

filtered and washed with 2 ml. of cold glacial acetic acid and with alcohol and dried, giving 0.8 g. (75.5%), m.p. 241–242°. One recrystallization from toluene (Darco) gave an analytical sample, m.p. 243.5–244°.

Anal. Calcd. for $C_{13}H_8FNO_2$: F, 7.81; N, 5.76. Found: F, 8.00; N, 5.85.

The infrared spectrum of this compound was identical with the spectrum mentioned above,¹³ although our melting point is somewhat higher.

N-2-(5-Fluoro-3-nitrofluorenyl)acetamide (7-acetamido-4-fluoro-6-nitrofluorene). To a solution of 1 g. of *N-2-(5-fluoro-fluorenyl)acetamide* in 10 ml. of glacial acetic acid at 50°, 1 ml. of nitric acid (d. 1.42) was added with stirring. The mixture was heated to 55°, then removed from the heat. The temperature rose to 60° and a yellow precipitate formed. After cooling, filtration, and washing with 2 ml. of cold glacial acetic acid and water, the product was dried, giving 1.0 g. (84.5%), m.p. 240–246° dec. One recrystallization from alcohol (Darco) gave an analytical sample, m.p. 241–246° slow dec.

Anal. Calcd. for $C_{12}H_{11}FN_2O_3$: C, 62.90; H, 3.87; N, 9.79. Found: C, 63.03; H, 4.21; N, 10.00.

5-Fluoro-3-nitro-2-fluorenamine. Hydrolysis of the above compound in refluxing concd. hydrochloric acid-alcohol for 15 hr. gave a yield of 88% of the amine, m.p. 233–235°. One recrystallization from alcohol gave an analytical sample, m.p. 238–239°.

Anal. Calcd. for $C_{13}H_9FN_2O_2$: N, 11.47. Found: N, 11.34.

N-2-(5-Fluoro-3-nitrofluorenyl)trifluoroacetamide (7-trifluoroacetamido-4-fluoro-6-nitrofluorene). Acylation with trifluoroacetic anhydride in benzene solution gave a quantitative yield, m.p. 201.5–202.5°. A mixture melting point with

the lesser (11%) product of nitration of 4-fluoro-7-trifluoroacetamidofluorene¹ was not depressed, 201.5–202.5°.

Diazotization and Schiemann decomposition of 2-N,N-dimethylamino-1-fluorenamine. A mixture of 5 g. of 2-dimethylamino-1-fluorenamine, 38 ml. of 50% fluoboric acid, and 15 ml. of water was heated to effect solution then cooled in an ice-salt bath. To this, an aqueous solution (5 ml.) of 1.75 g. of sodium nitrite was added with stirring at 0°. The brick-colored diazonium salt was filtered, washed with 5% fluoboric acid, methanol, and then ether, and dried, giving 7.2 g. (80%), dec. 110°. The salt (7.2 g.) was heated in 140 ml. of benzene at the boiling point, and gradual decomposition took place. After 30 min. no more white fumes were apparent and a small amount of dark material had formed. Darco treatment of the filtrate was followed by evaporation to dryness. Ammonium hydroxide (10 ml.) was added and the white precipitate was extracted with 100 ml. of toluene in several portions, and the toluene solution was dried with a little anhydrous sodium sulfate and boiled down to near dryness. The precipitate was recrystallized from petroleum ether (b.p. 30–60°, Darco), giving 1.35 g. (31% based on the starting compound) of 2-methylaminofluorene, m.p. 77.5–78°. One recrystallization from cyclopentane raised the melting point to 78–78.5°. A mixture melting point with authentic 2-methylaminofluorene was not depressed. Acetylation of this product gave authentic *N-methyl-N-2-fluorenylacetamide*¹⁹ (melting point and mixture melting point).

SEATTLE 5, WASH.

(19) T. L. Fletcher, M. E. Taylor, and A. W. Dahl, *J. Org. Chem.*, **20**, 1021 (1955).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

Organophosphorus Chemistry. Addition Reactions of Diethyl Phosphonate and the Oxidation of Triethyl Phosphite¹

M. S. KHARASCH,² ROBERT A. MOSHER,³ AND IRVING S. BENGELSDORF⁴

Received October 1, 1959

The reactions of dialkyl phosphonates, with aldehydes and ketones to give dialkyl α -hydroxyalkylphosphonates, and with olefins to yield dialkyl alkylphosphonates are discussed. Trialkyl phosphites react smoothly and vigorously with hydroperoxides (oxidation-reduction) to yield the trialkyl phosphate and the corresponding alcohol. Cryoscopic molecular weight data reveal that the $P=O$ dipole readily enters into hydrogen-bonded associations with hydroxylic groups.

A series of stimulating lectures and discussions on newly discovered phosphorylation techniques⁵ presented by Professor Alexander R. Todd in the autumn of 1948 led to the instant investigation of

both heterolytic and homolytic reactions of phosphonic and phosphorous esters.⁶

Both chemical and physical evidence strongly support the existence of diethyl phosphonate as the keto structure (I) instead of the enol (II).⁷

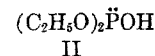
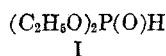
(1) Presented before the Symposium on Organophosphorus Chemistry at the 134th meeting of the American Chemical Society in Chicago, Illinois, September 1958.

(2) Deceased, October 1957. This paper is presented as a memorial tribute to the pioneering efforts in organophosphorus chemistry of the late Professor Kharasch.

(3) Present address: Standard Oil Research Department, Seymour, Indiana.

(4) Present address: TEXUS Research Center, Parsippany, New Jersey. To whom inquiries regarding this paper should be sent.

