In a similar manner, the adduct **4** of methyl deuteriopropiolate **2** and anthracene was hydrogenated to ester **7**, whose pyrolysis afforded methyl *cis*-β-deuterioacrylate **9**.

Propiolic acid was prepared inexpensively by the decarboxylation[9] of the monopotassium salt of acetylenedicarboxylic acid in water; conducting the decarboxylation in D_2O afforded a simple preparation of deuteriopropiolic acid containing 88% deuterium. The combination of these methods allows a rapid and highly stereospecific preparation of β-deuterated acrylic esters.

Experimental Section

Methyl 3-Deuteriopropiolate (2).—Acetylenedicarboxylic acid monopotassium salt (34 g, 0.224 mol) in deuterium oxide (100 g, 99.8% D_2O) was stirred under nitrogen for 2 hr. The temperature was increased slowly over 6 hr to 100°, and the solution refluxed 1 additional hr. After cooling in an ice bath, the solution was acidified with dilute deuteriosulfuric acid, extracted with five 200-ml portions of ether, dried over magnesium sulfate, concentrated, and distilled *in vacuo* affording 11 g (70%) of 3-deuteriopropiolic acid, bp 45–55° (15 mm).

The 3-deuteriopropiolic acid in methylene chloride (100 ml) and methanol (50 ml) containing a trace of concentrated sulfuric acid was refluxed for 3 days. After being poured into ice water, the organic layer was washed with 10% sodium bicarbonate solution, water, and dried over magnesium sulfate. Removal of the solvent afforded a colorless oil, which was distilled from a spinning-band column giving 10.2 g (77%) of pure methyl 3-deuteriopropiolate, bp 100–101° (740 mm). The ir spectrum (CCl_4) showed strong peaks at 1720 (ester $C{=}O$) and 1975 cm^{-1} ($-C{\equiv}CD$). The nmr spectrum (neat) showed peaks at δ 3.41 (s, $-CO_2CH_3$) and 2.90 (s, $C{\equiv}CH$); integration of these peaks showed the presence of 87.5–88.5% of one deuterium.

Methyl Propiolate–Anthracene Adduct (3).—The published procedure[10] for the preparation of the ethyl propiolate adduct was followed. A mixture of anthracene (40 g, 0.225 mol) and methyl propiolate (22 g, 0.262 mol) in anhydrous xylene (100 ml) was refluxed under nitrogen for 7 days. After cooling slowly to room temperature, the crystalline product was filtered and recrystallized from absolute ethanol, affording 39 g (66%) of adduct (**3**), mp 174–175°. Further recrystallization from ethanol raised the melting point to 177–178°: nmr ($DCCl_3$) δ 3.70 (s, 3, $-CO_2CH_3$), 5.20 (d, 1, $J = 6$ Hz, H_2), 5.68 (d, 1, $J = 3$ Hz, H_1), 7.85 (dd, 1, $J = 6.0$ and 3.0 Hz, $R = H$), and 6.85–7.45 (m, 8, aromatic). Hydrolysis of **3** with alcoholic potassium hydroxide gave in quantitative yield the known acid, mp 248–250° dec (lit.[10] mp 249–250.2° dec).

Methyl 3-Deuteriopropiolate–Anthracene Adduct (4).—Adduct **4** was prepared in the same way from anthracene and methyl 3-deuteriopropiolate (**2**): it melted at 172–174° and showed the parent peak in the mass spectrum at *m/e* 263; nmr ($DCCl_3$) δ 3.70 (s, 3, $-CO_2CH_3$), 5.20 (s, 1, H_2), 5.68 (s, 1, H_1), and 6.85–7.45 (m, 8, aromatic). Comparison of the integrated intensities of the methoxyl and olefinic protons indicated 88% olefinic deuterium.

Catalytic Deuteration of 3.—A solution of adduct **3** (8 g, 30 mmol) in 200 ml of ethyl acetate was stirred with 50 mg of 5% palladium on calcium carbonate under an atmosphere of deuterium (99.9%). The catalyst was filtered after the theoretical consumption of deuterium and the solvent was removed *in vacuo*, affording **6** in quantitative yield, mp 114–115°. Recrystallization from methanol raised the melting point to 117–118° (lit.[11] mp 117–118°): nmr ($DCCl_3$) δ 2.15 (d, 1, $J = 5$ Hz, $R_1 = H$), 3.53 (s, 3, $-CO_2CH_3$), 4.66 (s, 1, H_1), 4.30 (d, 1, $J = 5$ Hz, H_2), and 7.0–7.5 (m, 8, aromatic).

Hydrogenation of Adduct 4.—Ester **7** was prepared in the same manner by catalytic hydrogenation of adduct **4** in 91% yield: mp 114–116°; nmr ($DCCl_3$) δ 3.53 (s, 3, $-CO_2CH_3$), 4.29 (d, 1, $J = 5$ Hz, H_2), 4.65 (d, 1, $J = 5$ Hz, H_1), 2.85 (dd, 1, $J = 5$ and 10.0 Hz, $R_3 = H$), 1.98 (m, 1, $R_2 = H$), and 7.0–7.5 (m, 8, aromatic).

