[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE COLLEGE OF ARTS AND SCIENCES OF THE UNIVERSITY OF LOUISVILLE, AND THE BIOMEDICAL RESEARCH GROUP, LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

2-Pyrones. XXV. 3,6-Diaryl-2-pyrones as Heterocyclic Analogs of Terphenyl

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The synthesis of 6-phenyl-2-pyrone from phenylpropargyl aldehyde and malonic acid has been re-examined. Previous structural assignments for the products of the reaction have been revised on the basis of additional analytical data and infrared absorption characteristics. The principal product is 4-phenylbuten-3-yne-1,1-dicarboxylic acid (I) which can be cyclized to 3-carboxy-6-phenyl-2-pyrone (II). Decarboxylation gives 6-phenyl-2-pyrone (III). This reaction sequence has been extended to the condensation of phenylpropargyl aldehyde with three arylacetic acids to give 2,5-diphenylpenten-2-yne-4-oic acid (V), 3,6-diphenyl-2-pyrone (VI) and the related β-naphthyl-, *p*-biphenylyl and *p*-methoxyphenyl analogs. Introduction of the electron donor methoxy group results in lowered yields in both the condensation and cyclization.

The use of some of their heterocyclic analogs as replacements for *p*-terphenyl and *p*-quaterphenyl solutes in liquid scintillation counters has been sufficiently successful[2] to justify the continued exploration of related structural types. Such an effort is complicated by the fact that the *p*-polyphenyl structure, which is desired because the maximum scintillation response appears to be associated with the maximum resonance stabilization of the *para* structure, corresponds to a 1,4-diaryl heterocyclic structural type which is comparatively unknown. This study was undertaken to develop syntheses for a variety of 1,4-(*p*-)diaryl heterocycles to be examined in terms of their effectiveness as scintillators relative to *p*-terphenyl as a standard. In the present paper we wish to describe the preparation and characterization of a series of 3,6-diaryl-2-pyrones.

The possibility of preparing a 3,6-diaryl-2-pyrone by a modification of the synthesis originally described by Kalff[3] for the synthesis of 6-phenyl-2-pyrone was selected as the most attractive route to these structures. This synthesis as originally described involved the condensation of phenylpropargyl aldehyde with malonic acid to form an unstable compound, m.p. 208–218°, assigned the structure 6-phenyl-2-pyrone-3-carboxylic acid (II). This was reported to undergo decarboxylation in acetic acid at room temperature to give 6-phenyl-2-pyrone (III), m.p. 68°, and at steam-bath temperatures to give a compound, m.p. 218°, assigned the structure of a dilactone (IV) on the basis of its insolubility in bicarbonate, solubility in sodium hydroxide and stability toward decarboxylation.

On repeating the condensation we obtained only one product, m.p. 214–218°, regardless of the temperatures used, which could not possibly be II or IV on the basis of its characteristics. These include the presence of a strong maximum at 2210 cm.$^{-1}$ in the infrared absorption spectrum, which establishes that it is a disubstituted acetylene,[4] and a neutral equivalent of 108. Together these data indicate that the structure of this compound is 4-phenyl-1-buten-3-yne-1,1-dicarboxylic acid (I). It is soluble in bicarbonate and shows no tendency to undergo cyclization either on recrystallization or heating in acetic acid. Whether or not Kalff's acid is identical with this product cannot be determined since neutral equivalent data were not reported, but it does not show the instability toward cyclization observed by Kalff. On refluxing in 50% sulfuric acid for 3 hr., the acid I was converted to 6-phenyl-2-pyrone (III) in 54% yield. On refluxing with a dilute aqueous solution of mercuric sulfate, the acid I was converted in 80% yield to a compound, m.p. 214°, which is soluble in warm bicarbonate and has a neutral equivalent of 216. The infrared spectrum for this compound shows no absorption in the triple bond region, typical 2-pyrone carbonyl absorption at 1735 cm.$^{-1}$ and associated carboxyl carbonyl absorption at 1775 cm.$^{-1}$.[5] It shows absorption maxima in the ultraviolet at 240 mμ (log ε 3.73) and 345 mμ (log ε 4.17) as does also 6-phenyl-2-pyrone (235 mμ, log ε 3.92 and 330 mμ, log ε 4.12). It is readily converted in 67.5% yield to 6-phenyl-2-pyrone on refluxing with 50% sulfuric acid. On the basis of these data we believe this product to be 6-phenyl-2-pyrone-3-carboxylic acid (II). Again absence of a neutral equivalent for the compound obtained by Kalff makes it impossible to say definitely that the material he had is identical with ours.