(5) (a) F. R. Atherton, H. T. Openshaw, and A. R. Todd, *J. Chem. Soc.*, 382, 660 (1945); (b) F. R. Atherton and A. R. Todd, *J. Chem. Soc.*, 674 (1947).



(6) (a) The work presented in this paper was performed in the period 1948–1950; (b) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

(7) The latest physical evidence still corroborates these conclusions. See infrared analyses by L. W. Daasch, *J. Am. Chem. Soc.*, **80**, 5301 (1958) and deuterium exchange studies by R. B. Fox and W. J. Bailey, Symposium on Organophosphorus Chemistry, 134th meeting of the American Chemical Society, Chicago, Illinois, September 1958, Abstracts, p. 70P.

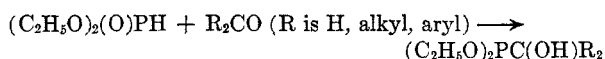
TABLE I
PREPARATION OF DIETHYL α -HYDROXYPHOSPHONIC ESTERS, $(C_2H_5O)_2(O)PC(OH)RR'$

Formula	R	R'	Reaction			B.P., °C/mm.	n_D^{20}	P, %		C_2H_5O , %	
			Temp.	Time, hr.	Yield, %			Calcd., Found	Calcd., Found		
$C_5H_{13}O_4P$	H	H	85 ^a	3	30	103-105/0.2	1.4342	18.4	53.5	—	—
$C_6H_{15}O_4P$	CH ₃	H	80	3	51	108-110/0.5	1.4348	17.0	49.5	16.9	48.6
$C_8H_{19}O_4P$	<i>n</i> -C ₃ H ₇	H	80	9	50	111-112/0.3	1.4378	14.7	42.8	14.4	—
$C_8H_{19}O_4P$	<i>i</i> -C ₃ H ₇	H	80-85	8	43 ^b	96-97/0.3	1.4392	14.7	42.8	14.5	42.8
$C_{11}H_{17}O_4P$	C ₆ H ₅	H	100-110	8	54	83-83.2 ^c	—	12.7	36.9	12.5	—
$C_{13}H_{19}O_4P$	C ₆ H ₅ CH=CH	H	80-100	11	20	106.5-107 ^{c,d}	—	11.5	33.3	11.4	32.9
$C_7H_{17}O_4P$	CH ₃	CH ₃	160	10	17	80-100/0.2 ^e	1.4320	15.8	45.9	15.9	—

^a As paraformaldehyde. ^b Same reaction for 12 hr. in a sealed tube gives rise to a non-volatile viscous oil which presumably arises by condensation of the α -hydroxy ester. ^c Melting points. ^d Absorbs bromine in carbon tetrachloride; other esters do not. ^e Molecular distillation bath temperature.

The physical and chemical properties of triethyl phosphite, however, are in agreement with a structure containing a trivalent-phosphorus atom which bears a free electron pair. The structures of these esters suggested that the phosphorus-hydrogen bond in the former may undergo both heterolytic and homolytic reactions. Most reactions of triethyl phosphite, however, are heterolytic in nature, e.g., Arbuzov-Michaelis type, although free-radical reactions⁸ recently have become recognized.

Thermal non-catalyzed addition of diethyl phosphonate to carbonyl compounds. This reaction repre-



sents a one-step synthesis of dialkyl α -hydroxy phosphonates.⁹

The esters are high-boiling liquids or crystalline solids whose water solubility decreases as the molecular weight increases. Table I summarizes the experimental data.

The most striking feature of the diethyl α -hydroxyphosphonates is their anomalous behavior in the cryoscopic determination of their molecular weights in benzene. The observed values indicate that the compounds are associated to a dimeric structure. Molecular weights determined in re-

fluxing carbon tetrachloride (Swietoslawski ebullioscopic apparatus) are also indicative of associated structures; their persistence at the higher temperatures suggests strongly hydrogen-bonded structures involving intermolecular reactions between the hydroxyl group and the strong $\overset{+}{P}-\overset{-}{O}$ dipole.¹⁰

That the α -hydroxyl group is an integral and necessary requirement for the observed intermolecular association is supported by esterification studies. The α -acetoxyphosphonates are monomeric in benzene solution and possess lower boiling points than the parent hydroxylic esters. The molecular weight determinations are summarized in Tables IIa and IIb.

The saturated α -hydroxyphosphonic esters are readily hydrolyzed in 18% aqueous hydrochloric acid to the corresponding α -hydroxyphosphonic acids; the latter are crystalline solids. The first few members of the aliphatic series are very hygroscopic, however, and the crystalline salts formed with aromatic amines are useful in their characterization.¹¹ In strong alkali, however, the α -hydroxyphosphonates are not hydrolyzed, but quantitatively regenerate the starting aldehyde. The reaction, undoubtedly, proceeds by the removal of a proton by the base to yield the intermediate

(8) C. Walling and R. Rabinowitz, *J. Am. Chem. Soc.*, **81**, 1243 (1959) present a detailed review of this field.

(9) V. S. Abramov and co-workers, simultaneously and independently observed the base-catalyzed addition of dialkyl phosphonates to carbonyl compounds. Their first paper in a continuing series is *Doklady Akad. Nauk S.S.S.R.*, **73**, 487 (1950). Other reports on this reaction are by W. E. Craig and W. F. Hester, U. S. Pat. 2,485,573, 25 October 1949; *Chem. Abstr.*, **44**, 3005h (1950), A. R. Stiles, U. S. Pat. 2,593,213, April 15, 1952; *Chem. Abstr.*, **46**, 11228e (1952), and R. L. McConnell and H. W. Coover, Jr., *J. Am. Chem. Soc.*, **78**, 4450 (1956).

