by base, it is necessary to avoid an excess of alkali in the neutralization of the amine salt. After stirring for 15 min. a yellow solid had separated. The water was decanted and the product was water-washed by decantation. The solid was dissolved in 200 ml. of hot methanol, the solution cooled to 30° and 12.1 g. (0.15 mole) of 37% formaldehyde added. The reaction mixture was stirred for 1 hr. at which time a light yellow solid had separated. The product was collected and dried, 16.2 g. (over-all yield of 40.8%), m.p. 114–118°. Recrystallization from chloroform gave yellow rods, m.p. 119–121°.

1-(3',3'-Dinitrobutyl)-3,6-dinitro-1,3,6-triazacycloheptane. A solution of 0.8 g. (0.02 mole) of sodium hydroxide in 30 ml. of water was added to a suspension of 3.2 g. (0.02 mole) of ethylenedinitramine, 3.2 g. (0.04 mole) of 37% formalin, and 30 ml of water. After stirring for 15 min. the solid had dissolved. A solution of 4.0 g. (0.02 mole) of 3,3-dinitrobutylamine hydrochloride[6] in 20 ml. of water was added dropwise. There was an immediate precipitate of a white solid. The product was collected and dried, 6.7 g. (99.3%) m.p. 140–146°. Recrystallization from ethylene dichloride raised the m.p. to 146–147°.

1,3,5-Tris(3',3',3'-trinitropropyl)perhydro-1,3,5-triazine. To a solution of 34.5 g. (0.15 mole) of 3,3,3-trinitropropylamine hydrochloride, 75 ml. of water, and 12.1 g. (0.15 mole) of 37% formaldehyde was added dropwise a solution of 12.3 g. (0.15 mole) of sodium acetate in 50 ml. of water. A yellow solid was immediately precipitated. The product was collected, washed with water, and dried to give 30.7 g. (99.4%), m.p. 118–123°. Recrystallization from methanol gave yellow plates, m.p. 121–123°.

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The Preparation of Diethylphosphonoalkyl Acrylates

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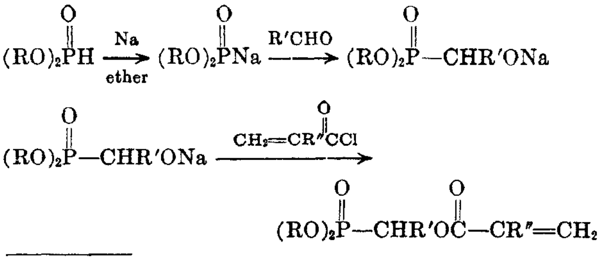
A recent patent by O'Brien, Park, and Lane[1] concerning the preparation of dialkylphosphonoalkyl acrylates prompts us to report our preparation of these compounds and simple polymers derived therefrom. We have found that the acrylate or methacrylate esters can be prepared directly from the sodium salts of the hydroxyalkylphosphonic esters[2] *via* the following sequence of reactions:



$$(RO)_2\overset{O}{\overset{\|}{P}}H \xrightarrow[\text{ether}]{Na} (RO)_2\overset{O}{\overset{\|}{P}}Na \xrightarrow{R'CHO} (RO)_2\overset{O}{\overset{\|}{P}}-CHR'ONa$$

$$(RO)_2\overset{O}{\overset{\|}{P}}-CHR'ONa \xrightarrow{CH_2=CR''\overset{O}{\overset{\|}{C}}Cl} (RO)_2\overset{O}{\overset{\|}{P}}-CHR'O\overset{O}{\overset{\|}{C}}-CR''=CH_2$$

In the reactions studied, R' and R'' was either H or CH_3. These compounds have been polymerized using free radical initiators. The polymerization and copolymerization behavior of these materials is currently under study and will be reported in detail at a later date.

EXPERIMENTAL[3]

Diethyl hydroxymethylphosphonate. This alcohol was prepared by the method of Abramov[2] except that acetic acid was used instead of hydrochloric acid to acidify the sodium salt. From 11.5 g. (0.5 g.-atom) of sodium, 69 g. (0.5 mole) of diethyl hydrogen phosphite and 18 g. (0.6 mole) of paraformaldehyde, there was obtained on distillation in vacuum, 55 g. (65%) of colorless product, b.p. 112–115° (1.5 mm.); n_D^{25} 1.4310 (b.p. 123° (3 mm.), no yield reported, n_D^{20} 1.4322).[2]

Anal. Calcd. for $C_5H_{13}O_4P$: C, 35.72; H, 7.81; P, 18.42. Found: C, 35.47; H, 7.87; P, 18.22.

