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Synthesis and evaluation of some new oxazolones and imidazolones as antioxidant additives for Egyptian lubricating oils

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Abstract: Oxazolone derivative **2** was utilized as a key intermediate for synthesis of some new oxazolone and imidazolone derivatives. Reaction of oxazolone derivative **2** with diamines under different conditions afforded the corresponding imidazolone derivatives **3-8**, respectively. Moreover, oxazolone **2** reacted with some heterocyclic amines in glacial acetic acid giving the corresponding imidazolone derivatives **9-14**, respectively. Cyclocondensation of thiosemicarbazide with compound **2** in dry pyridine afforded compound **15**. Addition of secondary amines to olefin double bond of compound **2** gave the corresponding addition products **16-19**, respectively. Michael addition of compound **2** with some active methylene compounds afforded oxazolone derivatives **20-23**, respectively. These prepared products were evaluated as antioxidant and corrosion inhibitors for gasoline lubricating oil and compounds **6a-c**, **10** and **15** exhibited the highest antioxidant and anticorrosive activities. The effect of concentration of additives was studied to recommend the optimum concentration to be used. The results showed, for additive **15**, 0.1 g for 1 L oil was the more effective concentration. Measurements for thermal analysis and of surface tension of oil after oxidation were also carried out.

Key words: Oxazolone, imidazolone, benzoimidazole, surface tension, thermal stability, antioxidant additives.

1 Introduction

Lubricating oils produced by solvent refining of high boiling petroleum distillates consist mainly of long chain hydrocarbon molecules. In internal combustion engines, lubricating oils suffer from autoxidation as a result of contact at elevated temperatures with air for a long period and with metals, from which the engine was made.

These metals act as catalysts for oxidation of lubricating oil and are responsible for the formation of oxygenated oil-soluble and insoluble products which exert an adverse effect on the performance of the lubricating oils (Hassan et al, 1985; 2000; Hassan, 1998; Façanha et al, 2007; Aucelio et al, 2007; Suzuki et al, 2009). With increasing demands being placed on lubricants for automotive engines and transmissions and high-speed machinery, much research has been devoted to the development of improved lubricants. Not only petroleum-based lubricants, but also synthetic lubricants require additives to improve their lubricating and aging properties when exposed to many severe end use conditions, e.g., for extreme pressure applications where metal to metal contact may be encountered, additives must be used to form low shear strength surface films to minimize wear. Other additives inhibit oxidation; prevent rusting and improve the viscosity index and pour points of the lubricants.

2 Experimental section

2.1 Synthesis

The melting points (uncorrected) of all the compounds were determined on Gallenkamp electric melting point apparatus, and Fourier transform Infrared Spectroscopy (FT-IR) (KBr disk) was performed on a Mattson 5000 FTIR spectrometer which has spectral resolution of 4 cm^{-1} and scan number of 64 in the spectral range 400-4000 cm^{-1}using the Win first program. Calibration of the frequency reading was carried out using polystyrene film at the Microanalytical unit, Faculty of Science, Mansoura University, Mansoura, Egypt. ^{1}H-NMR spectra, were determined on a Brucker WPSY 300 MHZ spectrometer with TMS as internal standard and the chemical shifts are in σ ppm. Mass spectra were recorded at 70 ev with a Varian MAT 311. Elemental analysis was satisfactory for all the synthesized compounds **2-23**, and elemental analysis was carried out in the Faculty of Science, Cairo University, Egypt. (Z)-4-((5–Oxo-2-phenyloxazol-

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4(5H)–ylidene)methyl)phenyl-4-methylbenzene sulfonate (**2**) was prepared according to the previously reported method (Girges et al, 1989).

2.1.1Reaction of oxazolone (2) with *o*-phenylenediamine

a) By fusion at 140 ºC and at 190 ºC

A mixture of oxazolone **2** (0.003 mol), *o*-phenylenediamine (0.003 mol) and freshly fused sodium acetate (0.2 gm) was fused at 140 °C and/or 190 °C for 3 h. In each case, the reaction mixture was cooled, washed with dilute HCl, and the separated solid product was dried and recrystallized from methanol to give compounds **3** and **4**, respectively. Their characteristic spectral data are as follows:

4-(2-Benzamido-2-(1H-benzo[d]imidazol-2-yl)vinyl) phenyl4-methylbenzene sulfonate (**3**). IR (KBr), ν/cm^{-1}: 1680 (CO, amidic), 3174-3289 (2NH), 1360 (SO_3), 1600 (C=N), 1590 (C=C). EIMS (m/z, %): 509 (M^+, 20), 422 (54), 353 (23), 268 (11), 263 (16), 191 (32), 104 (100), 77 (37).

(Z)-4-((1-Phenyl-3H-benzo[d]imidazo[1,5-a]imidazol-3-ylidene)methyl)phenyl-4-methyl benzenesulfonate (**4**). IR (KBr), ν/cm^{-1}: 1360 (SO_3), 1620 (C=N). EIMS (m/z, %): 489 (M^+-2, 18), 341 (38), 295 (25), 213 (40), 193 (48), 147 (73), 91 (38), 44 (100). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 7.1-8.2 (m, 18H, Ar-H, CH=C).

b) By refluxing in ethyl alcohol

A mixture of oxazolone **2** (0.003 mol) and *o*-phenylenediamine (0.003 mol) in absolute ethanol (20 mL) was refluxed for 6 h. The solid product that separated on cooling was filtered off and recrystallized from ethanol to give compound **5**.

(Z)-4-(3-((2-Aminophenyl)amino)-2-benzamido-3-oxoprop-1-en-1-yl)phenyl-4-methyl benzenesulfonate (**5**). IR (KBr), ν/cm^{-1}: 1680 (CO, amidic), 3430, 3490 (2NH), 3225-3370 (NH_2), 1360 (SO_3), 1620 (C=N). EIMS (m/z, %): 527 (M^+, 30), 495 (11), 480 (14), 422 (27), 380 (56), 268 (16), 253 (100), 105 (52). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 4.5 (br, 2H, NH_2), 6.9-8.3 (m, 20H, Ar-H, CH=C, 2NHCO).

c) By refluxing in glacial acetic acid

A mixture of oxazolone **2** (0.003 mol) and *o*-phenylenediamine (0.003 mol) in glacial acetic acid (20 mL) containing freshly fused sodium acetate (0.2 gm) was heated under reflux for 7 h. The reaction mixture was left to cool, and then poured over ice. The solid that separated was filtered off, dried and recrystallized from ethanol-ether was compound **6**.

(Z)-4-((1-(2-Acetamidophenyl)-5-oxo-2-phenyl-1H-imidazol-4(5H)-ylidene) methyl)phenyl 4-methylbenzenesulfonate (**6**). IR (KBr), ν/cm^{-1}: 1698 (CO, amidic), 1665 (CONH), 3133 (NH), 1360 (SO_3), 1610 (C=N). EIMS (m/z, %): 551 (M^+, 45), 451 (42), 368 (25), 282 (26), 197 (19), 148 (40), 78 (51), 63 (100). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 2.2 (s, 3H, CH^3CO), 7.1-8.2 (m, 19H, Ar-H, CH=C, NH).

2.1.2 Reaction of oxazolone (2) with *p*-phenylenediamine

A mixture of oxazolone **2** (0.003 mol) and *p*-phenylenediamine (0.003 mol) in glacial acetic acid (30 mL) containing freshly fused sodium acetate (0.2 gm) was heated under reflux for 5 h. The reaction mixture was left to cool, and the solid that separated was filtered off, dried and recrystallized from acetic acid to give compound **7**.