(10) The trimeric association of benzenephosphonic acid $C_6H_5PH(O)OH$ in benzene has been described by G. M. Kosolapoff and J. S. Powell, *J. Am. Chem. Soc.*, **72**, 4291 (1950). C. D. Miller, R. C. Miller, and W. Rogers, Jr., *J. Am. Chem. Soc.*, **80**, 1562 (1958) present evidence based upon infrared spectral band shifts that dialkyl α -hydroxyalkyl phosphonates show both inter- and intramolecular hydrogen bonding; molecular weight determinations are not described.

(11) (a) J. B. Conant and A. D. Macdonald, *J. Am. Chem. Soc.*, **42**, 2343 (1920); (b) I. S. Bengelsdorf and L. B. Barron, *J. Am. Chem. Soc.*, **77**, 2869 (1955).

TABLE II
MOLECULAR WEIGHT DATA
(a) DIETHYL α -HYDROXYPHOSPHONIC ESTERS (C₂H₅O)₂ OPC(OH)RR'

R	R'	Molecular Weight			
		Monomer Calcd.	Dimer Calcd.	Cryoscopic (C ₆ H ₆)	Ebullioscopic (CCl ₄)
H	H	168	336	352	355
CH ₃	H	182	364	365	372
<i>n</i> -C ₃ H ₇	H	210	420	393	330
<i>i</i> -C ₃ H ₇	H	210	420	400	—
C ₆ H ₅	H	244	488	536, 550	—
C ₆ H ₅ CH=CH	H	270	540	500	—
CH ₃	CH ₃	196	392	350	—

(b) DIETHYL α -ACETOXYPHOSPHONIC ESTERS (C₂H₅O)₂ OPCH(OCOCH₃)R

R	Formula	B.p., °C/mm.	<i>n</i> _D ²⁰	P, % Calcd. Found	Molecular Weight	
					Monomer Calcd.	Found (C ₆ H ₆)
CH ₃	C ₈ H ₁₇ O ₅ P	77-78/0.3	1.4268	13.8 13.7	224	229
<i>n</i> -C ₃ H ₇	C ₁₀ H ₂₁ O ₅ P	80-81/0.3	1.4303	12.3 12.0	252	259
<i>i</i> -C ₃ H ₇	C ₁₀ H ₂₁ O ₅ P	76-77/0.3	1.4310	12.3 12.0	252	261
C ₆ H ₅ CH=CH	C ₁₃ H ₂₁ O ₅ P	135-140/0.3 ^a	—	9.9 9.8	—	—

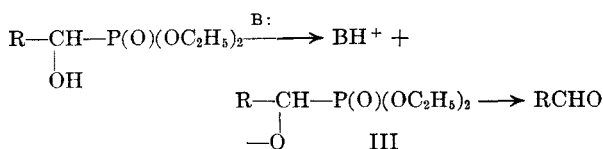
^a Molecular distillation.

TABLE III
ACIDIC HYDROLYSES OF DIETHYL α -HYDROXYPHOSPHONIC ESTERS^a

RCH(OH)P(O)(OH) ₂ R	Formula	M.P. °C.	P, % Calcd., Found	Remarks
H	CH ₅ O ₄ P	87-88	27.7 27.5	Anilinium salt (from ethanol), m.p. 167-168°. <i>Anal.</i> Calcd. for C ₇ H ₁₂ NO ₄ P: P, 15.1. Found: P, 15.0.
CH ₃	C ₂ H ₇ O ₄ P	—	—	Acid isolated as oil which slowly crystallized. Attempts to purify unsuccessful. <i>Anal.</i> Calcd. for C ₂ H ₇ O ₄ P: Neut. equiv., 63; Found: Neut. equiv., 63.5. Anilinium salt, m.p. 168-169°. <i>Anal.</i> Calcd. for C ₈ H ₁₄ NO ₄ P: P, 14.1%. Found: P, 14.1.
<i>n</i> -C ₃ H ₇	C ₄ H ₁₁ O ₄ P	154.5-155 ^b	20.1 20.0	Shiny plates from benzene-glacial HOAc (2:1) mixture.
<i>i</i> -C ₃ H ₇	C ₄ H ₁₁ O ₄ P	165-166	20.1 19.8	Same solvent as above.
C ₆ H ₅	C ₇ H ₉ O ₄ P	167-168 dec. ^c	16.5 16.3	Same solvent as above.
C ₆ H ₅ CH ₂ CH ₂	C ₉ H ₁₃ O ₄ P	173-173.5 ^d	14.4 14.2	Attempted hydrolysis of original unsaturated ester from cinnamaldehyde only led to gummy materials. Hydrolysis proceeded smoothly after hydrogenation.

^a All hydrolyses were conducted with 18% aqueous hydrochloric acid. ^b Fossek-Page method, acid m.p. 154.5-155°. ^c Fossek-Page method, acid m.p. 165-166°. ^d Fossek-Page method, acid m.p. 174.5-175°.

III; the latter undergoes phosphorus-carbon bond cleavage to yield the aldehyde.¹²



Thus, diethyl α -hydroxy-*iso*-butylphosphonate, diethyl α -hydroxybenzylphosphonate, and diethyl α -hydroxy- γ -phenyl-2-propenylphosphonate give isobutyraldehyde (96.2%), benzaldehyde (99.3%),

and cinnamaldehyde (94.5%), respectively, when treated with a 10% sodium hydroxide solution. The aldehydes were isolated as their 2,4-dinitrophenylhydrazone derivatives.