Diethyl 1-hydroxyethylphosphonate. This alcohol can be prepared as described above except that acetaldehyde is used in place of paraformaldehyde. Another convenient method is that of Fields.[4] To a stirred solution of 69 g. (0.5 mole) of diethyl hydrogen phosphite and 10.1 g. (0.1 mole) of triethylamine was added slowly and with external cooling, 27 g. (0.6 mole) of acetaldehyde. After addition of the aldehyde, the solution was heated at 75° for 0.5 hr. using a Dry Ice-condenser. Vacuum distillation gave 64 g. (70%) of a colorless liquid, b.p. 116–119° (1.5 mm.); n_D^{25} 1.4298 (b.p. 139–140° (6 mm.); n_D^{20} 1.4308).[2]

Diethylphosphonomethyl acrylate. The acrylic esters can be prepared directly from the sodium salt of the corresponding alcohol without prior isolation of the alcohol. To the ice-cooled ether solution of sodium diethyl hydroxymethylphosphonate, 45 g. (0.5 mole) of acrylyl chloride containing 0.1% cuprous chloride, was added dropwise. The reaction mixture was stirred for 1 hr. after which time it was refluxed an additional 0.5 hr. The precipitate was removed and the ether evaporated. The resulting yellow oil was distilled in the presence of *t*-butylcatechol to give 39 g. (35%) of a colorless liquid, b.p. 108–110° (0.6 mm.); n_D^{25} 1.4340.

Anal. Calcd. for $C_8H_{15}O_5P$: P, 13.94. Found: P, 13.90.

1-Diethylphosphonoethyl acrylate. The acrylic ester of diethyl 1-hydroxyethylphosphonate was prepared as described above. Distillation gave 35 g. (30%) of a colorless liquid, b.p. 90–93° (0.05 mm.); n_D^{25} 1.4333.

Anal. Calcd. for $C_9H_{17}O_5P$: P, 13.11. Found: P, 12.82.

Diethylphosphonomethyl methacrylate. The methacrylate derivative can be prepared as described above, using 52 g. (0.5 mole) of methacrylyl chloride in place of acrylyl chloride. This procedure affords 54 g. (46%) of a clear liquid, b.p. 92–94° (0.3 mm.); n_D^{23} 1.4398.

Anal. Calcd. for $C_9H_{17}O_5P$: P, 13.11. Found: P, 12.73.

Polydiethylphosphonomethyl acrylate. Polymerizations were carried out in an evacuated sealed tube at 75° for 12 hr., using 0.1 mole % of azobisisobutyronitrile as an initiator. A white, rubbery, benzene-soluble polymer was obtained after precipitation from ether and freeze-drying from benzene; $[\eta]$, 0.13 in benzene at 28.2°.

Anal. Calcd. for $C_8H_{15}O_5P$: C, 43.24; H, 6.81; P. 13.94. Found: C, 43.25; H, 7.05; P, 13.79.

Poly-1-diethylphosphonoethyl acrylate. Polymerization as described above gave a white, rubbery, benzene-soluble polymer; $[\eta]$, 0.33 in benzene at 28.2°.

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(1) J. L. O'Brien, E. Park, and C. A. Lane, U. S. Patent **2,934,555** (to Rohm and Haas Co.), April 26, 1960.

(2) V. S. Abramov, *J. Gen. Chem.*, **22**, 647 (1952); *Chem. Abstr.*, **47**, 5351 (1953).

(3) Analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(4) E. K. Fields, U. S. Patent **2,579,810** (to Research Corp), December 25, 1951; *Chem. Abstr.*, **46**, 6140 (1952).

Anal. Calcd. for $C_9H_{17}O_5P$: C, 45.77; H, 7.26; P, 13.11. Found: C, 45.88; H, 7.76; P, 12.77.

Polydiethylphosphonomethyl methacrylate. Polymerization as described above gave a white, powdery, benzene-soluble polymer.

Anal. Calcd. for $C_9H_{17}O_5P$: C, 45.77; H, 7.26; P, 13.11. Found: C, 45.50; H, 7.62; P, 12.64.

Infrared spectra.[5a,b] The infrared spectra of the prepared compounds exhibit the customary ester (1735 cm.$^{-1}$), carbon-carbon double bond (1640 cm.$^{-1}$), P → O (1250 cm.$^{-1}$), P-O-C (1020 cm.$^{-1}$), 1050 cm.$^{-1}$ and 815 cm.$^{-1}$), and P–O (965 cm.$^{-1}$) absorption. In addition, an OH peak (3500 cm.$^{-1}$) probably due to traces of water is also observed.