(Z)-4-((1-(4-acetamidophenyl)-5-oxo-2-phenyl-1H-imidaz-ol-4(5H)-ylidene) methyl)phenyl 4-methylbenzenesulfonate (**7**). IR (KBr), ν/cm^{-1}: 1700 (CO, amidic), 1660 (CON), 3350 (NH), 1360 (SO_3), 1640 (C=N). EIMS (m/z, %): 552 (M^+, 15), 446 (12), 342 (15), 256 (25), 157 (16), 109 (35), 84 (63), 40 (100). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 2.6 (s, 3H, CH_3CO), 7.1-8.4 (m, 19H, Ar-H, CH=C, NH).

A mixture of oxazolone **2** (0.006 mol) and *p*-phenylenediamine (0.003 mol) in glacial acetic acid (30 mL) containing freshly fused sodium acetate (0.5 gm) was heated under reflux for 8 h. The reaction mixture was left to cool, and then poured over ice, the solid that separated out was filtered off, dried and recrystallized from dimethylformamide giving bis imidazolone **8**.

((1Z,1′Z)-(1,1′-(1,4-phenylene)bis(5-oxo-2-phenyl-1H-imi-dazole-1(5H)-yl-4(5H)-ylidene))bis(methanylylidene))-bis(4,1-phenylene)bis(4-methyl benzenesulfonate) (**8**). IR (KBr), ν/cm^{-1}: 1675-1688 (2CON), 1360 (SO_3), 1620 (C=N). EIMS (m/z, %): 911 (M^+, 22), 788 (33), 540 (11), 382 (100), 364 (44), 301 (8), 285 (53), 218 (17), 155 (25), 75 (33). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (br, 6H, $2CH_3$), 6.9-8.3 (m, 32H, Ar-H, 2CH=C).

2.1.3 Reaction of oxazolone (2) with heterocyclic amines

A mixture of **2** (0.01 mol) and the appropriate heterocyclic amines namely 2-aminopyridine, 3-aminopyridine, 2-aminothiazole, 2-amino benzothiazole, 4-aminoantipyrine and 3-amino-4-(phenyldiazenyl)-1H-pyrazol-5(4H)-one (0.01 mol) and freshly fused sodium acetate (0.5gm) in glacial acetic acid (40 mL) was refluxed for 5-8 h, then cooled and the reaction mixture was poured into ice-water. The solids separated were filtered off and recrystallized from methanol to give imidazolone derivatives **9-14**.

(Z)-4-((5-Oxo-2-phenyl-1-(pyridin-2-yl)-1H-imidazol-4(5H)-ylidene)methyl) phenyl-4-methyl benzenesulfonate (**9**). IR (KBr), ν/cm^{-1}: 1680 (CO, amidic), 1360 (SO_3), 1620 (C=N). EIMS (m/z, %): 496 (M^++1, 16), 267 (14), 232 (13), 195 (18), 153 (14), 101 (12), 86 (47), 74 (100).

(Z)-4-((5-Oxo-2-phenyl-1-(pyridin-3-yl)-1H-imidazol-4(5H)-ylidene)methyl) phenyl-4-methyl benzenesulfonate (**10**). IR (KBr), ν/cm^{-1}: 1680 (CO, amidic), 1360 (SO_3), 1620 (C=N). EIMS (m/z, %): 495 (M^+, 24), 378 (23), 256 (41), 202 (37), 184 (12), 126 (15), 88 (43), 58 (100).

(Z)-4-((5-Oxo-2-phenyl-1-(thiazol-2-yl)-1H-imidazol-4(5H)-ylidene)methyl) phenyl-4-methylbenzenesulfonate (**11**). IR (KBr), ν/cm^{-1}: 1680 (CO, amidic), 1360 (SO_3), 1620 (C=N). EIMS (m/z, %): 501 (M^+, 41), 445 (38), 404 (48), 388 (71), 347 (41), 294 (66), 263 (33), 191 (11), 105 (81), 58 (100).

(Z)-4-((1-(Benzo[d]thiazol-2-yl)-5-oxo-2-phenyl-1H-imidazol-4(5H)-ylidene) methyl)-phenyl-4-methyl benzenesulfonate (12). IR (KBr), ν/cm-1: 1680 (CO, amidic), 1360 (SO3), 1620 (C=N). EIMS (m/z, %): 553 (M++2, 20), 423 (20), 383 (41), 305 (59), 256 (25), 227 (48), 186 (11), 156 (10), 122 (15), 75 (100).

(Z)-4-((1-(1,5-Dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl)-5-oxo-2-phenyl-1H-imidazol-4(5H)-ylidene)-methyl)phenyl-4-methylbenzenesulfonate (**13**). IR (KBr), ν/cm^{-1}: 1680 (CO, amidic), 1360 (SO_3), 1620 (C=N). EIMS (m/z, %): 604 (M^+, 32), 450 (13), 347 (26), 290 (11), 263 (16), 231 (39), 156 (62), 105 (100).

4-((1Z)-(5-Oxo-1-(5-oxo-4-(phenyldiazenyl)-4,5-dihydro-1H-pyrazol-3-yl)-2-phenyl-1H-imidazol-4(5H)-ylidene)-methyl)phenyl-4-methylbenzenesulfonate (**14**). IR (KBr), ν/cm^{-1}: 1680 (CO, amidic), 3320 (NH), 1360 (SO_3), 1620 (C=N). EIMS (m/z, %): 605 (M^+, 21), 495 (16), 449 (12), 369 (23), 255 (12), 196 (16), 104 (73), 91 (100).

2.1.4 Reaction of oxazolone (2) with thiosemicarbazide

Thiosemicarbazide (0.03 mol) was added to a solution of compound **2** (0.01 mol) in 30 mL dry pyridine, and the reaction mixture was heated under reflux for 8 h, left to cool and then poured into cold water with stirring. The solid product was filtered off, washed with water several times and recrystallized from dimethylformamide to give compound **15**.

(Z)-4-((5-phenyl-2-thioxo-2H-imidazo[1,5-b][1,2,4]-triazol-7(3H)-ylidene)methyl) phenyl 4-methylbenzenesulfonate (**15**). IR (KBr), ν/cm^{-1}: 1376 (C=S), 3442 (NH), 1340 (SO_3), 1640 (C=N). EIMS (m/z, %): 475 (M^+, 42), 411 (75), 320 (18), 275 (53), 167 (57), 139 (27), 91 (100), 50 (49). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 9.8 (s, 1H, NH), 7.2-8.3 (m, 14H, Ar-H, CH=C).

2.1.5 Reaction of oxazolone (2) with secondary amines and thiophenol

A mixture of oxazolone **2** (0.05 mol) and the appropriate reagent namely piperidine, morpholine, piperazine, and thiophenol (0.05 mol) in dry benzene (30 mL) was heated at 60 ºC with stirring for 3-5 h. The reaction mixture was left to stand overnight at room temperature, then petroleum ether (40-60 ºC) was added and the precipitated solid products were filtered off and recrystallized from benzene-hexane (2:1) to give **16-19**, respectively.

4-((5-Oxo-2-Phenyl-4,5-dihydrooxazol-4-yl)(piperidin-1-yl)methyl)phenyl-4-methyl benzenesulfonate (**16**). IR (KBr), ν_{max}/cm^{-1}: 1770 (CO, lactone), 1644 (C=N), 1360 (SO_3). EIMS (m/z, %): 504 (M^+, 12), 478 (7.1), 365 (58), 282 (10), 161 (14), 85 (100), 72 (28). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 2.46-2.47 (t, 4H, N(CH_2)2), 1.48-1.49 (m, 6H, 3CH_2 of piperidine), 4.51-4.52 (m, 2H, N-CH, CH of oxazolone), 6.9-8.1 (m, 14H, Ar-H, CH=C).