The acidic hydrolytic reactions of α -hydroxyphosphonates are described in Table III.

(12) If the R-group contains an appropriate leaving group, such as chlorine, or an electron-withdrawing group, such as carbonyl, one observes instead phosphorus-carbon bond cleavage with the formation of a phosphoric ester [cf. I. S. Bengelsdorf, *J. Org. Chem.*, **21**, 475 (1956); V. A. Kukhtin, V. S. Abramov, and K. M. Orekhova, *Doklady Akad. Nauk S.S.S.R.*, **128**, 1198 (1959)].

TABLE IV
 FREE RADICAL ADDITION OF DIETHYL PHOSPHONATE TO 1-OCTENE

Initiator	Temp.	Time, hr.	1:1 Product ^a			2:1 Product ^b		
			B.p.	n_D^{20}	Yield, %	B.p.	n_D^{20}	Yield, %
Benzoyl peroxide ^c	85	4	105–106°/0.5	1.4354	43	150–153°/0.5	1.4472	28 ^d
Azo bisisobutyronitrile ^e	100	4	105–108°/0.5	1.4344	45	155°/0.5	1.4458	28 ^f
Acetyl peroxide ^g	75–80	6	92°/0.5	1.4340	55	125–135°/0.001	1.4432	3 ^h

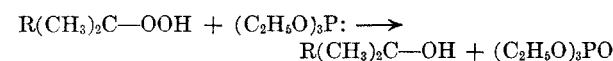
^a The 1:1 product is diethyl *n*-octylphosphonate. A typical analysis is *Anal.* Calcd. for C₁₂H₂₇O₃P: P, 12.4; mol. wt., 250; sapon. equiv., 250. Found: P, 12.4, 12.5; mol. wt., 255 (Benzene); sapon. equiv., 246, 256. ^b The 2:1 product is diethyl hexadecylphosphonate. The specific structure of the hexadecyl radical was not determined. *Anal.* Calcd. for C₂₀H₄₃O₃P: P, 8.5. Found: P, 8.2, 9.2. ^c 0.1 Mole ester to 0.1 mole olefin; 5 mole % initiator. ^d Also obtained 2.3 g. of non-volatile residue. ^e 0.19 Mole ester to 0.19 mole olefin; 4.75 mole % initiator. ^f Less than 1.0 g. non-volatile residue. ^g 0.36 Mole ester to 0.24 mole olefin; 5 mole % initiator. ^h Reaction was conducted in the presence of dimethyl fumarate (0.12 mole); residue is a clear, glassy, polymeric material consisting of diethyl phosphonate, 1-octene, and dimethyl fumarate units. *Anal.* Found: P 3.5; mol. wt., 847 (benzene); sapon. equiv., 136.

Free-radical initiated addition of diethyl phosphonate to olefins. The observation that phosphorus trichloride adds to olefins by homolytic cleavage of a phosphorus-chlorine bond¹³ suggests that one may observe the homolytic cleavage of a phosphorus-hydrogen linkage as well.

This is indeed the case. The reaction of diethyl phosphonate with 1-octene in the presence of 5 mole % of benzoyl peroxide, acetyl peroxide, or azobisisobutyronitrile leads to synthesis of diethyl *n*-octylphosphonate as the primary product, (Table IV). This type of reaction has been described subsequently in the literature.¹⁴

Neither homolytic nor heterolytic fission of the phosphorus-chlorine bond in diethyl phosphorochloridate¹⁵ was achieved, however, in the treatment of the latter with 1-octene, employing either benzoyl peroxide as the free radical initiator or aluminum chloride as the ionic catalyst. The starting 1-octene was recovered in the former case, whereas the latter experiment yielded monoethyl phosphate.

The reduction of hydroperoxides with triethyl phosphite. The smooth and vigorous reaction of triethyl phosphite with hydroperoxides leads to but two products, the alcohol derived from the reduction of the hydroperoxide, and triethyl phosphate from the simultaneous oxidation of the triethyl phosphite.



(13) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Am. Chem. Soc.*, **67**, 1864 (1945).

(14) C. Walling, *Free Radicals in Solution*, John Wiley and Sons, Inc., New York, New York, 1957, p. 342–343 gives an excellent account of such research. More recent results are reported by A. R. Stiles, W. E. Vaughan, and F. F. Rust, *J. Am. Chem. Soc.*, **80**, 714 (1958), and L. A. Hamilton, Symposium on Organophosphorus Chemistry, 134th Meeting of the American Chemical Society, Chicago, Illinois, September 1958, Abstracts, p. 68P.

Cryoscopic measurements in benzene solution indicated association between triethyl phosphate and α -cumyl alcohol (R = C₆H₅). In order to determine whether the association of triethyl phosphate and alcohols was a general phenomenon,¹⁶ cryoscopic molecular-weight determinations were performed on a series of triethyl phosphate-alcohol mixtures. The results are tabulated in Table V.

 TABLE V
 MOLECULAR WEIGHTS OF EQUIMOLAR MIXTURES OF TRIETHYL PHOSPHATE AND ALCOHOLS IN BENZENE

Alcohol	Molecular Weight		Molecular Weight (Mixtures)	
	Calcd.	Found	Calcd. ^a	Found
None	182	188	—	—
Triphenylcarbinol	260	266	221	280
Isopropyl alcohol	60	85	121	171
1-Octanol	130	—	156	207
α , α -Dimethylbenzyl alcohol	136	148 ^b	159	192

^a Based upon the assumption that there is no association of the solute molecules. ^b M. S. Kharasch and A. C. Poskus, unpublished work.

