

The following compounds were prepared. Their chemical shifts are shown in Table I.

N,N'-Bis(methylsulfonylmethyl)urea, $(\text{CH}_3\text{SO}_2\text{CH}_2\text{NH})_2\text{CO}$, was prepared in 38% yield, mp 178–179°, from water. *Anal.* Calcd for $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_6\text{S}$: C, 24.58; H, 4.95; N, 11.47; S, 26.25. Found: C, 24.39; H, 5.51; N, 11.22; S, 26.22.

N-(Methylsulfonylmethyl)benzamide, $\text{CH}_3\text{SO}_2\text{CH}_2\text{NHCOC}_6\text{H}_5$, was prepared in 42% yield, mp 181–182°. *Anal.* Calcd for $\text{C}_9\text{H}_{11}\text{NO}_3\text{S}$: C, 50.69; H, 5.20; N, 6.57; S, 15.04. Found: C, 50.96; H, 5.21; N, 6.85; S, 14.90.

N-(Methylsulfonylmethyl)acetamide, $\text{CH}_3\text{SO}_2\text{CH}_2\text{NHCOC}_2\text{H}_5$, was prepared in 21% yield, mp 110–111°, from chloroform-carbon tetrachloride. *Anal.* Calcd for $\text{C}_4\text{H}_9\text{NO}_3\text{S}$: C, 31.78; H, 6.00; N, 9.27; S, 21.21. Found: C, 32.02; H, 6.13; N, 9.30; S, 20.96.

N-(Methylsulfonylmethyl)methanesulfonamide, $\text{CH}_3\text{SO}_2\text{CH}_2\text{NH}_2$, was prepared in 37% yield, mp 106–107°, from ethyl

acetate. *Anal.* Calcd for $\text{C}_3\text{H}_9\text{NO}_4\text{S}_2$: C, 19.24; H, 4.85; N, 7.48; S, 34.25. Found: C, 18.75; H, 4.92; N, 7.71; S, 34.56.

N,N-Bis(methylsulfonylmethyl)-*p*-toluidine, $(\text{CH}_3\text{SO}_2\text{CH}_2)_2\text{NC}_6\text{H}_4\text{CH}_3$, was prepared on a 0.1-mole scale from *p*-toluidine, mp 141–144° dec. The pmr spectrum of a 10% solution in trifluoroacetic acid showed four singlets at 2.37 (CH_3C_6), 2.90 (CH_3SO_2), 5.48 (NCH_2SO_2), and 7.32 ppm (C_6H_4). The areas of the four peaks were in the ratio of 3:6:4:4. *Anal.* Calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_4\text{S}_2$: C, 45.34; H, 5.88; N, 4.81; S, 22.01. Found: C, 45.31; H, 5.98; N, 4.96; S, 21.84.

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The Photolysis of Diazomethane and Ethyl Diazoacetate in the Presence of 4-Octyne¹

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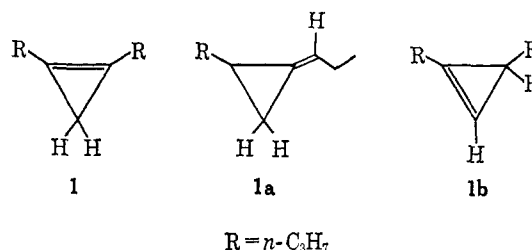
The addition of methylene and carboethoxycarbene, generated photochemically from diazomethane and ethyl diazoacetate, to 4-octyne yielded 1,2-di-*n*-propylcyclopropene and ethyl 1,2-di-*n*-propylcyclopropene-3-carboxylate, respectively. It is shown that a close to statistical reaction of methylene and a more discriminate reaction of carboethoxycarbene with the carbon-hydrogen bonds occur together with addition to the acetylenic bond. Diels-Alder reaction of 1,2-di-*n*-propylcyclopropene and 1,2-di-*n*-propylcyclopropene 3-carboxylate with cyclopentadiene afforded the *endo* adducts in both cases.