4-(Morpholino(5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-methyl)phenyl-4-methyl benzene sulfonate (**17**). IR (KBr), ν_{max}/cm^{-1}: 1780 (CO, lactone), 1640 (C=N), 1360 (SO_3). EIMS (m/z, %): 506 (M^+, 16), 420 (16), 265 (19), 161 (100), 117 (45), 93 (46), 57 (18). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 2.67-2.68 (t, 4H, N(CH_2)$_2$), 3.58-3.59 (t, 4H, O(CH_2)$_2$), 4.51-4.52 (m, 2H, N-CH, CH of oxazolone), 6.9-8.1 (m, 14H, Ar-H, CH=C).

4-((5-Oxo-2-phenyl-4,5-dihydrooxazol-4-yl)(piperazin-1-yl)methyl)phenyl-4-methylbenzenesulfonate (**18**). IR (KBr), ν_{max}/cm^{-1}: 1780 (CO, lactone), 3423 (NH), 1638 (C=N), 1360 (SO_3). EIMS (m/z, %): 505 (M^+, 22), 441 (26), 395 (52), 315 (12), 277 (53), 200 (61), 148 (79), 105 (100), 48 (61). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 2.65-2.66 (m, 8H, N(CH_2)$_4$), 4.51-4.52 (m, 2H, N-CH, CH of oxazolone), 6.9-8.1 (m, 15H, Ar-H, CH=C, NH).

4-((5-Oxo-2-phenyl-4,5-dihydrooxazol-4-yl)(phenylthio)-methyl)phenyl-4-methyl benzene sulfonate (**19**). IR (KBr), ν_{max}/cm^{-1}: 1780 (CO, lactone), 1640 (C=N), 1360 (SO_3). EIMS (m/z, %): 529 (M^+, 25), 401 (19), 316 (47), 257 (29), 213 (37), 188 (15), 101 (12), 77 (20), 43 (100).

2.1.6 Reaction of oxazolone (2) with active methylene compounds

A mixture of oxazolone 2 (0.03 mol), ethylcyanoacetate (0.05 mol) and few drops of piperidine in dry chloroform (50 mL) was heated under reflux for 8 hours. The solvent was evaporated under reduced pressure. The obtained solid product was filtered off and recrystallized from methanol to obtain 20.

ethyl2-cyano-3-(5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-3-(4-(tosyl-oxy)phenyl) propanoate (**20**). IR (KBr), ν_{max}/cm^{-1}: 1780 (CO, lactone), 1730 (CO, ester), 2110 (CN), 1640 (C=N), 1360 (SO_3). EIMS (m/z, %): 533 (M^+, 10), 413 (19), 341 (42), 304 (25), 280 (14), 189 (17), 168 (42), 105 (44), 77 (59), 43 (100). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 1.29-1.30 (t, 3H, CH_3CH_2), 4.37-4.43 (q, 2H, CH_3CH_2), 4.31-4.32 (m, 3H, CH-CH, CH of oxazolone), 6.9-8.1 (m, 14H, Ar-H, CH=C).

A mixture of **2** (0.005 mol) and ethylacetoacetate (0.01 mol) in 30mL ethanol was added dropwise to 10 mL sodium hydroxide (10%), the mixture was stirred at room temperature for 24 h, then poured into 5 mL of 5% HCl. The formed solid was filtered, washed with water and recrystallized from ethanol to give **21**.

2-acetyl-4-benzamido-3-(4-(tosyloxy)phenyl)pentanedioic acid (**21**). IR (KBr), ν_{max}/cm^{-1}: 1670 (CO, amidic), 1700 (CO), 3400 (OH), 3300 (NH), 1640 (C=N), 1360 (SO_3). EIMS (m/z, %): 539 (M^+, 46), 457 (10), 382 (100), 298 (10), 254 (35), 181 (27), 147 (16), 111 (15), 91 (56).

A mixture of compound **2** (0.005 mol), the appropriate nitroalkane namely, nitromethane and/or nitroethane (0.01 mol) and few drops of triethylamine in ethanol (30 mL) was refluxed with stirring for 12 h, then poured onto ice-water, The solid that separated was filtered off and recrystallized from ethanol to give **22** and **23**, respectively.

4-(2-Nitro-1-(5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-ethyl)phenyl-4-methyl benzene sulfonate (**22**). IR (KBr), ν_{max}/cm^{-1}: 1770 (CO, lactone), 1350 (NO_2), 1640 (C=N), 1360 (SO_3). EIMS (m/z, %): 482 (M+2, 19), 411 (28), 344 (36), 218 (55), 275 (100), 197 (45), 155 (47), 129 (46), 91 (67).

4-(2-Nitro-1-(5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)-propyl)phenyl-4-methyl benzene sulfonate (**23**). IR (KBr), ν_{max}/cm^{-1}: 1770 (CO, lactone), 1350 (NO_2), 1640 (C=N), 1360 (SO_3). EIMS (m/z, %): 495 (M^+, 23), 455 (16), 419 (80), 384 (46), 350 (63), 334 (12), 295 (60), 238 (100), 155 (36). ^{1}H NMR (DMSO) (δ, ppm), 2.4 (s, 3H, CH_3), 1.7 (d, 3H, CH_3-CH), 3.3 (t, 1H, CH), 4.31-4.32 (m, 2H, O_2NCH-, CH of oxazolone), 6.9-8.1 (m, 14H, Ar-H, CH=C).

2.2 Evaluation of the prepared compounds as lubricating oil additives

2.2.1 Evaluation of the prepared compounds as antioxidant additives for the tested lubricating oil

A lubricating sample free from additives, as well as lubricating oil samples containing different concentrations of prepared products, were subjected to severe oxidation with an air rate of 10 L·h^{-1} at 155 °C for 36 h. Samples were taken at regular intervals in 3-36 h of oxidation. The oxidation stability of these samples is expressed in terms of total acid number (TAN) according to (ASTMD-3242) (Figs.1-4)

2.2.2 Evaluation of the prepared compounds as corrosion inhibitor additives for the tested lubricating oil

In order to evaluate the corrosion inhibition of the tested lubricating oil samples containing the prepared compounds, strips of three metals: iron, copper and aluminum with surface area of 1 cm^2, were used in this study. Every metal was weighed and immersed in the oxidation system for 36 h under the previous conditions (155 ºC with air rate of 5 L/h). Then every metal was cleaned and weighed again. The difference in weight was calculated and the efficiency of the used products as corrosion inhibitors was evaluated by using weight loss technique according to ASTMD-130 (Table 3).

2.2.3 Effect of concentration

The effect of concentration of additive, which gave the highest antioxidant efficiency for the tested lubricating oil, was studied in order to find the optimum concentration. In our work, three different concentrations of additive **15** namely, 0.01, 0.05 and 0.1 $g \cdot L^{-1}$, were used (Fig. 5).

2.2.4 Surface tension of lubricating oil after oxidation

Surface tension was measured for the lubricating oil with and without additives after 36 h at 155 °C with air rate of 10 $L \cdot h^{-1}$ in order to determine the detergency effect of the additives on oil, by using surface tension apparatus (Torsion Balance White Elec. Co Ltd. No 0/17604f) (Table 4).

2.2.5 Thermal stability of prepared antioxidant additives

In order to study the stability of effective antioxidant and anticorrosive additives towards heating, thermal analysis using thermogravimetric analysis (TGA) and differential thermal gravimetric analysis (DTGA) techniques were conducted by using Shimadzu TGA apparatus.