The data definitely indicate a degree of association of the triethyl phosphate molecule with that of the alcohol (*cf.* diethyl α -hydroxyalkylphosphonates above).

There is no definite evidence to determine whether the oxidation-reduction reaction proceeds *via* a homolytic or a heterolytic intermediate. The exothermicity and instantaneousness of the reaction, and the fact that it is not affected by the

(15) F. R. Atherton, H. T. Howard, and A. R. Todd, *J. Chem. Soc.*, 1106 (1948).

(16) G. B. King and J. H. Walton, *J. Phys. Chem.* **35**, 1745 (1931) previously had observed "onium" addition compounds between phosphoric acid and oxygenated organic compounds.

presence of trinitrobenzene⁸ an inhibitor of homolytic reactions, strongly suggest that the reaction of trialkyl phosphites with hydroperoxides chiefly occurs by an ionic mechanism. The trialkyl phosphite-hydroperoxide reaction should be useful as a quick nonaqueous analytical determination for either phosphites or hydroperoxides (volumetric or infrared). Triethyl phosphite can also serve to distinguish between hydroperoxidic and peroxidic content, as the former reacts at ambient temperatures while the latter requires heating.^{8,17}

EXPERIMENTAL

Purification of materials. The diethyl phosphonate employed was prepared either by the interaction of phosphorus trichloride with ethanol,¹⁸ or by purification of a generous sample supplied by the Victor Chemical Company (b.p. 77°/18 mm., n_D^{20} 1.4080). Aldehydes were distilled prior to use. The 1-octene was purified by distillation through a vacuum-jacketed column, b.p. 120–121°, n_D^{20} 1.4090. Acetyl peroxide was prepared in ether solution,¹⁹ while azoisobutyronitrile (Rohm & Haas), benzoyl peroxide, and tank nitrogen were commercial products used without purification.

Triethyl phosphite was prepared by the interaction of phosphorus trichloride with ethanol in anhydrous ether in the presence of quinoline (b.p. 237°); this is a modification of the original method which employed pyridine.²⁰ The phosphite now is commercially available. It is a clear, mobile liquid with an obnoxious odor (b.p. 51–53°/13 mm., n_D^{20} 1.4138, 72% yield). Commercial (72%) α -cumyl hydroperoxide (Hercules Powder Company) was purified by precipitation as its sodium salt and its careful regeneration with acid.²¹ The hydroperoxide, thus obtained, is of 98–99% purity (iodometric titration). Commercial *t*-butyl hydroperoxide was distilled through a vacuum-jacketed tantalum wire column, (b.p. 44°/27, 80% purity by iodometric titration).

Determination of phosphorus. The micro method described by Niederl and Niederl²² was used, but sample weights were in the semimicro range. Ammonium phosphomolybdate was determined gravimetrically. Consistently low results for phosphorus were obtained for some compounds, e.g., diethyl phosphonate, triethyl phosphate; the difficulty was eliminated by the use of a sulfuric-nitric acid wet combustion procedure followed by reflux with perchloric acid.

Diethyl α -hydroxyalkylphosphonates. Typical experimental procedures for the preparation, acetylation, acidic and basic hydrolyses, and proofs of structures are described below. Detailed information is in the tables (above).

Preparation: reaction of diethyl phosphonate with isobutyraldehyde. Diethyl phosphonate (20 g., 0.145 mole) and isobutyraldehyde (14.2 g., 0.197 mole) were placed in a 100-ml. two necked flask equipped with a gas inlet tube and a condenser fitted with a calcium chloride tube. The reagents were heated for 8 hr. at 80–85° (oil bath), under nitrogen. The diethyl α -hydroxyisobutylphosphonate distilled at 96–97°/

0.3 mm. A distillation residue (4.7 g.) remained in the flask. Similar results can also be obtained if the two reagents are mixed, degassed, and sealed in glass reaction tubes (vacuum line) and heated in a cylindrical metal container in an oil bath.

Acetylation. Diethyl α -hydroxyethylphosphonate (5 g.) and acetic anhydride (10 g.) were refluxed for 4 hr. The dark-brown reaction product was distilled to give diethyl α -acetoxyethylphosphonate in 84% yield. The α -acetoxy derivatives give a positive qualitative hydroxamic acid test for carboxylic esters, whereas the original phosphonic esters react negatively.

Acidic hydrolysis. Diethyl α -hydroxy-*n*-butylphosphonate (1.0 g.) was refluxed with 18% aqueous hydrochloric acid. The α -hydroxy-*n*-butylphosphonic acid separated as shiny plates.

Basic hydrolysis. Ten milliliters of 10% sodium hydroxide were placed in a 100-ml. steam-distillation flask equipped with a dropping funnel. Steam passage was begun; a small flame under the flask prevented excessive dilution of the sodium hydroxide. A weighed sample of diethyl α -hydroxybenzylphosphonate, dissolved in 15 ml. of methanol, was slowly introduced into the flask (15 min.). Twenty milliliters of methanol was added to the 30–35 ml. distillate, followed by 10 ml. of 2,4-dinitrophenylhydrazine solution (2 g. of reagent in 5 ml. concd. sulfuric acid and 50 ml. methanol). After standing for 5 hr., 10 ml. of 6*N* sulfuric acid was added. The precipitate was collected the next day and washed with dilute methanolic sulfuric acid followed by 20% aqueous methanol. The hydrazone was dried to constant weight under reduced pressure over calcium chloride.²³

Anal. Calcd. for 0.233 g. of ester: 0.273 g. hydrazone. Found: 0.271 g. hydrazone (aldehyde, 99.3%). The benzaldehyde 2,4-dinitrophenylhydrazone melted at 240–241° (lit., m.p. 237°). Other aldehydes and the melting points of their 2,4-dinitrophenylhydrazone derivatives are: isobutyraldehyde, 179–180° (lit. m.p. 182°, 187°); cinnamaldehyde, 245–246° (lit., m.p. 248°, 255°).