One of the many outgrowths of the chemistry of divalent carbon² has been the synthesis of cyclopropenes, especially the reactions of metal-catalyzed decomposition of diazoacetic esters³ with acetylenes. Photolytic decomposition of diazomethane and methyl diazoacetate in the presence of 2-butyne has been reported⁴ to yield 1,2-dimethylcyclopropene and methyl 1,2-dimethylcyclopropene-3-carboxylate, respectively. Because there was an interest in a one-step synthesis of ¹⁴C-3 labeled cyclopropenes in this laboratory, the photoinduced reaction of diazomethane and ethyl diazoacetate with 4-octyne was investigated.

The photodecomposition of diazomethane was carried out at -78° with a high-pressure mercury lamp giving light only above 300 m μ by use of a filter. No solvent was used in order to keep the number of reaction products as low as possible. 1,2-Di-*n*-propylcyclopropene (1) was isolated in yields up to 25% based on *N*-nitrosomethylurea. Its half-life at room temperature is about 4 weeks, and it can be stored in the refrigerator without polymerization.⁵

Structural proof of 1 is based on elemental analysis, and infrared and nmr spectra. The empirical formula C_9H_{16} could imply three structural isomers, 1-1b. The nmr spectrum shows two equivalent *n*-propyl groups and two allylic protons but no vinyl proton,

thus supporting structure 1. The infrared spectrum contains absorption at 1865⁶ and 1007 cm^{-1} ⁷ with no absorption around 910 cm^{-1} ⁸ eliminating vinylcyclopropanes of the type 1a. There is no ultraviolet absorption above 200 m μ . In accordance with structure 1, a positive Halphen test⁹ is observed.



The addition of 1 with excess cyclopentadiene¹⁰ was carried out directly in the photolysis mixture to give the adduct 5a in 75% yield. Elemental analysis and infrared and nmr spectra are in accord with the tricyclic structure. A choice between the *endo* or *exo* configuration for the tricyclooctene 5a was accomplished by nmr spectroscopy. The cyclopropyl proton of *endo* form 5a should be shielded by the double bond and therefore shifted to a higher field compared to that

(1) This work was supported by Public Health Research Grant EF00499-03 from the Division of Environmental Engineering and Food Protection.

(2) P. Migoniac, *Bull. Soc. Chim. France*, 2000 (1962); E. Chinoporos, *Chem. Rev.*, **63**, 235 (1963); W. Kirmse, *Organic Chemistry*, Vol. I, Academic Press Inc., New York, N. Y., 1964.

(3) (a) I. A. D'yakonov and M. I. Komendatov, *Zh. Obshch. Khim.*, **29**, 1749 (1959); (b) R. Breslov, R. Winter, and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959); (c) see F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964), for further reference.

(4) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

(5) Cyclopropene itself cannot be stored at -75°: M. J. Schlatter, *J. Am. Chem. Soc.*, **63**, 1733 (1941).

(6) Faure and Smith⁷ found a weak absorption in sterculic acid at 1865 cm^{-1} and anticipate that the carbon-carbon double-bond stretching frequency in cyclopropenes should lie between those of simple olefins and acetylenes; for further references, see ref 3c.

(7) P. K. Faure and J. C. Smith, *J. Chem. Soc.*, 1818 (1956).

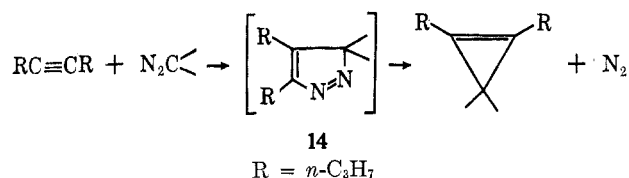
(8) This absorption is due to vinylic carbon-hydrogen out-of-plane vibrations: cf. L. F. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 51.

(9) F. C. Magne, *J. Am. Oil Chemists' Soc.*, **42**, 332 (1965).