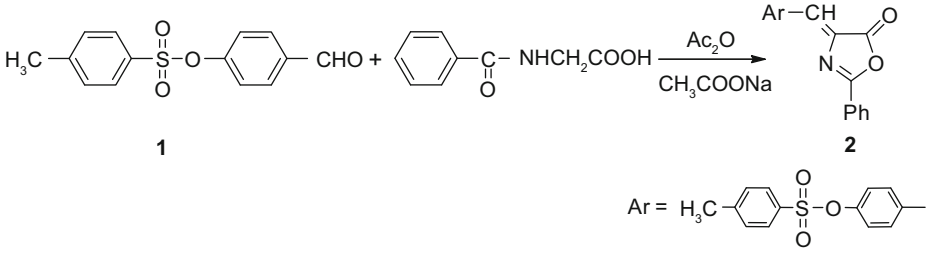
2.2.6 A comparison of the oxidation stability between lubricating oil containing the prepared products and lubricating oil containing a commercial additive

The oxidation stability was compared between the lubricating oil containing the highly efficient prepared antioxidants (0.1 $g \cdot L^{-1}$)and the lubricating oil containing a commercial antioxidant additive purchased from the local market (CO-OP Cosf/cc 21 w/51 oil). The results obtained after 36 h oxidation at 155 °C with air rate of 10 $L \cdot h^{-1}$ (Fig. 6).

3 Results and discussion

3.1 Chemistry

Many types of organic heterocyclic compounds have been used as antioxidant and anticorrosive additives for lubricating oils. In continuation of our previous studies in the field of antioxidant and anticorrosive additives (Hassan et al, 2010; 2011a; 2011b; Hassan, 2011; Amer et al, 2011; Habib et al, 2010; Habib et al, in press; Cameron, 1966), new additives **2-23** were prepared and their antioxidant and anticorrosive activities were evaluated for some Egyptian local lubricating oils. Thus, the required (Z)-4-((5-oxo-2-phenyloxazol-4(5H)-ylidene)methyl)phenyl-4-methyl benzenesulfonate **2**, was prepared by means of the reaction of 4-toluenesulfonyloxy benzaldehyde **1** with hippuric acid and acetic anhydride in the presence of freshly fused sodium acetate according to the method reported in literature (Girges et al, 1989).



Scheme 1 Synthesis of oxazolone derivative **2**

Fusion of oxazolone **2** with *o*-phenylenediamine in the presence of freshly fused sodium acetate at 140 °C and 190 °C respectively gives different products. When fusion was carried out at 140 °C, compound **3** was obtained, while fusion at 190 °C leads to the formation of compound **4**. Moreover, reaction of oxazolone **2** with *o*-phenylenediamine in absolute ethanol under reflux afforded compound **5**. Furthermore, treatment of oxazolone **2** with *o*-phenylenediamine in glacial acetic acid under reflux in the presence of fused sodium acetate gives imidazolone derivative **6** (Table 1) (Scheme 2).

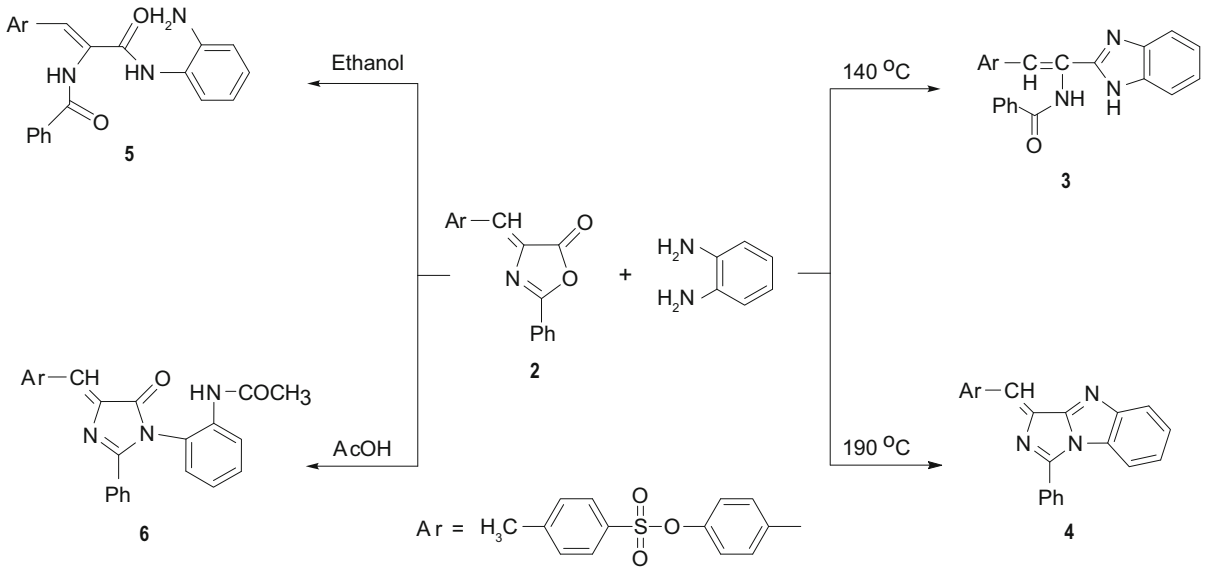
On the other hand, refluxing of one mole of oxazolone **2** with one mole of *p*-phenylenediamine in the presence of glacial acetic acid and fused sodium acetate afforded imidazolone **7**, but using two moles of compound **2** to one mole of the other give bis imidazolone **8** (Table 1) (Scheme 3).

In the present investigation, oxazolone **2** reacted with some heterocyclic amines, namely 2-aminopyridine, 3-aminopyridine, 2-aminothiazole, 2-aminobenzothiazole, 4-aminoantipyrine or 5-amino-4-phenylazo-2,4-dihydropyrazol-3-one, in glacial acetic acid and fused sodium acetate giving imidazolone derivatives **9-14** (Table 1) (Scheme 4), respectively.

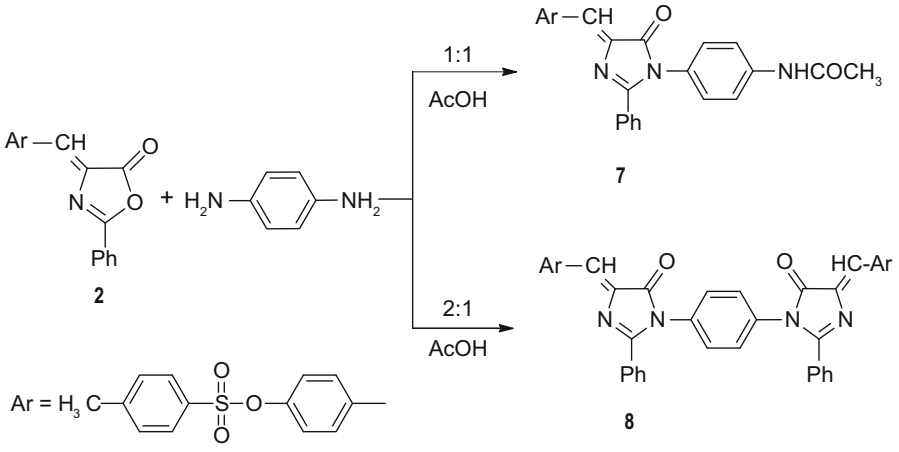
Cyclocondensation of thiosemicarbazide with oxazolone **2** in dry pyridine afforded (Z)-4-((5-phenyl-2-thioxo-2H-imidazo[1,5-b][1,2,4]triazol-(3H)-ylidene)methyl)phenyl-4-methylbenzene sulfonate **15** (Table 1) (Scheme 5).

The reactivity of the exocyclic (C=C) bond in the four position of the oxazolone ring is due to conjugation with the adjacent carbonyl group (Habib et al, 1989). In the present work, the addition of piperidine, morpholine, piperazine or thiophenol to the olefinic double bond in the four position of compound **2** gives the corresponding addition products **16-19** (Table 1) (Scheme 6), respectively.