Proof of structure. The structure of an α -hydroxyalkylphosphonate was proved by its hydrolysis to the corresponding α -hydroxyalkylphosphonic acid and the demonstration that this acid was identical with an authentic sample prepared by the independent Fossek-Page method.²⁴ Thus, the reaction of *n*-butyraldehyde with phosphorus trichloride gave an acid which had the same phosphorus content (P, 20.1%) and did not depress the melting point of the acid obtained from the acidic hydrolysis of diethyl α -hydroxy-*n*-butylphosphonate.

Attempts to isolate an acid derivative from the hydrolysis of diethyl α -hydroxy- γ -phenyl-2-propenylphosphonate were unsuccessful. The ester (2.0 g.) was then hydrogenated in 60 ml. absolute ethanol (0.5–1.0 g. Raney nickel) under 30 lbs./sq. in. hydrogen pressure. The residual oil slowly crystallized on standing. It was washed with ligroin to give diethyl α -hydroxy- γ -phenylpropylphosphonate.

Anal. Calcd. for $C_{13}H_{21}O_4P$: P, 11.4. Found: P, 11.2.

The saturated ester (0.5 g., did not absorb bromine in carbon tetrachloride) was hydrolyzed to give shiny plates of α -hydroxy- γ -phenylpropylphosphonic acid (m.p. 173–173.5°). Dihydrocinnamaldehyde (b.p. 87–88°/8 mm.), prepared by the hydrogenation of cinnamaldehyde²⁵ (Raney nickel, absolute ethyl alcohol, room temperature), was treated with phosphorus trichloride to give α -hydroxy- γ -phenylpropylphosphonic acid. This acid had the same phosphorus content (P, 14.2%) and did not depress the melting point of the acid obtained from the acidic hydrolysis of the above hydrogenated ester.

(23) M. S. Kharasch and J. H. Cooper, *J. Org. Chem.*, **10**, 48 (1945).

(24) (a) W. Fossek, *Monatsh.*, **5**, 636 (1884); (b) H. J. Page, *J. Chem. Soc.*, **101**, 423 (1912).

(25) H. A. Weidlich and M. Meyer-Delius, *Ber.*, **74B**, 1195 (1941).

(17) I. S. Bengelsdorf, unpublished work.

(18) P. Nylen, *Studien über organische Phosphorverbindungen*, Almqvist and Wiksells, Uppsala, Sweden, (Thesis), 1930.

(19) H. Friedlander, Ph. D. Dissertation, Dept. of Chemistry, University of Chicago, 1947.

(20) T. Milobedzki and A. Sachnowski, *Chem. Polski*, **15**, 34 (1917); *Chem. Abstr.* **13**, 2865 (1919).

(21) M. S. Kharasch, A. Fono, and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

(22) J. B. Niederl and V. Niederl, *Micromethods of Quantitative Organic Analysis*, John Wiley and Sons, New York, 1942, p. 199.

High-boiling residues from the diethyl phosphonate-aldehyde reactions. The experimental data concerning the residues remaining after the distillation of the α -hydroxyphosphonates are summarized in Table VI.

TABLE VI
HIGH-BOILING RESIDUES FROM $(C_2H_5O)_2P(O)H-RCHO$
REACTIONS^a

RCHO R	P, %	C ₂ H ₅ O, %	Mol. wt.
H	19.0	—	—
CH ₃	21.3	33.3	—
<i>n</i> -C ₃ H ₇	18.3	31.4	747
<i>i</i> -C ₃ H ₇ ^b	15.7, ^c 19.3 ^d	38.0, ^c 32.3 ^d	528, ^c 717 ^d

^a All of the residues are viscous, colorless oils which are hydrolyzable with 18% hydrochloric acid to give α -hydroxyalkylphosphonic acids identical with those obtained from the acidic hydrolyses of the distillable diethyl α -hydroxyphosphonates. ^b Residue is major product if reaction time is prolonged (12 hr.). ^c Sealed tube reaction. ^d Flask reaction.

*Preparation of diethyl *n*-octylphosphonate.* The free-radical reactions of diethyl phosphonate with 1-octene were conducted in a 125-ml. three necked round bottomed flask equipped with a gas inlet tube, and a reflux condenser fitted with a calcium chloride tube. An atmosphere of nitrogen was maintained during the reaction period. The reaction with azoisobutyronitrile serves as a typical experimental procedure (further details and analyses are in Table IV).

A solution of azoisobutyronitrile (1.6 g., 0.009 mole) in a mixture of diethyl phosphonate (12.9 g.) and 1-octene (10.4 g.) was slowly added over a 3-hr. period to a mixture of diethyl phosphonate (13.8 g., 0.19 mole total) and 1-octene (11.2 g., 0.19 mole total) maintained at 97°. After heating for an additional hour at 100° the unchanged 1-octene (10.3 g.) and diethyl phosphonate (14.7 g., b.p. 45°/0.5 mm.) were removed at reduced pressure. The residue was distilled to give the following fractions: Fraction 1: Diethyl *n*-octylphosphonate (1:1 addition product), Fraction 2: Diethyl hexadecylphosphonate (2:1 addition product), Fraction 3: A residue (1.0 g.) which did not distill.