(10) Cyclopropenes readily undergo Diels-Alder additions: (a) K. W. Wiberg and W. J. Bartley, *J. Am. Chem. Soc.*, **82**, 6375 (1960); (b) M. A. Battiste, *Chem. Ind. (London)*, 550 (1961); *J. Am. Chem. Soc.*, **85**, 2175 (1963); (c) M. A. Battiste, *Tetrahedron Letters*, No. 50, 3795 (1964).

ported the tricyclooctene ester structure. Catalytic hydrogenation gave the saturated product (6b). Comparison of nmr spectra for 5b and 6b revealed the same relationship for the cyclopropyl proton resonance that was observed for 5a with similar shielding of 0.62 ppm. The configuration of the adduct 5b is therefore considered to be *endo*.

The mechanism of the photolytic reaction of diazomethane and ethyl diazoacetate with 4-octyne is not understood at this time. It is uncertain whether direct addition of free carbenes to the acetylenic bond or photolytic decomposition of intermediate pyrazolen-



ines 14 occurs, or if both species are involved in formation of cyclopropenes and products of insertion reactions into the carbon-hydrogen bond.²²

Experimental Section

All boiling points are uncorrected. Infrared spectra were taken on Perkin-Elmer, Model 337 or Beckman IR-4 spectrophotometers. Nuclear magnetic resonance spectra were taken on a Varian A-60 spectrometer, using tetramethylsilane as an internal standard. Chemical shifts are measured to the estimated center of moment of a multiplet or singlet. Elemental analysis was carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

The Photolytic Reaction of Diazomethane with 4-Octyne.—A solution of diazomethane in decalin was prepared by adding 30 g of *N*-nitrosomethylurea to a well-stirred, ice-cold mixture of 600 ml of decalin and 120 ml of 40% aqueous potassium hydroxide over a 30-min period. After separation of the two-layer system and drying of the decalin phase over potassium hydroxide pellets, the diazomethane was transferred into 300 ml of chilled (−78°) 4-octyne by passing a stream of dry nitrogen through the diazomethane solution and allowing it to come to room temperature. The irradiation of the diazomethane-4-octyne system was accomplished by means of a water-cooled (25°), high-pressure mercury immersion lamp (75 w, designed and built in this laboratory) surrounded by a transparent Pyrex glass dewar vessel, which served as both a heat shield and light filter. This complete unit was immersed in the reaction solution which was maintained at −78°. A total of four doses of diazomethane was introduced at intervals sufficiently long to permit the decomposition of the preceding dose. The diazomethane content of each run was determined by titration against benzoic acid, and varied from 65 to 70% with the average concentration of 0.4 *M* in the 4-octyne.

Gas chromatography [15% tricyanoethylpropane on Chromosorb P (TCEP), 45°] of the photolyzed reaction mixture indicated 38% of 1,2-di-*n*-propylcyclopropene (1), 19% of 7-methyl-4-octyne (3), and 23% of 4-nonyne (4)²³ corresponding to 25, 12, and 15% of theory based on *N*-nitrosomethylurea (acetone as internal standard). Chromatography (15% TCEP, 45°) did not resolve 6-methyl-4-octyne (2) from 4-octyne but easily separated this mixture from the other compounds in a concentrate after distilling off most of the 4-octyne; in this case analysis was made by chromatography with known mixtures of the authentic acetylenes. Thus in a normal run 19% of 6-methyl-4-octyne (2) (12% based on *N*-nitrosomethylurea) was detected.

1,2-Di-*n*-propylcyclopropene (1).—Samples of 1 were collected on a preparative gas chromatography column (5 ft × 0.5 in. i.d.,

(22) The formation of cyclopropenes by photodecomposition of pyrazolones is well established: G. L. Closs and W. A. Böll, *Angew. Chem.*, **75**, 640 (1963); *J. Am. Chem. Soc.*, **85**, 3904 (1963); R. Anet and F. A. L. Anet, *ibid.*, **86**, 525 (1964).

(23) Identified by comparison with commercially obtained 4-nonyne from K & K Laboratories, Inc.