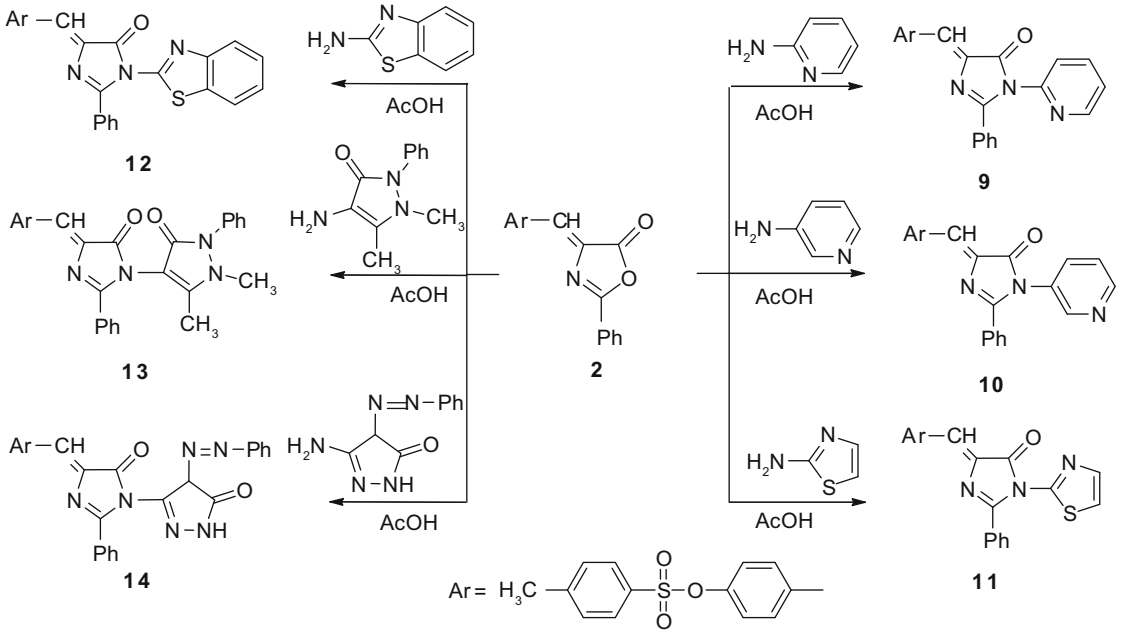
The present investigation deals also with the Michael addition on the exocyclic double bond in compound **2**. Thus addition of ethylcyanoacetate to compound **2** in chloroform afforded oxazolone derivative **20**, but the addition of ethylacetoacetate in the presence of sodium hydroxide afforded compound **21**. On the other hand, addition of nitromethane and nitroethane to oxazolone **2** leads to the formation of compounds **22** and **23** (Table 1)(Scheme 7), respectively.



Scheme 2 Reaction of oxazolone **2** with *o*-phenylenediamine under different conditions



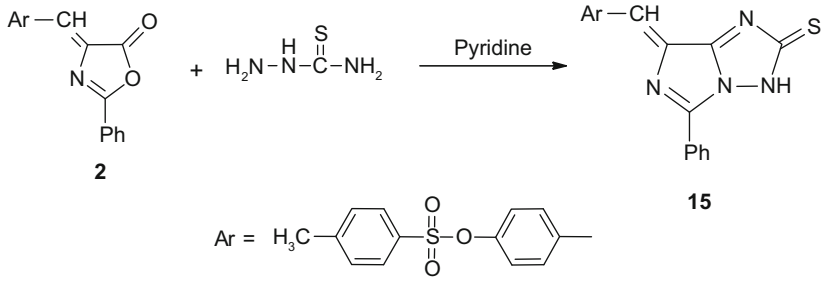
Scheme 3 Reaction of oxazolone **2** with *p*-phenylenediamine under different moles



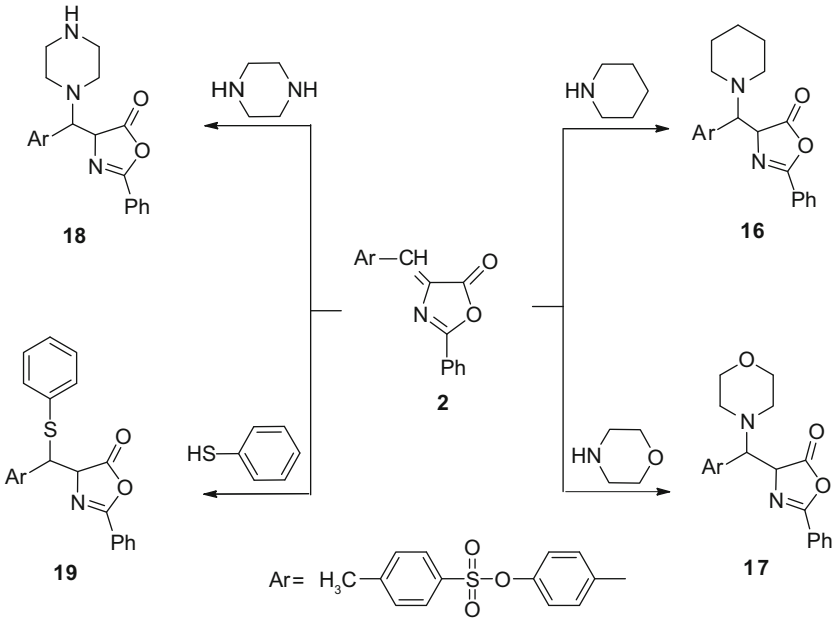
Scheme 4 Reaction of oxazolone **2** with different heterocyclic amines