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[5] (a) L. J. Bellamy, *The Infrared Spectra of Complex Molecules,* Wiley, New York, 1958. (b) R. Sasin, R. M. Nauman, and D. Swern, *J. Am. Chem. Soc.,* 81, 4335 (1959).

Effect of Ring Size on the Spectra of Some Ketocycloalkano[a]pyrroles

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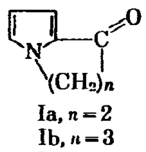
During an investigation of the chemistry of substituted pyrroles, some ketocycloalkano[*a*]pyrroles of the type were synthesized as intermediates



Ia, *n* = 2
Ib, *n* = 3
Ic, *n* = 4

Because of the recent interest in the spectra of pyrrole compounds[1] the ultraviolet spectra and carbonyl absorption frequencies of these compounds are reported herein. These spectral data are recorded in Table I.

For convenience the bands will be designated by an adaptation of the method used by Doub and Vandenbelt[2,3] in the substituted benzene series.

TABLE I
ULTRAVIOLET MAXIMA AND CARBONYL FREQUENCIES OF THE PYRROLES

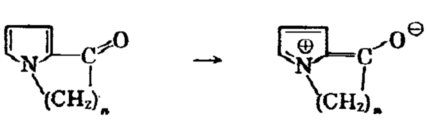
	95% Ethanol		Cyclohexane		Carbonyl Frequencies, Cm.$^{-1}$
	λ (mμ)	ε × 10^{-3}	λ (mμ)	ε × 10^{-3}	
1-Methyl-2-acetylpyrrole	287[a,b]	10.4	—	—	—
Ia	288	19.1	276[c] 282.5	29.6 39.6	1700
Ib	294	17.3	278[c] 288	19.5 21.8	1650
Ic	294[c]	4.74	279.5[c] 288.5	1.71 1.68	1645

[a] Also λ = 245 mμ; ε × 10^{-3} = 4.89. [b] Reference 1a. [c] Shoulder appears in the range 250–270 mμ.

The most displaced intense bands, relative to those of pyrrole, are designated as primary bands and the less intense bands as secondary bands. In the terminology of Eisner and Gore[1c] the primary band is called the K-band and the secondary band is called the B-band. A primary band (λ, 287 mμ) and a secondary band (λ, 245 mμ) have been reported[1a] for 1-methyl-2-acetylpyrrole. In the spectra reported here, only the primary band is observed; the secondary band is either masked completely or appears as a poorly defined shoulder of the primary band. The interpretation of these spectra will be limited to the primary band.

The ultraviolet maxima shifts and ε variations parallel those reported by Schubert and Sweeney[4] and those of Hedden and Brown[5] for the benzocyclanone series. The results can be rationalized by the application of the ideas used by Braude[6] in the substituted acetophenone series.

The primary band is usually ascribed to the nonpolar-polar transition[1a–1c] illustrated below. A



comparison of the spectra of 1-methyl-2-acetylpyrrole and 4-ketocyclopentano[*a*]pyrrole (Ia) shows only an increase in the intensity of the primary band and a masking of the secondary band. The increase in the transition probability can be attributed to the fixing of the carbonyl group in the plane of the pyrrole ring system.

With 5-ketocyclohexano[*a*]pyrrole (Ib) a shift, relative to the five-membered ketone system, of the primary band to longer wave lengths along with a slight decrease in the transition probability

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[1] (a) R. Andrisano, G. Pappalardo and L. Bolognari, *Gazz. chim. ital.,* 85, 1430 (1955). (b) G. H. Cookson, *J. Chem. Soc.,* 2789 (1953). (c) U. Eisner and P. H. Gore, *J. Chem. Soc.,* 922 (1958). (d) U. Eisner and R. L. Erskine, *J. Chem. Soc.,* 971 (1958).

[2] L. Doub and J. M. Vandenbelt, *J. Am. Chem. Soc.,* 69, 2714 (1947).

[3] The referee points out that the "secondary" bands identified by Doub and Vandenbelt in benzenoid spectra have no analogs in the pyrrole spectra and that it is possible that both intense bands of the pyrroles are "primary" bands. It has not been established that the transitions involved are equivalent to those of the benzene series.

[4] W. M. Schubert and W. A. Sweeney, *J. Am. Chem. Soc.,* 77, 2297 (1958).

[5] G. D. Hedden and W. G. Brown, *J. Am. Chem. Soc.,* 75, 3744 (1953).

[6] E. A. Braude and E. S. Wright, *Progress in Stereochemistry,* Vol. 1, W. Klyne, ed., Butterworth, London, 1954, pp. 144–153.