Reaction of Ethylene with C_{18} Monocarboxylic Dienoic Acids

ETHYLENE, the simplest dienophile, reacts with various diene systems to give cyclic adducts in moderate yields (1). We discovered that ethylene will react almost quantitatively with 9,11-t,t-octadecadienoic acid (I) to yield a new C_{20} monocarboxylic acid (II). Its I.V. (Table I) indicates the presence of one double bond, and the infrared absorption at 673 cm^{-1} is characteristic of cyclohexenes.

A 500-ml stainless steel autoclave containing 200 ml of spectral grade 2,2,4-trimethyl pentane and 14.4 g of I prepared by the method of Schneider, et al. (2) was flushed with ethylene and pressurized to 500 psig at room temp with stirring. The autoclave was heated to 260C, which produced a final pressure of 3,400 psig. The temp was maintained for 13 hr. The isolated acids from this reaction contained a neutral fraction presumed to be polymerized ethylene (condensation product). This material was removed by converting the acids to their sodium salts and extracting with petroleum ether. The salts were acidified and distilled under vacuum to give II in 93% yield. The gas chromatogram of II is shown in Figure 1, the physical constants in Table I.

Reaction of ethylene with linoleic acid [1] in the presence of 100% excess NaOH (above that required to produce the salt) and three volumes of ethylene glycol as solvent for 15½ hr at 260C under an initial pressure of 900 psig yielded a similar product (III, Fig. 1), which was isolated in the same manner as II. A residue (19%) was obtained by distillation of the crude acids isolated from this reaction. This material had a neutralization equivalent of 820. Saponification yielded a product with a neutralization equivalent of 346, indicating that the polymer was composed largely of polyester. This finding is in agreement with the previously reported observation in the alkaline isomerization and cyclization of linseed oil (3). The overall yield of C_{20} monomeric adduct based on linoleic acid was 76%.

TABLE I

Physical Constants of the Ethylene Adduct of Methyl 9,11-t,t-Octadecadienoate

	Exp.	Theory
Neutralization equivalent	309	309.5
I.V.	85.5	83.9
Boiling point (a) 20 μ	174C	.....
Refractive Index (a) 30C	1.4739	.....
(C) %	77.83	77.87
(H) %	11.62	11.76

Reaction of ethylene with soybean oil in the presence of 100% excess NaOH and three volumes of ethylene glycol as solvent for 3 hr at 295C under an initial pressure of 800 psig yielded a product (IV, Fig. 1) after distillation of the crude acids. An overall yield of 40.7% C_{20} monomeric adduct was obtained with 6.8% undistillable residue.

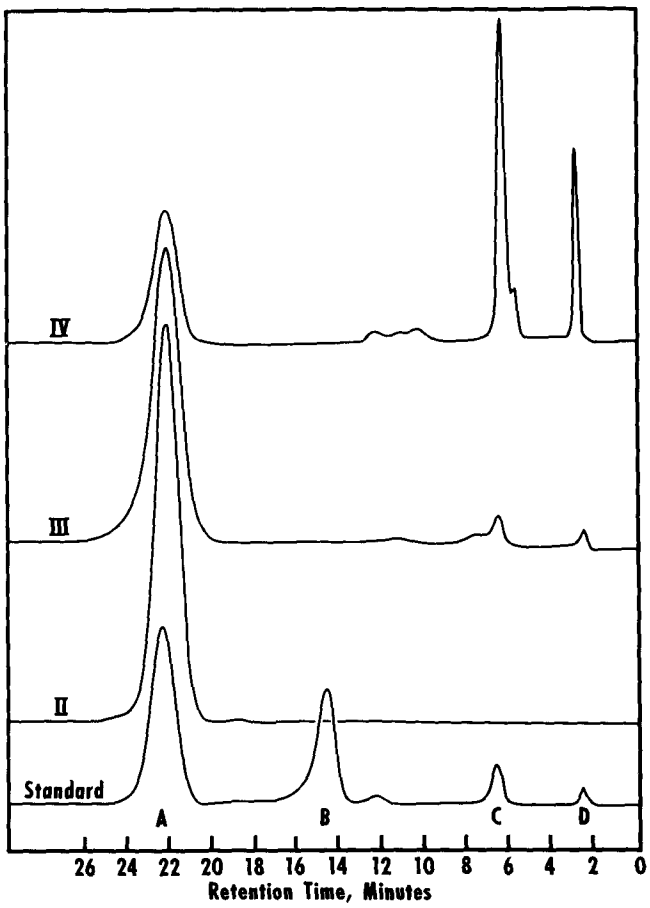

FIG. 1. Gas chromatograms of ethylene adducts from a Pye-Argon chromatograph, column 4 ft x ¼ inch, stationary phase 10% polyester succinate, temp 184C. A = ethylene adduct of methyl 9,11-t,t-octadecadienoate, B = methyl 9,11-t,t-octadecadienoate, C = methyl stearate, D = methyl palmitate.

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[1] The linoleic acid was 96% pure. Some palmitic, stearic, and oleic acids were present.