Table 1 Characterization data of newly prepared compounds

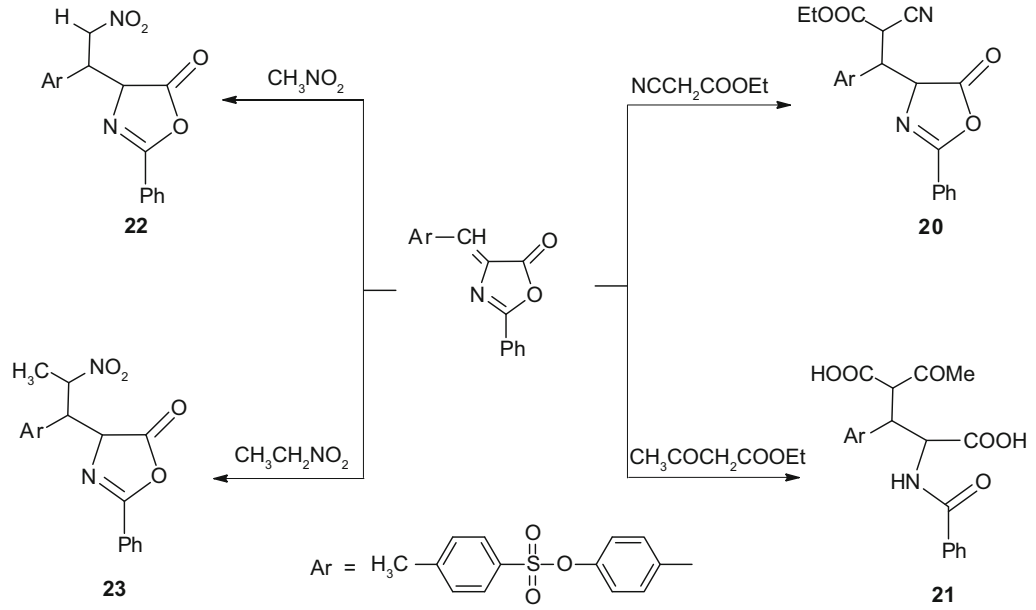
Cpd. No.	m.p. (°C)	Yield (%), Color	Mol. Formula (wt)	Elemental analysis Calc. (Found)		
				C%	H%	N%
3	149-151	53, Gray powder	$C_{29}H_{23}N_3O_4S$ (509.5)	68.35 (68.31)	4.55 (4.50)	8.25 (8.15)
4	238-240	63, Brown powder	$C_{29}H_{21}N_3O_3S$ (491.5)	70.86 (70.81)	4.31 (4.30)	8.55 (8.45)
5	218-220	65, Grey powder	$C_{29}H_{25}N_3O_5S$ (527.5)	66.02 (66.01)	4.78 (4.80)	7.96 (7.86)
6	180-182	65, Yellow powder	$C_{31}H_{25}N_3O_5S$ (551.6)	67.5 (67.4)	4.57 (4.50)	7.62 (7.65)
7	225-227	80, Yellow powder	$C_{31}H_{25}N_3O_5S$ (551.6)	67.5 (67.1)	4.57 (4.49)	7.61 (7.62)
8	271-273	75, Grey powder	$C_{52}H_{38}N_4O_8S_2$ (911)	68.56 (68.48)	4.2 (4.1)	6.15 (6.11)
9	158-160	62, Yellow crystals	$C_{28}H_{21}N_3O_4S$ (495.5)	67.86 (67.81)	4.27 (4.20)	8.48 (8.35)
10	166-168	72, Yellow powder	$C_{28}H_{21}N_3O_4S$ (495.5)	67.86 (67.78)	4.27 (4.25)	8.48 (8.49)
11	181-183	52, Yellow crystals	$C_{26}H_{19}N_3O_4S_2$ (501.5)	62.26 (62.28)	3.82 (3.80)	8.38 (8.28)
12	163-165	60, Grey powder	$C_{30}H_{21}N_3O_4S_2$ (551.6)	65.32 (65.28)	3.84 (3.80)	7.62 (7.55)
13	194-196	42, Yellow crystals	$C_{34}H_{28}N_4O_5S$ (604.6)	67.53 (67.58)	4.67 (4.60)	9.27 (9.24)
14	172-174	46, Yellow powder	$C_{32}H_{24}N_6O_5S$ (604.6)	63.57 (63.58)	4.0 (3.80)	13.90 (13.88)
15	181-183	41, Grey powder	$C_{24}H_{18}N_4O_3S_2$ (474.5)	60.74 (60.71)	3.82 (3.79)	11.81 (11.78)
16	186-188	25, Yellow powder	$C_{28}H_{28}N_2O_5S$ (504.6)	66.65 (66.55)	5.59 (5.55)	5.55 (5.54)
17	160-162	31, Yellow crystals	$C_{27}H_{26}N_2O_6S$ (506.5)	64.02 (64.0)	5.17 (5.15)	5.53 (5.53)
18	221-223	34, Yellow powder	$C_{27}H_{27}N_3O_5S$ (505.5)	64.14 (64.13)	5.38 (5.35)	8.31 (8.24)
19	196-198	41, Yellow crystals	$C_{29}H_{23}NO_5S_2$ (529.6)	65.77 (65.73)	4.38 (4.35)	2.64 (2.54)
20	297-299	28, Yellow powder	$C_{28}H_{24}N_2O_7S$ (532.5)	63.15 (63.13)	4.54 (5.55)	5.25 (5.21)
21	285-287	51, White powder	$C_{27}H_{25}NO_9S$ (539.5)	60.10 (60.13)	4.67 (4.65)	2.60 (2.54)
22	205-207	38, Yellow crystals	$C_{24}H_{20}N_2O_7S$ (480.4)	59.99 (60.03)	4.20 (4.25)	5.83 (5.84)
23	165-167	25, Yellow powder	$C_{25}H_{22}N_2O_7S$ (494.5)	60.72 (60.73)	4.48 (4.45)	5.66 (5.56)



Scheme 5 Reaction of oxazolone **2** with thiosemicarbazide



Scheme 6 Reaction of oxazolone **2** with secondary amines and thiophenol



Scheme 7 Reaction of oxazolone **2** with active methylene compounds

3.2 Antioxidant and anticorrosive additives

3.2.1 Evaluation of the prepared compounds as antioxidant additives for the tested lubricating oil

As mentioned in the literature survey, air oxidation of aliphatic hydrocarbons proceeds by a series of free radical reactions as shown by the following scheme:

Initiation:

$$RH + O_2 \rightarrow R^{\bullet} + {}^{\bullet}OOH$$

Propagation:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$
$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$
$$ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$$
$$RO^{\bullet} + RH \rightarrow ROH + R^{\bullet}$$

Termination:

$$RO^{\bullet} + R^{\bullet} \rightarrow ROR$$
$$RO^{\bullet} + RO^{\bullet} \rightarrow ROOR$$

The principle requirement for the majority of antioxidants is the presence of a labile hydrogen in their chemical structure or the presence of sulphur or phosphorous. It was stated that, the antioxidant molecule reacts with the peroxy radicals which form during oxidation and leads to the formation of inactive products as shown in the following scheme:

$$ROO^{\bullet} + AH \rightarrow ROOAH$$

Followed by:

$$ROOAH + ROO\cdot \rightarrow \text{inactive product}$$

or:

$$ROO^{\bullet} + AH \rightarrow ROOH + A\cdot$$

$ROO^{\bullet} + A^{-} \rightarrow$ inactive product

where, AH is the antioxidant molecule and A is an antioxidant radical. Thus, as the labile hydrogen atoms increase, the efficiency of the antioxidant effect would also be increased.

To verify the effectiveness of the synthesized compounds as antioxidants, we prepared different solutions by adding 0.1 g of the selected compound to 1 L of the additive-free tested lubricating oil, then the lubricating oil with and without additives was subjected to severe oxidation at 155 °C with air at a rate of 10 $L \cdot h^{-1}$ for 36 h. Samples were taken at regular intervals of 3 h for testing their oxidation stability, which is expressed in terms of the total acid number (TAN) according to ASTMD 3242, and recorded their UV spectra and then compared them with the lubricating oil sample free from additives. The results showed that, in the absence of additives, the oxidation products increased with time. When the prepared additives **2-23** were added to the tested lubricating oil at a concentration of 0.1 $g \cdot L^{-1}$, the oxidation products increased at a rate much lower than that without additives, as shown in Figs. 1-4 and Table 2. The highest antioxidant activity was observed in the presence of **11-15** compounds due to the presence of some antioxidant groups in each of them. Compound **14**, which were the most effective antioxidant additive have many antioxidant moieties, such as imidazolone and pyrazolone moieties, and some antioxidant groups such as N=N and NH groups, while, compound **15** contains imidazolone and thiotriazole moieties. On the other hand, compounds **11-13** exhibited the highest antioxidant activity because they contain thiazole, benzothiazole, and pyrazole moieties, respectively, beside the imidazolone moiety in each of them.