In extending this reaction to the condensation of acrylacetic acids with phenylpropargyl aldehyde, it was found that this modification of the reaction proceeds best as a Perkin reaction. In acetic anhydride solution with sodium acetate as a catalyst 30–90% yields of the acetylenic acid V were obtained. Table I summarizes the yields obtained and the data characterizing the products from phenylacetic acid and the four substituted phenylacetic acids used. It can be seen that electron donor substituents in the aryl nucleus of the arylacetic acid decrease the yield significantly. The best yields and an increased reaction rate resulted using the *p*-biphenyl and α-naphthyl derivatives in which the *p*-biphenyl and α-naphthyl groups presumably are more effective electron-attracting groups than is the unsubstituted phenyl group. What little information is available[6] indicates that this is contrary to the effect usually produced by electron-attracting substituents in the aryl nucleus of the arylacetic acid in Perkin reactions.

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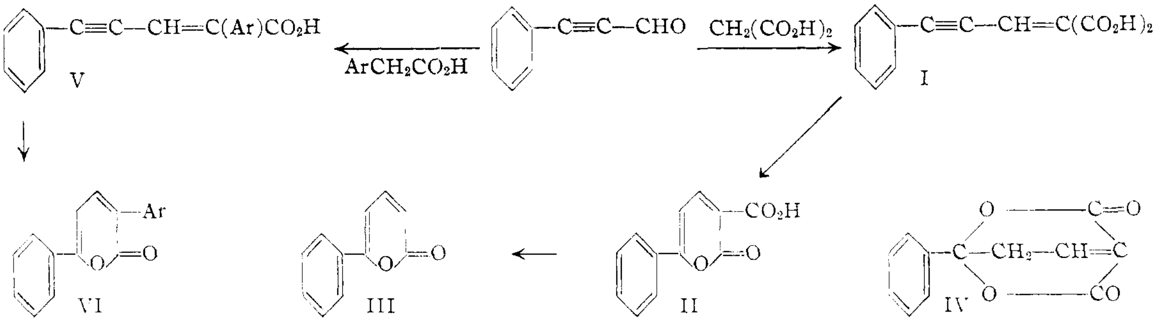
(2) F. N. Hayes, D. G. Ott and V. N. Kerr, *Nucleonics*, **14**, No. 1, 44 (1956); F. N. Hayes, D. G. Ott, V. N. Kerr and Betty S. Rogers, *ibid.*, **13**, No. 12, 38 (1955).

(3) J. Kalff, *Rec. trav. chim.*, **46**, 599 (1927)

(4) L. J. Bellamy, "Infra Red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 49.

(5) L. J. Bellamy, ref. 4, p. 139.

(6) P. H. Leake, *Chem. Revs.*, **56**, 33 (1956).



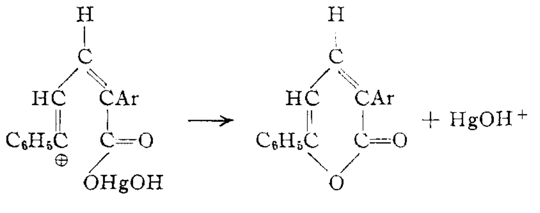
Such comparisons are of questionable validity since the available data are almost exclusively those for reactions using *o*-nitrobenzaldehydes in which steric effects must be important. Electron-attracting substituents should, however, facilitate the formation of the carbanion derived from the mixed anhydride which is to add to the aldehyde in accordance with usually accepted concepts of the mechanism of the Perkin reaction and therefore should, if this is an important factor, facilitate the reaction. This apparent inconsistency indicates that more precise data defining this effect would provide a more adequate understanding of the factors involved in the mechanism of the Perkin reaction.