Similar results are obtained in the use of benzoyl peroxide or acetyl peroxide as the free radical initiator.

*Identification of the 1:1 addition product as diethyl-*n*-octylphosphonate.* Triethyl phosphite (5 g., 0.03 mole) and *n*-octyl bromide (5.84 g., 0.03 mole) were heated for 7 hr. at 150° (Arbuzov-Michaelis reaction).²⁶ The liberated ethyl bromide was collected in a trap (3.0 g.) and diethyl *n*-octylphosphonate was recovered by distillation (b.p. 91.8°/0.3 mm., n_D^{20} 1.4361, 65% yield).

Anal. Calcd. for C₁₂H₂₇O₃P: P, 12.4%; Found: P, 12.4%.

Hydrolysis with 18% aqueous hydrochloric acid gave *n*-octylphosphonic acid (m.p. 102–102.5°), which did not depress the melting point of the alkylphosphonic acid obtained from a similar acidic hydrolysis of the product obtained from the free radical addition of diethyl phosphonate to 1-octene.

The latter sample of *n*-octylphosphonic acid was crystallized as small white platelets from 65°-petroleum ether (m.p. 101.8–102.8°).

Anal. Calcd. for C₈H₁₉O₃P: P, 15.9. Found: P, 15.6.

Treatment of an ethereal solution of the acid with aniline gave the monoanilinium salt of *n*-octylphosphonic acid. It was recrystallized from water (m.p. 143–145°).

Anal. Calcd. for C₁₄H₂₉O₃NP: P, 10.8. Found: P, 10.7.

The monocyclohexylammonium salt of *n*-octylphosphonic acid was prepared in a similar manner (m.p. 187–188°).

Anal. Calcd. for C₁₄H₃₂O₃NP: P, 10.5. Found: P, 10.5.

(26) A. H. Ford-Moore and J. H. Williams, *J. Chem. Soc.*, 1465 (1947).

Reaction of diethyl phosphorochloridate with 1-octene in the presence of aluminum chloride. Diethyl phosphorochloridate was prepared by the interaction of diethyl phosphonate with sulfuric chloride²⁵ in 71% yield (b.p. 72–73°/8 mm.). It was characterized by its reaction with aniline to give diethyl anilinophosphate (m.p. 95–96°).²⁷

Anal. Calcd. for C₁₀H₁₆O₃NP: P, 13.4. Found: P, 13.4.

Aluminum chloride (2.1 g., 0.016 mole) was added to diethyl phosphorochloridate (9 g., 0.052 mole) and 1-octene (5.86 g., 0.052 mole) at room temperature. The reaction mixture was then heated for 4 hr. at 90°. The liquid decantate was distilled to give a volatile material (presumably ethyl chloride) and unchanged 1-octene (5.3 g.).

The residual solid was washed with an 18% aqueous hydrochloric acid solution. Concentration of the aqueous solution and treatment of the residue with aniline gave a gelled solid. The latter was extracted with ethanol to yield the monoanilinium salt of monoethyl phosphate (m.p. 163–164°).

Anal. Calcd. for C₈H₁₄O₄NP: P, 14.1. Found: P, 13.9, 14.2. This salt was prepared in an independent manner by treating an alcoholic suspension of barium monoethyl phosphate²⁸ with the calculated amount of sulfuric acid. The barium sulfate was collected and the treatment of the ethanolic filtrate with aniline precipitated monoanilinium monoethyl phosphate. This salt had the same phosphorus content (P, 14.1%) and did not depress the melting point of the salt obtained from the above aluminum chloride reaction.

Reaction of triethyl phosphite with α -cumyl hydroperoxide. The reaction was conducted in a 500-ml. three necked round bottomed flask fitted with a mechanical stirrer, dropping funnel, and reflux condenser. A solution of α -cumyl hydroperoxide (49.2 g., 0.323 mole) in 98 ml. of toluene was slowly added over a 1-hr. period to a solution of triethyl phosphite (53.7 g., 0.323 mole) in 100 ml. toluene. A cooling bath maintained the temperature at 25–30°. The toluene was removed at reduced pressure and the residue was distilled as an equimolar mixture of triethyl phosphate and α -cumyl(α , α -dimethylbenzyl) alcohol (b.p. 47–50°/0.1 mm., n_D^{20} 1.4571).

Anal. Calcd. for C₉H₁₂O·C₆H₁₀O₄P: C, 56.6; H, 8.5; P, 9.7; sapon. equiv., 318; mol. wt., 159. Found: C, 56.6; H, 8.6; P, 9.6; sapon. equiv., 324; mol. wt., 206, 216.

Identification of the α -cumyl hydroperoxide-triethyl phosphite product. The presence of α -cumyl alcohol was shown when the above mixture (3 g.) was heated for 7 hr. with a mixture of thioglycolic acid (3 g.) and 24 ml. of 2*N* hydrochloric acid to give a quantitative yield of long white needles of α -cumylmercaptoacetic acid (m.p. 69–70° from benzene-ligroin).²⁹ This acid did not depress the melting point of α -cumylmercaptoacetic acid prepared by the reaction of thioglycolic acid with α -methylstyrene.

The presence of triethyl phosphate was not primarily verified (see below), but the product of the reaction was compared with a synthetic mixture of α -cumyl alcohol (0.68 g., 0.005 mole) and triethyl phosphate (0.91 g., 0.005 mole), as follows: Reaction product: n_D^{20} 1.4571; sapon. equiv., 324. Synthetic mixture: n_D^{20} 1.4573; sapon. equiv., 324.