3.2.2 Evaluation of the prepared compounds as corrosion inhibitors for the tested lubricating oil

Once more, the prepared compounds were tested as corrosion inhibitors for the corresponding lubricating oil using three different strips of copper, iron and aluminum with an area of 1 cm^2. The results showed a loss in the weight of metal strips for oil without additives. While in the presence of the compounds 2-23, higher corrosion inhibition was

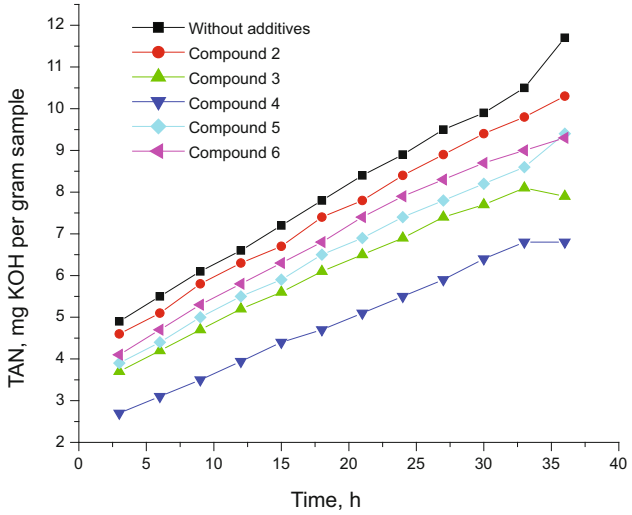


Fig. 1 Variation of total acid number (TAN) with oxidation time of lubricating oil sample without and with additives **2-6** at 0.1 g/L concentration at 155 ºC in 3-36 h

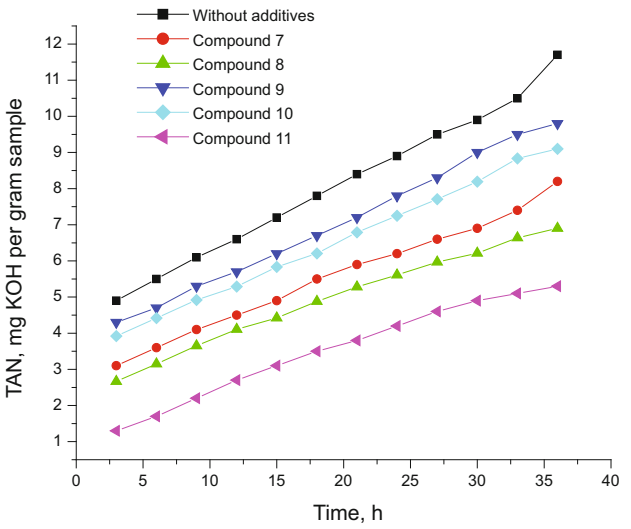


Fig. 2 Variation of the TAN with oxidation time of the lubricating oil sample without and with additives **7-11** at 0.1 g/L concentration at 155 ºC in 3-36 h

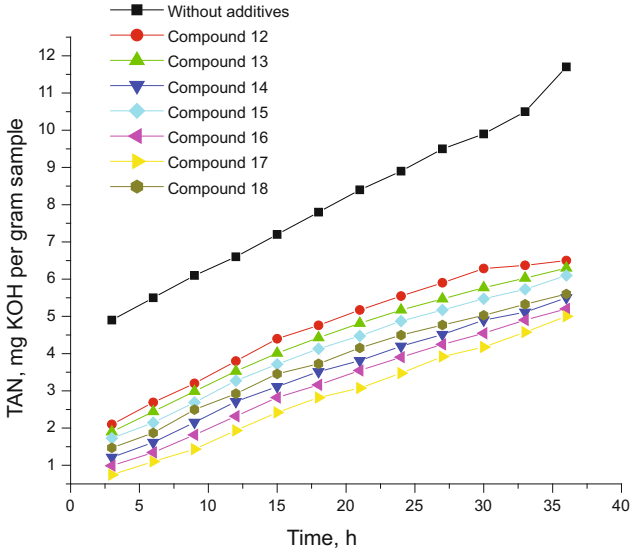


Fig. 3 Variation of the TAN with oxidation time of the used lubricating oil sample without and with additives **12-18** at 0.1 g/L concentration at 155 ºC in 3-36 h

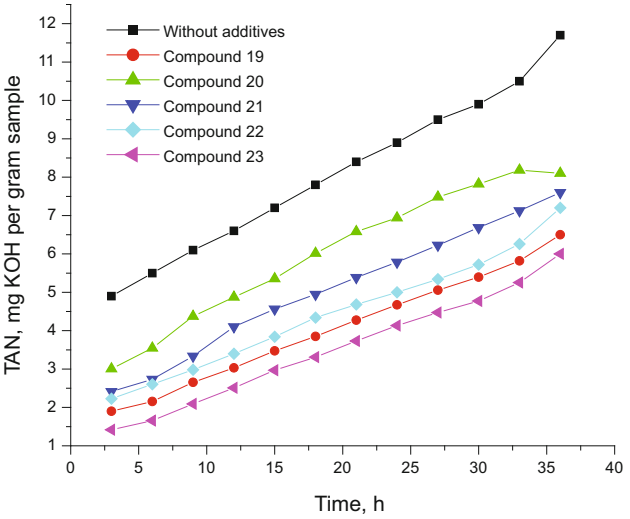


Fig. 4 Variation of the TAN with oxidation time of the lubricating oil sample without and with additives **19-23** at 0.1 g/L concentration at 155 ºC in 3-36 h

Table 2 Comparison of oxidation stability of lubricating oil in the presence and absence of additives **2-23**

Compound No.	Acid value gm KOH/g	Peroxide value gm (KI)/g oil	Carbonyl value gm (O)/g oil	Ester value gm (KOH)/g oil	Hydroxyl value gm (KOH)/g oil
Without additives	11.7	16.5	36.0	60.0	125.0
With additive **2**	10.3	8.2	30.6	54.4	111.3
3	7.9	11.2	25.6	41.5	63.6
4	6.8	8.9	10.9	40.3	39.5
5	9.4	9.5	21.2	51.3	66.7
6	9.3	10.5	22.8	46.7	71.5
7	8.2	9.9	15.4	40.5	66.8
8	6.9	9.8	14.4	48.4	57.8
9	9.8	11.2	30.2	44.6	91.5
10	9.1	10.1	22.2	50.6	86.7
11	5.3	13.4	18.7	34.6	74.7
12	5.2	7.8	12.5	49.6	66.7
13	5.5	12.4	28.5	50.4	75.0
14	5.0	10.4	27.6	44.5	85.7
15	5.6	10.3	15.3	44.5	92.5
16	6.3	6.8	10.3	45.4	37.8
17	6.5	7.4	9.7	40.4	46.7
18	6.1	6.8	7.8	33.6	39.5
19	7.2	9.5	30.2	41.5	71.5
20	6.5	10.5	22.2	40.3	66.8
21	6.0	9.9	18.7	51.3	57.8
22	8.1	9.8	12.5	46.7	91.5
23	7.6	11.2	28.5	40.5	86.7

observed, as shown in Table (3).

3.2.3 Mechanism of corrosion inhibition

In lubricating oil, compounds **2-23** exist as neutral molecules, in general, the mode of adsorption could be considered. The neutral form may be adsorbed on the metal surface via a chemisorption mechanism, involving the displacement of oil molecules from the metal surface and the sharing electrons between the N, O and S atoms and metal. In addition, lone-pair electrons of N and O atoms in the investigated compounds **2-23** may combine with freshly generated M^{2+} or M^{3+} ions on metal surface, forming metal inhibitor complexes.

$$M \rightarrow M^{2+} + 2e \quad (1)$$

$$Inh. + M^{2+} \leftrightarrow [Inh.\text{-}M]^{2+} \quad (2)$$

$$[Inh.]n^{+} + M^{2+} \leftrightarrow [Inh._{n}\text{-}M]^{(2+n)+} \quad (3)$$

M= Fe and Cu

In case of aluminum as metal the equations will be as follows:

$$Al \rightarrow Al^{3+} + 3e \quad (4)$$

$$Inh. + Al^{3+} \leftrightarrow [Inh.\text{-}Al]^{3+} \quad (5)$$

$$[Inh.]n^{+} + Al^{3+} \leftrightarrow [Inh._{n}\text{-}Al]^{(3+n)+} \quad (6)$$

These complexes might be adsorbed onto the metal surface by van der Waal's forces to form protective films. On the other hand, the surface coordination is through the nitrogen atoms. It can be concluded that the mode of adsorption depends on the affinity of the metal towards the π-electron clouds of the ring system. Metals such as Cu and Fe, which have a greater affinity towards aromatic moieties, were found to adsorb benzene rings in a flat orientation. Thus, it is reasonable to assume that the tested inhibitors are adsorbed in a flat orientation through the N- and O-atoms. It was found that, the prepared compounds (**2-23**) showed good corrosion inhibition for all the metals used. This could be explained by the presence of heterocyclic moieties in their structures. Also, in the presence of NH, C=N groups and sulfur atom which may react with these metals to form the corresponding sulphides.