15% TCEP, 55°) from a fraction²⁴ boiling from 140 to 145° (760 mm) of the above photolysis solution and were stable when stored at 0° under nitrogen. At room temperature 1 polymerized slowly, and could not be detected²⁵ by means of the Halphen reaction after a period of 8 weeks. Pure 1 (*n*_D²⁰ 1.4310) showed no absorption in the ultraviolet (10^{−3} *M*, in ethanol). Infrared (CCl₄) showed 1865 (cyclopropenyl C=C stretch)⁷ and 1007 cm^{−1}.⁸ Nmr (CCl₄) showed 2.48 (triplet, *J* = 7.0 cps, 4 H, allylic), 1.66 (sextet, *J* = 7.0 cps, 4 H, CH₂), 1.0 (triplet, *J* = 6.5 cps, 6 H, CH₃), and 0.78 ppm (singlet, 2 H, cyclopropenyl), consistent with the structure assigned.

Anal. Calcd for C₉H₁₆: C, 87.02; H, 12.97. Found: C, 87.17; H, 13.02.

6-Methyl-4-octyne (2).—Lithium-1-pentyne²⁶ (0.15 mole in 140 ml of dry dioxane) was heated with *sec*-butyl bromide (41.1 g, 0.30 mole) in an autoclave for 17 hr at 150°. After cooling to room temperature the reaction mixture was poured into 1000 ml of water and the resulting mixture was extracted with ether. The extracts were neutralized with 10% sulfuric acid and dried over anhydrous calcium chloride. Evaporation of the ether and distillation of the residue afforded 1.5 g (4%) of product, bp 136–138° (760 mm). Purification by gas chromatography (15% TCEP, 90°) showed little contamination by 2-bromobutane. Collection of the major product afforded pure 2, *n*_D²⁰ 1.4237. Nmr (CCl₄) showed 2.21 (multiplet, 3 H, allylic), 1.41 (broad multiplet, 4 H, CH₂), and 0.81 ppm (multiplet, 9 H, CH₃).

Anal. Calcd for C₉H₁₆: C, 87.02; H, 12.97. Found: C, 86.96; H, 13.17.

Both authentic and original 2 had the same analytical data.

7-Methyl-4-octyne (3).—To a slightly brown solution of lithium-1-pentyne²⁶ (0.15 mole in 140 ml of dry dioxane) was added dropwise at 90° isobutyl *p*-toluenesulfonate (32 g, 0.14 mole). After 1 hr at this temperature the reaction mixture solidified. On working up as shown for 6-methyl-4-octyne (2) the residue was distilled to yield 3.0 g (17%) of acetylene 3, bp 55° (27 mm); *n*_D²⁰ 1.4250. Nmr (CCl₄) showed 2.20 (multiplet, 4 H, allylic), 1.60 (multiplet, 3 H, CH₂), 1.01 (multiplet, 9 H, CH₃) with superimposed peaks at 0.99 (triplet, *J* = 7.0 cps), and 0.98 ppm (doublet, *J* = 6.0 cps) consistent with 7-methyl-4-octyne (3).

Anal. Calcd for C₉H₁₆: C, 87.02; H, 12.97. Found: C, 87.05; H, 12.74.

Authentic and original 3 were identical in infrared and nmr spectroscopy.

The Reaction of 1,2-Di-*n*-propylcyclopropene (1) with Cyclopentadiene. Adduct 5a.—Freshly distilled cyclopentadiene (15 g, 0.227 mole) was added to 148 g of a reaction mixture from the photolysis of diazomethane with 4-octyne which contained 20 g of 1. After 24 hr at 50° the fraction boiling from 96 to 100° (5 mm) was collected; redistillation of this fraction yielded the pure adduct 5a (23 g, 75%), bp 98.5–100° (5 mm), *n*_D²⁰ 1.4759. Infrared (neat) showed 3065, 1102, 1044, 995, 903, and 741 cm^{−1}. Nmr^{27,28} (CCl₄) showed 5.76 (triplet), 2.57 (multiplet), 1.68 (multiplet), 1.43 (multiplet), 0.62 (doublet, cyclopropyl), and 0.91 ppm (triplet).