Anthracene–Methyl Acrylate Adduct (5).—Adduct **5** was prepared as described by Wawzonek and Hallum[11] and, after recrystallization from methanol, had mp 117–118°; nmr ($DCCl_3$) δ 1.98 (dd, 1, $J = 12$ and 5 Hz, $R_2 = H$), 2.10 (dd, 1, $J = 5$ and 4 Hz, $R_1 = H$), 2.7–3.0 (m, 1, $R_3 = H$), 3.53 (s, 3, CO_2CH_3), 4.30 (*t*, 1, $J = 5$ Hz, H_2), 4.66 (d, 1, $J = 5$ Hz, H_1), and 7.0–7.5 (m, 8, aromatic).

Methyl α-*trans*-β-Dideuterioacrylate (8).—Ester **6** (8.0 g, 30 mmol) was heated slowly to 290–300° at atmospheric pressure in a simple 25-ml distillation flask equipped with a nitrogen inlet. The volatile ester (bp *ca.* 80°) was slowly released over a 1-hr period and was collected in a receiver cooled to −80°; anthracene sublimed slowly to the neck of the distillation flask and was discarded. The colorless distillate was redistilled, affording 2.4 g (94.5%) of pure **8**: bp 78–80°; nmr (neat) δ 6.3 (1:1:1 t, 1, $J = 2.7$ Hz, *cis*-β proton) and 3.70 (s, 3, CO_2CH_3). Integrated intensities of these two peaks showed the presence of greater than 98% of two deuteriums in **8**.

Methyl *cis*-β-Deuterioacrylate (9).—Ester **7** (18.0 g, 0.068 mol) was heated to 300° at atmospheric pressure under nitrogen as outlined above, distilling the volatile ester **9** (5.5 g, 93% yield): bp 79–80°; nmr (neat) δ 3.70 (s, 3, CO_2CH_3) and 5.7–6.4 (m, 2.15, olefinic protons). The olefinic region of the nmr spectrum was very similar to the published[5b] spectrum of the corresponding isopropyl ester.

Methyl α-*cis*-β-Dideuterioacrylate (10).—The ester with *trans* deuteriums was prepared by the method used by Schuerch and Fowells[6,12] for the isopropyl ester.

Methyl propiolate (8.5 g, 0.102 mol) was added rapidly to a stirred blue-green solution of chromous chloride (25 g) in deuterium oxide (100 ml, 99.9% D_2O) at 5° under nitrogen. The mixture was stirred at ambient temperature overnight, then saturated with solid ammonium sulfate, extracted with ten 100-ml portions of ether, dried over magnesium sulfate and carefully concentrated. The residual oil was distilled, affording 400 mg (4.5%) of **10**: bp 78–80°; nmr (CCl_4) δ 3.70 (s, 3, $-CO_2CH_3$) and 5.80 (1:1:1 t, 1, $J = 1.5$ Hz, *trans*-β H). The nmr spectrum was the same in the vinyl region as that reported[6a] for the corresponding isopropyl ester, and showed greater than 98% incorporation of two deuteriums.

Registry No.—**2**, 18910-46-8; **3**, 18910-47-9; **4**, 18910-48-0; **5**, 13294-86-5; **7**, 18916-93-3; **8**, 3321-61-7; **9**, 18910-51-5; **10**, 3321-60-6; 3-deuteriopropiolic acid, 18910-53-7.

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[9] K. Alder and G. Stein, *Ann.*, **525**, 183 (1936).

[10] W. R. Vaughan and K. M. Milton, *J. Amer. Chem. Soc.*, **74**, 5623 (1952).

[11] S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

[12] We thank Professor Schuerch for his kindness in sending us detailed directions from the Ph.D. thesis of W. Fowells for the chromous chloride reduction.

Concerning Chlorocarbonium Ions as Intermediates in the Reaction of Ketones with Phosphorus Pentachloride

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In an earlier article,[1] the formation of the products which result from the reaction of ketones with phosphorus pentachloride was explained by assuming that chlorcarbonium ions, R_2ClC^+, were the reactive intermediates. In two later papers,[2,3] arguments that

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[1] M. S. Newman and L. L. Wood, Jr., *J. Amer. Chem. Soc.*, **81**, 4300 (1959).

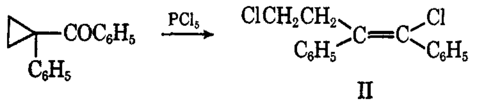
[2] M. S. Newman and G. Kaugars, *J. Org. Chem.*, **31**, 1379 (1966).

[3] M. S. Newman and G. Kaugars, *ibid.*, **31**, 3105 (1965).