3.2.4 Effect of concentration

For the compound that gave the highest antioxidant efficiency, the effect of its concentration was investigated to find the optimum concentration recommended to be used. Thus, three different concentrations of additive **15**, namely 0.01, 0.05 and 0.1 g, for 1 L lubricating oil were used.

Table 3 Effect of additive types at 0.1 g/L concentration in the oil on the weight loss of metals (iron, copper, and aluminum) after 36 h oxidation at 155 ºC with air rate of 5 L/h

Compound No.	Weight loss (10^{-3} g)		
	Cu	Fe	Al
Without additives	11.8	14.7	9.2
With additive **2**	2.5	7.8	1.8
3	2.6	5.1	1.5
4	2.7	7.9	1.3
5	4.6	4.6	3.7
6	3.7	6.5	5.4
7	2.2	6.2	4.3
8	5.8	4.8	3.6
9	4.2	6.7	4.6
10	6.1	7.7	1.3
11	6.8	2.4	1.2
12	3.5	3.5	2.6
13	2.2	6.8	6.4
14	2.8	6.9	4.4
15	4.3	8.9	1.8
16	1.8	1.7	1.9
17	1.7	15.5	1.6
18	4.2	6.4	1.5
19	2.8	7.7	4.3
20	4.3	2.4	3.6
21	1.8	3.5	4.6
22	1.7	6.8	1.3
23	4.2	6.9	1.2

The obtained results showed that, increasing the additive concentration led to decrease of oxidative products, indicating that that concentration of 0.1 g for 1 L oil is the more effective concentration to be used for additives **15** (Fig. 5).

3.2.5 Measurement of surface tension of lubricating oil after oxidation

Surface tension was measured for lubricating oil with and without additives after heating for 36 h at 155 °C with air rate of 10 L·h^{-1} in order to determine the detergency effect of additives. As shown in Table (4), we can see that, the surface tension decreased for the lubricating oil in the presence of additives after oxidation compared to that of the additive-free oil. This means that, in presence of compounds **2-23**, the need of oil for detergency additives are decreased in comparison with other additives.

3.2.6 Thermal stability of the prepared antioxidant additives

Some of the highly effective antioxidant additives, namely additives **11-15**, were subjected to thermal analysis using TGA and DTGA techniques. The data indicated that, the first

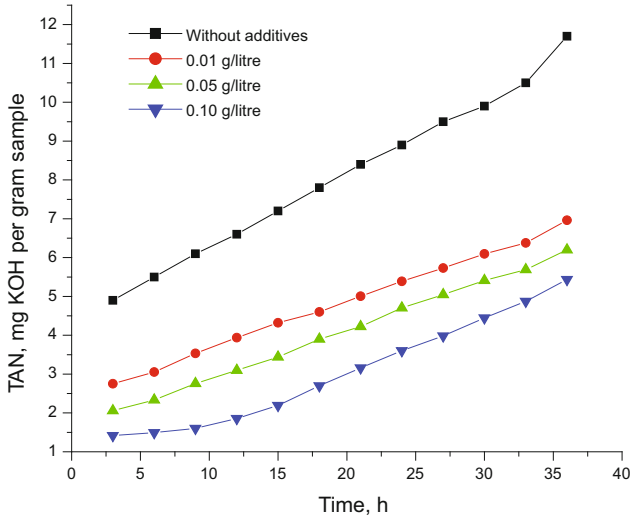


Fig. 5 Variation of the acid value with oxidation time of the lubricating oil samples without or with different concentrations of additive **15** at 155 ºC in 3-36 h

stage of decomposition began at 185.1 °C for compound **11** and at 241.2 °C for compound **12**, and ended at 251.1 °C and 272.2 °C with weight loss of 11.2% and 16.4%, respectively. Compounds **13-15** began their decomposition in the first stage at 165.5 °C, 188.7 °C, 199.1 °C, and ended them at 237.5 °C, 245.5 °C, 275.3 °C with weight loss of 11.7%, 13.3% and 10.0%, respectively.

3.2.7 A comparison of the oxidation stability between the tested oil containing the prepared products and lubricating oil containing a commercial additive

The oxidation stability of the tested lubricating oil containing the highly efficient prepared antioxidants (0.1 g·L^{-1}) is compared with that of the lubricating oil containing a commercial antioxidant additive purchased from the local market. The results obtained after 36 h oxidation at 155 °C with air rate 10 L h^{-1} are shown in Fig. 6. It can be seen that the lubricating oil containing the compounds **11-15** showed better oxidation stability than the commercial lubricating oil.

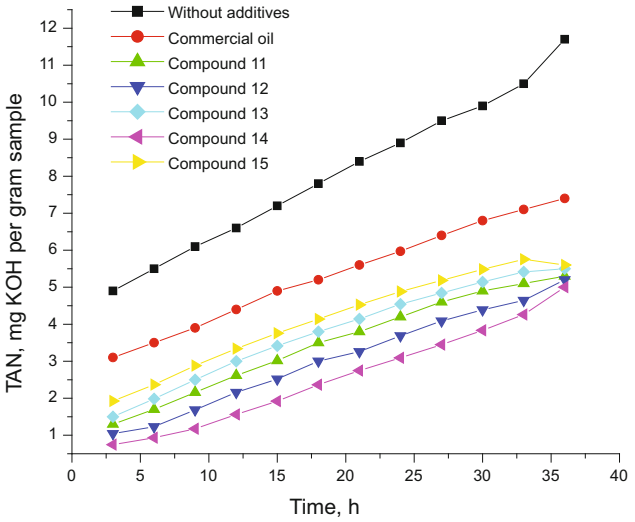


Fig. 6 Evaluation of the tested lubricating oil additives compared with the commercial lubricating oil sample

Table 4 Surface tension for lubricating oil with and without additives (0.1 g·L^{-1} concentration) at 155 °C after 36 h of oxidation for additives **2-23**

Additive used	Surface tension dyn·cm^{-1}	Additive used	Surface tension dyn·cm^{-1}
Lubricating oil before oxidation	45.0	Lubricating oil before oxidation	45.0
Lubricating oil without additives after oxidation	54.0	Oil without additives after oxidation	54.0
Lubricating oil with **2** after oxidation	42.0	13	45.0
3	40.0	14	43.5
4	38.4	15	40.0
5	37.6	16	40.0
6	40.0	17	38.4
7	38.0	18	37.6
8	41.5	19	41.5
9	45.0	20	45.0
10	40.0	21	43.5
11	38.4	22	40.0
12	37.6	23	42.0

4 Conclusion

Newly synthesized imidazolone derivatives seem to be interesting for antioxidant and anticorrosive studies. The present investigation offers rapid and effective new procedures for the synthesis of novel imidazolone derivatives incorporating sulfonate moiety. It is clear that incorporation of aryl sulfonate, oxazolone and imidazolone moieties in the same molecule provide high antioxidant and anticorrosive characteristics. On the other hand, incorporation of pyridine, thiazole, benzothiazole and pyrazole rings into imidazolone compounds was crucial for antioxidant and anticorrosive characteristics as in case of compounds **9-14**.

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