Anal. Calcd for C₁₄H₂₂: C, 88.35; H, 11.65. Found: C, 88.44; H, 11.76.

Hydrogenation of Adduct 5a.—A mixture of 5% palladium on charcoal (2 g) and 5a (9.0 g, 0.0474 mole) in 100 ml of ethyl acetate was hydrogenated under a hydrogen pressure of 200 psi at room temperature. After hydrogen uptake the solvent was removed. On distillation with a short-path still the pure, saturated adduct 6a was obtained (8.8 g, 97%), bp 93–94° (2.3 mm), *n*_D²⁰ 1.4725. Infrared (neat) showed 3065 (cyclopropyl CH), 1102, 1036, 986, and 903 cm^{−1}. Nmr²⁷ (CCl₄) showed 2.06 (broad singlet), 1.29 (doublet, cyclopropyl), and 1.17 ppm (broad singlet).

(24) This fraction contained approximately 38% of 1, determined by nmr spectroscopic comparison of the cyclopropenyl-H singlet at 0.78 ppm in a pure sample of 1 and the above, distilled fraction.

(25) Cf. A. J. Deutschman, Jr., and I. S. Klaus, *Anal. Chem.*, **32**, 1809 (1960).

(26) Lithium-1-pentyne was prepared by adapting the procedure of Schlubach and Repenning¹⁸ for lithium-1-hexyne.

(27) The spectrum had a rather complex pattern and only clearly distinguishable absorptions are listed. The relative peak areas agreed with the structure assigned. In all cases the CH₂ protons were masked and thus not identified.

(28) These values should be compared with the reported frequencies for the adduct cyclopropene-cyclopentadiene.^{10a}

Anal. Calcd for $C_{14}H_{24}$: C, 87.40; H, 12.58. Found: C, 87.42; H, 12.58.

The Photolytic Reaction of Ethyl Diazoacetate with 4-Octyne.—Ethyl diazoacetate (10 g, 0.87 mole) in 90 ml of degassed 4-octyne was irradiated under oxygen-free nitrogen with a water-cooled, high-pressure mercury immersion lamp (quartz ultraviolet) at room temperature until the diazoester could no longer be detected in the infrared (2130 cm^{-1} , diazo stretching). After removal of excess 4-octyne by vacuum distillation [bp up to 55° (20 mm)] the residue was fractionated using gas chromatography (15% TCEP, 120° , nitrobenzene as internal standard). The major fraction (61%) had the following spectra: infrared (neat) showed 1900 cm^{-1} (cyclopropenyl C=C stretching), 1725 cm^{-1} (ester C=O), and 1025 cm^{-1} ; nmr (CCl_4) showed 4.32 (quartet, $J = 7.0\text{ cps}$, 2 H, OCH_2), 2.51 (triplet, $J = 7.5\text{ cps}$, 4 H, allylic), 2.13 (singlet, 1 H, cyclopropenyl), 1.41 (broad multiplet, 13 H, aliphatic), with superimposed peaks at 1.26 (triplet, $J = 7.4\text{ cps}$) and 0.98 ppm (triplet, $J = 7.0\text{ cps}$), consistent with ethyl 1,2-di-*n*-propylcyclopropene-3-carboxylate (7)¹⁶ (58%).

The first minor product (14%) was identical with authentic 8 in infrared and nmr spectra (15% yield).

The second minor product (15%) exhibited these spectra: infrared (neat) showed 1740 cm^{-1} (ester C=O); nmr (CCl_4) showed 4.39 (quartet, $J = 7.0\text{ cps}$, 2 H, OCH_2), 2.30 (multiplet, 6 H, allylic), and 1.39 ppm (broad multiplet, 13 H, aliphatic), consistent with ethyl 3-methyl-5-nonynoate (9, 16%).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.30; H, 10.25. Found: C, 73.20; H, 10.15.