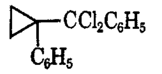
chlorocarbonium ions were not involved were presented. The experimental facts were that different products resulted when certain ketones were brought into contact with phosphorus pentachloride in carbon tetrachloride or in methylene chloride. Acting on information that phosphorus pentachloride was a dimer, P_2Cl_{10}, in carbon tetrachloride and a monomer, PCl_5, in chloroform[4] we accounted for the products isolated by using differences in behavior of P_2Cl_{10} and PCl_5 with the ketones involved. We assumed that PCl_5 was the species present in methylene chloride as this was expected to be more like chloroform than carbon tetrachloride as a solvent.[2,3]

In a recent conversation Professor Shore told me that phosphorus pentachloride is mainly (*ca.* 80%) monomer in *both* CCl_4 and $CHCl_3$ at about 30–35°.[5] Assuming that PCl_5 is mainly monomeric in methylene chloride, new interpretations of the reactions previously discussed[2,3] must be made.

On reaction of phenyl 1-phenylcyclopropyl ketone (I) with phosphorus pentachloride *cis*-1,4-dichloro-1,2-diphenyl-1-butene (II) and phenyl(1-phenylcyclopropyl)dichloromethane (III) were formed.[2] In carbon tetrachloride at room temperature only III was obtained (60% of I recovered after 3 days) while at reflux (1.5 hr) 26% II and 70% III were obtained. In methylene chloride II was the main product under all conditions. Furthermore, the rate of reaction in methylene chloride was considerably greater, although not exactly measured.

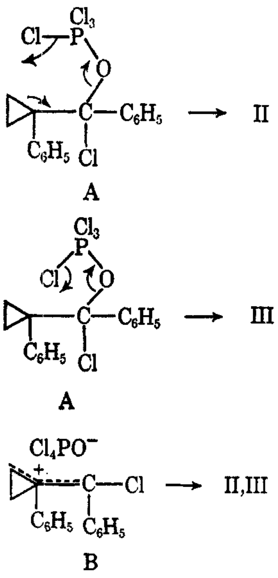


I II



III

Instead of the explanation previously given[2] the following one, which uses only monomeric PCl_5, is given. In each solvent the complex A, formed by addition of PCl_5 to ketone, is produced. A can further collapse by intramolecular processes to yield II or III as shown. Alternatively A may go to a chlorocarbonium ion (or an ion pair) (B) which yields mainly II. The route *via* the carbonium ion or the ion pair would be favored in methylene chloride as compared to carbon tetrachloride because of the dielectric constant differences (8.7 *vs.* 2.2 D).



Similar explanations can be involved in other cases but will not be discussed in this Note. In conclusion, it is pointed out that arguments previously used to discount the probability of chlorocarbonium ions as reaction intermediates have been revised in the light of new information regarding the species present when phosphorus pentachloride is dissolved in carbon tetrachloride or methylene chloride. The likelihood that chlorocarbonium ions may be reaction intermediates is now favored in certain cases.

Registry No.—PCl_5, 10026-13-8.

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[4] In a conversation, Professor S. Shore of this department gave me this information. The experimental work was done at temperatures below 0° but I was unaware of this fact and assumed that the molecular weights had been determined at room temperature.

[5] These results have recently been obtained in an apparatus which allows for extremely accurate readings of vapor pressure and will be reported by Shore and coworkers.

The Preparation of Nopadiene and 2-Ethylidene-6,6-dimethylbicyclo[3.1.1]-3-heptene

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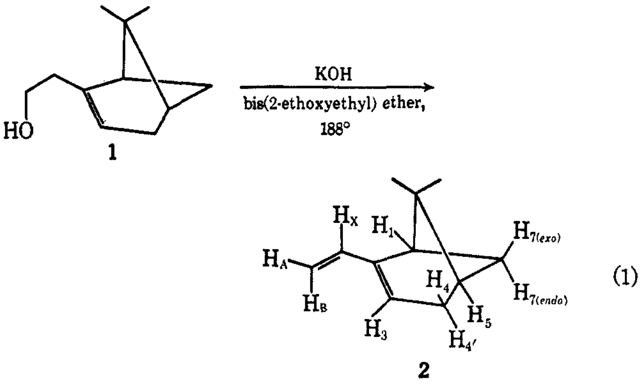
The preparation of nopadiene (**2**) was first reported by Kitchen,[1] who dehydrated the readily available terpene derivative nopol (**1**) using the conditions shown in eq 1. In 1955, Ohloff and Schade[2] reported their results on the dehydration of nopol using a similar procedure (alkali in heterogenous phase at 200°). Under these rather drastic conditions, the latter workers noted that, in addition to nopadiene, there was formed another hydrocarbon to which they tentatively assigned a monocyclic structure possessing three double bonds. In a subsequent publication,[3] however, the base-catalyzed dehydration of nopol was reported to yield,



(1)

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[1] L. J. Kitchen, *J. Amer. Chem. Soc.*, **73**, 2368 (1951).

[2] G. Ohloff and G. Schade, *Angew. Chem.*, **67**, 427 (1955).

[3] G. Ohloff, *Chem. Ber.*, **90**, 1554 (1957); *Ann. Chem.*, **627**, 79 (1959).