The structures of these acetylenic acids are confirmed by their infrared absorption characteristics. They show typical disubstituted acetylene stretching absorptions of medium intensity between 2188 and 2205 cm.$^{-1}$, bonded hydroxyl stretching vibrations of medium intensity and very broad at 2800–3200 cm.$^{-1}$, C—O stretching or O—H deformation vibrations at 1412 and 1430 cm.$^{-1}$, and very strong carbonyl stretching vibrations at 1660–1680 cm.$^{-1}$, and the characteristic acid bands in the 1250–1268 cm.$^{-1}$ region.

Cyclization of the 2-aryl-5-phenylpenten-2-yne-4-oic acids (V) to the corresponding 3-aryl-6-phenyl-2-pyrones (V) takes place in aqueous organic solvents with mercuric sulfate catalyst. The choice of solvent and temperature and the role of the substituents in the aryl group are all important factors in the reaction. The phenyl analog is formed in 40–60% yields in 2.5 hr. in aqueous acetone or dioxane. Under otherwise similar conditions, 12.5-hr. reaction times are required to obtain similar yields of the β-naphthyl compound. A reaction time of 24 hr. and a much higher catalyst concentration are required to obtain at best 20% yields of the *p*-biphenyl derivative, and it is necessary to use aqueous methanol as the solvent for the cyclization of the *p*-methoxyphenyl derivative since only resins were obtained using dioxane or acetone. No satisfactory conditions could be found for the cyclization of the *m*-methoxyphenyl compound. A crystalline mercuric salt of the acid precipitated from all reaction media tried and could not itself be successfully cyclized. Because these conditions are obviously highly critical, the details of each reaction are given in the Experimental section. Data upon which the selection of these conditions was based will not be recorded here.

The pyrones isolated from these reactions are all yellow, crystalline materials with infrared absorption in the carbonyl stretching range at 1695 to 1712 cm.$^{-1}$. This displacement to frequencies below the 1720 cm.$^{-1}$ carbonyl frequency usually associated with the carbonyl stretching vibration in 2-pyrones[7] has been observed in other 3-substituted 2-pyrones.[8] This carbonyl absorption is displaced much too far toward higher frequencies to be confused with the β-substituted-5-membered lactone carbonyl absorptions.[9] This eliminates the possibility that cyclization has given a γ-lactone. In contrast to the acetylenic acids, absorption in the conjugated carbon–carbon unsaturation region is noted at 1620–1650 cm.$^{-1}$ as a band of medium intensity. The ultraviolet spectra of the 3-aryl-6-phenyl-2-pyrones show two maxima, as do other 2-pyrones,[10] but the frequencies are displaced to 245–265 mμ (log ε 4.00–4.27) and 360–370 mμ (log ε 4.10–4.56). This shift to longer wave lengths presumably is due to the additional conjugation.

The cyclization of these acids may be visualized as proceeding through initial hydration of the triple bond followed by lactonization or through cyclic addition of the carboxylic acid to the triple bond. The fact that the reactions require aqueous media suggests that hydration may be involved. In the addition of acetic acid to acetylene, traces of water result in acetaldehyde formation indicating a more rapid rate for the hydration reaction than for the addition of the acid. Initial attack by a proton at the γ-carbon atom followed by cyclization through displacement of the oxymercuri group offers a more direct mechanism, but this simplicity is perhaps misleading.