The third minor product (10%) showed a band at 1740 cm^{-1} (ester C=O) in the infrared (neat). The nmr spectrum ($CDCl_3$) contained absorptions at 4.39 (quartet, $J = 7.0\text{ cps}$, 2 H, OCH_2), 2.50 (multiplet, 6 H, allylic), and 0.85 ppm (broad multiplet, 12 H, aliphatic), consistent with ethyl 6-decynoate (10, 11%).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.30; H, 10.25. Found: C, 73.01; H, 10.05.

When radiation of the above mixture was carried out in the presence of atmospheric air, the above products were obtained in yields of 38% for 7, 14% for 8, 14% for 9, and 10% for 10, and two additional fractions were collected. The infrared and nmr spectra of the lowest boiling fraction (17%) were identical with those of authentic 4-octyn-3-one (11, 9%) while the spectra of the next higher boiling fraction (21%) were identical with those of authentic 4-octyn-3-ol (12, 15%, based on ethyl diazoacetate).

4-Octyn-3-ol (12).—The Grignard reagent prepared from ethylmagnesium iodide (0.60 mole) and 1-pentyne (34 g, 0.50 mole) was treated with propionaldehyde (29 g, 0.50 mole) for 3 hr in refluxing ether. On working up with saturated ammonium chloride solution, 7.8 g (13%) of 12 was obtained, bp $92\text{--}92.5^\circ$ (24 mm), n_D^{20} 1.4505. Infrared (neat) showed 3400 cm^{-1} (asymmetric OH) and 2260 cm^{-1} ($C\equiv C$). Nmr (CCl_4) showed 4.27 (triplet, $J = 6.0\text{ cps}$, 1 H, $\equiv CCHO$), 3.90 (singlet, 1 H, OH), 2.20 (multiplet, 2 H, $CH_2C\equiv C$), 1.55 (multiplet, 4 H, CH_2), 0.98 (triplet, $J = 6.5\text{ cps}$), and 0.98 ppm (triplet, $J = 6.0\text{ cps}$), both together integrating for six protons (CH_3).

Anal. Calcd for $C_8H_{14}O$: C, 76.13; H, 11.18. Found: C, 76.37; H, 11.22.

4-Octyn-3-one (11).—To a suspension of active manganese dioxide²¹ (1.32 g) in 15 ml of light petroleum ether (bp $30\text{--}60^\circ$) was added 12 (0.150 g, 0.0012 mole) and the reaction mixture was stirred for 30 min at room temperature. Filtration and evaporation of the solvent yielded 11 (0.140 g, 95%). Gas chromatography (15% TCEP, 115°) indicated 95% purity. Infrared (neat) showed 2220 cm^{-1} (conjugated $C\equiv C$) and 1680 cm^{-1} (ketone C=O). Nmr (CCl_4) showed 2.30 (multiplet, 4 H, allylic), 1.10 (multiplet, 2 H, CH_2), 0.90 (triplet, $J = 7.0\text{ cps}$) and 0.86 ppm

(triplet, $J = 7.0\text{ cps}$) both together integrating for six protons (CH_3).

Anal. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.45; H, 9.71.

Ethyl 3-Ethyl-4-octynoate (8).—To a solution of 12 (6.0 g, 0.048 mole) and pyridine¹⁹ (0.1 ml) in 20 ml of anhydrous ether was added dropwise phosphorus tribromide (4.66 g, 0.017 mole) then refluxed for 3 hr. On work-up, the ether layer yielded 3-bromo-4-octyne (4.72 g, 52%), bp $89\text{--}93^\circ$ (19 mm), n_D^{20} 1.4860. Infrared (neat) showed 2262 cm^{-1} ($C\equiv C$). Nmr (CCl_4) showed 4.51 (triplet, $J = 6.5\text{ cps}$, 1 H, $\equiv CCHBr$), and 1.60 ppm (broad multiplet, 12 H, allylic and aliphatic).