*Reaction of triethyl phosphite with *t*-butyl hydroperoxide.* A solution of triethyl phosphite (23.5 g., 0.142 mole) in 50 ml. of toluene was treated with a solution of *t*-butyl hydroperoxide (16.4 g., 0.141 mole) in 50 ml. of toluene in the manner described for the α -cumyl hydroperoxide reaction.

A mixture of *t*-butyl alcohol and toluene was removed at reduced pressure. The residue was distilled to give triethyl

(27) H. McCombie, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 380 (1945).

(28) A sample was kindly supplied by Prof. F. H. Westheimer and Dr. W. W. Butcher.

(29) B. Holmberg, *J. prakt. Chem.*, 141, 93 (1934).

phosphate (b.p. 46–47°/0.3 mm., n_D^{20} 1.4058, quantitative yield).

Anal. Calcd. for $C_8H_{15}O_4P$: P, 17.0%; Found: P, 17.0%.

The *t*-butyl alcohol was identified as the 3,5-dinitrobenzoate ester (melting point and mixture melting point 139.5–140.0°).

Acknowledgments. The authors wish to thank Dr. W. Nudenberg for his invaluable suggestions and discussions during the course of the work.

CHICAGO, ILL.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & Co., INC.]

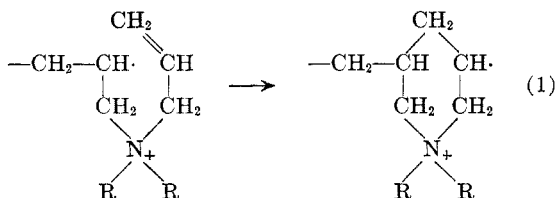
Intermolecular-Intramolecular Polymerization of 2,6-Diphenylheptadiene-1,6

N. D. FIELD

Received December 18, 1959

The synthesis of 2,6-diphenylheptadiene-1,6 from 1,3-dibenzoylpropane was accomplished in good yield utilizing the Wittig reaction. It was polymerized using free radical, cationic, anionic, and Ziegler-type initiation to give in all cases soluble polymers of essentially the same structure with few or no double bonds detectable in the infrared spectrum. This is the first example of a diene on which all known general types of initiation have led to intermolecular-intramolecular polymerization.

In order to explain the solubility of polymers obtained from diallyl quaternary ammonium salts, Butler and Angelo¹ proposed an intermolecular-intramolecular propagation mechanism in the free radical polymerization, the intramolecular step producing piperidinium units:

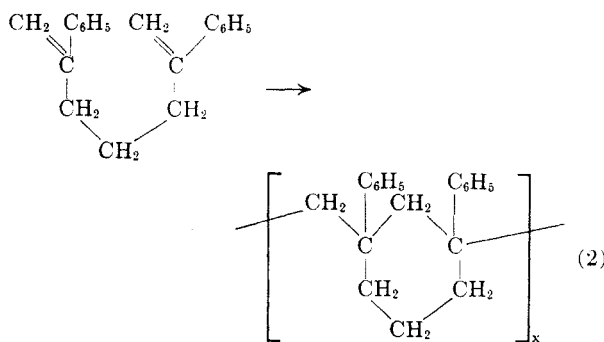


Strong evidence for this mode of polymerization is seen in Marvel's results on the polymerizations of 2,6-dicarboxyheptadiene-1,6 and its esters.² High molecular weight soluble polymers with no detectable residual unsaturation were obtained. For example, 2,6-dicarbomethoxyheptadiene-1,6 was polymerized using free radical initiation in an emulsion system to give polymer with an intrinsic viscosity in chloroform of 0.73. It was soluble in a number of organic solvents and showed no carbon-carbon double bonds in the infrared spectrum.

A number of examples of intermolecular-intramolecular polymerization have since appeared. These include, in addition to the free radical variety discussed above, Ziegler-type,³ anionic,⁴ and cationic.⁵

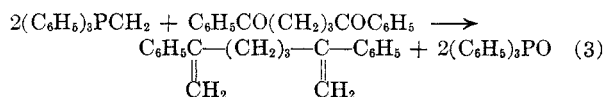
This paper reports the preparation of 2,6-diphenylheptadiene-1,6 and its polymerization. All the known general types of initiation mentioned

above were employed and resulted only in intermolecular-intramolecular polymerization. To our knowledge, this is the first example of a diene which responds in this fashion:



DISCUSSION

Monomer synthesis. A powerful synthetic tool for unequivocal olefin formation is the Wittig reaction⁶ in which a carbonyl group is converted to an ethylenic group via the action of a triphenylphosphinemethylene. The ethylenic linkage is reported to form only at the point where the carbonyl group existed originally. This reaction was conducted by us on 1,3-dibenzoylpropane to give 2,6-diphenylheptadiene-1,6 in 65% yield based on starting diketone:



The structure of the diene was confirmed by oxidation to the starting dione in 76% yield using sodium periodate and osmium tetroxide.⁷

(6) G. Wittig and E. Schollkopf, *Ber.*, **87**, 1308 (1954).

(7) R. Pappo, D. S. Allen, R. V. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

(1) G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, **79**, 3128 (1957).

(2) C. S. Marvel and R. D. Vest, *J. Am. Chem. Soc.*, **79**, 5771 (1957).

(3) C. S. Marvel and J. K. Stille, *J. Am. Chem. Soc.*, **80**, 1740 (1958).

(4) J. F. Jones, *J. Polymer Sci.*, **33**, 7 (1958).

(5) J. F. Jones, *J. Polymer Sci.*, **33**, 513 (1958).