In a malonic ester synthesis,²⁰ 3-bromo-4-octyne (4.1 g, 0.022 mole) and ethyl malonate (5.15 g, 0.32 mole) yielded 3-ethyl-4-octynoic acid (2.75 g, 77%), bp $132\text{--}135^\circ$ (5 mm), n_D^{20} 1.4542. Infrared (neat) showed broad absorption in the $3340\text{--}cm^{-1}$ region (asymmetric OH). Nmr (CCl_4) showed 12.17 (singlet, 1 H, COOH) and 2.45 ppm (broad multiplet, 5 H, allylic).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.41; H, 9.44.

Upon esterification of 3-ethyl-4-octynoic acid with excess ethanol containing small amounts of *p*-toluenesulfonic acid, 8 was obtained in 95% yield, bp $100\text{--}101^\circ$ (55 mm), n_D^{20} 1.4426. Infrared (neat) showed 1740 cm^{-1} (ester C=O). Nmr (CCl_4) showed 4.12 (quartet, $J = 7.5\text{ cps}$, 2 H, OCH_2), 2.65 (multiplet, 1 H, $C\equiv CCH$), 2.15 (multiplet, 4 H, allylic), and 1.32 (multiplet, 13 H, aliphatic) with these superimposed peaks: 1.23 (triplet, $J = 7.0\text{ cps}$) and 0.96 ppm (triplet, $J = 7.0\text{ cps}$).

Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.30; H, 10.25. Found: C, 73.43; H, 10.24.

Hydrogenation of Ethyl 3-Methyl-5-nonynoate (9) and Ethyl 6-Decynoate (10).—Samples of 9 and 10 in ethyl acetate were hydrogenated over 5% palladium on charcoal at room temperature and under atmospheric pressure. After purification by gas chromatography (SE 52, 155°) the hydrogenation product of 9 was identical with authentic ethyl 3-methylpelargonate (13)³⁰ and 10 with ethyl caprate.

The Reaction of 1,2-Di-*n*-propylcyclopropene-3-carboxylate (7) with Cyclopentadiene. Adduct 5b.—Freshly distilled cyclopentadiene (5 g, 0.076 mole) and 7 (5.05 g, 0.026 mole) were refluxed for 12 hr. After evaporation of excess cyclopentadiene the residue was distilled with a short-path still to yield the tricyclooctene ester 5b (5.75 g, 85%), bp $95\text{--}96.5^\circ$ (0.1 mm), n_D^{20} 1.4812. Infrared (neat) showed 3065 and 1730 cm^{-1} (ester C=O). Nmr (CCl_4)²⁷ showed 5.86 (triplet), 3.93 (quartet), 2.70 (multiplet), 2.04 (multiplet), 1.40 (singlet, cyclopropyl³¹), 1.15 (triplet), and 0.92 ppm (triplet).

Hydrogenation of Adduct 5b.—On hydrogenation of 5b (0.66 g) in 5 ml of ethyl acetate containing 5% palladium on charcoal (200 mg) at room temperature and atmospheric pressure the saturated adduct 6b (0.64 g, 96%) was obtained, bp 118° (0.65 mm), n_D^{20} 1.4752. Infrared (neat) showed 3066 cm^{-1} (cyclopropyl CH) and 1730 cm^{-1} (ester C=O). Nmr (CCl_4)²⁷ showed 4.0 (quartet), 2.18 (broad singlet), 1.82 (singlet, cyclopropyl), 1.25 (multiplet), 1.19 (triplet), and 0.89 ppm (triplet).

Anal. Calcd for $C_{17}H_{26}O_2$: C, 77.22; H, 10.67. Found: C, 77.22; H, 10.72.

(29) The general procedure of M. S. Newman and J. H. Wotiz, *J. Am. Chem. Soc.*, **71**, 1292 (1949).

(30) Authentic 13 was prepared according to the procedure in ref 20 and had the required analytical data.

(31) This assignment is supported by the work of Sauers and Sonnet who report the signal for the cyclopropyl proton in the *endo* adduct obtained from ethyl diazoacetate and norbornadiene at 1.34 ppm (τ 8.66): R. R. Sauers and P. E. Sonnet, *Chem. Ind. (London)*, 786 (1963).