These compounds were examined by the Biomedical Research Group of the Los Alamos Laboratories of the University of California for activity as solutes in standard liquid scintillation counting systems. The results of this testing indicate that even though these materials are strongly fluorescent, they are not effective as scintillators. None

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[8] R. H. Wiley and C. H. Jarboe, THIS JOURNAL, **78**, 2399 (1956).

[9] C. Djerassi, P. Sengupta, J. Herran and F. Walls, *ibid.*, **76**, 2967 (1954).

[10] R. H. Wiley, *et al.*, *ibid.*, **75**, 3715 (1953).

TABLE I

2-ARYL-5-PHENYLPENTEN-2-YNE-4-OIC ACIDS

									Absorption data								
									Ultraviolet[b]				Infrared[d]				
			Carbon, %		Hydrogen, %		Neut. equiv.										
Aryl	M.p., °C.	Yield,[a] %	Calcd.	Found	Calcd.	Found	Calcd.	Found	λ, mμ	log ε	λ, mμ	log ε	RC≡CR	C=O	C=O, OH		
Phenyl	159	79,L	82.24	82.12	4.87	5.18	248	247	225	3.34	315	4.20	2200m	1680s	3000–2500m,b	1415s	1268s
p-Biphenylyl	218	90,G	85.16	85.07	4.97	5.03	324	320	250	3.35	370	3.60[c]	2180m	1665s	3000–2500m,b	1425m	1620s
β-Naphthyl	195	85,G	84.54	84.74	4.73	5.12	298	295	290	3.08	315	3.07	2188m	1665s	3000–2500m,b	1412s	1255s
p-Methoxyphenyl	185	44,B	77.68	77.66	5.07	5.15	166	163	287	3.32	320	3.29	2190m	1665s	3000–2500m,b	1412m	1250s
m-Methoxyphenyl	138	30,H	77.68	77.70	5.07	5.09	166	162	..	..	..	..	2205	1660s	3000–2500m,b	1430m	1260s

[a] Recrystallized from L, ligroin (b.p. 66–75°); G, glacial acetic acid; B, benzene; H, *n*-heptane. [b] Methanol solutions. [c] Chloroform solution. [d] vs, very strong; s, strong; m, medium; w, weak; b, broad. Frequencies given in cm.$^{-1}$.

show relative pulse height values, determined as previously described,[2] over 0.12.

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Experimental[11]

The phenylpropargyl aldehyde, malonic acid and arylacetic acids used in the following experiments were obtained from commercial sources. The *p*-biphenylacetic acid was prepared by a previously described procedure.[12]

4-Phenyl-1-buten-3-yne-1,1-dicarboxylic Acid (I).—A solution of 2.6 g. of phenylpropargyl aldehyde and 2.1 g. of malonic acid in 20 ml. of glacial acetic acid was allowed to stand for 48 hr. The entire reaction mass was poured into 200 ml. of ice-water. The solid precipitate was filtered, dissolved in bicarbonate solution and decolorized two times with activated charcoal. The solution was acidified with dilute hydrochloric acid to precipitate 2.8 g., 65.2%, of yellow 4-phenyl-1-buten-3-yne-1,1-dicarboxylic acid, m.p. 214–218°. Similar yields were obtained when the reaction mixture was refluxed for 4 hr. Infrared absorption maxima occur at 2210, 1730, 1645, 1580, 1485, 1450, 1250, 764 and 685 cm.$^{-1}$.

Anal. Calcd. for $C_{12}H_8O_4$: C, 66.67; H, 3.73; neut. equiv., 108. Found: C, 66.66; H, 3.69; neut. equiv., 108.

3-Carboxy-6-phenyl-2-pyrone.—A catalyst prepared by heating 0.5 g. of yellow mercuric oxide in 4 ml. of concd. sulfuric acid until the color was discharged was dissolved in 50 ml. of distilled water and added to 1 g. of 4-phenyl-1-buten-3-yne-1,1-dicarboxylic acid in a 125-ml. round-bottom flask. This mixture was refluxed for 4 hr., cooled to room temperature and filtered. The crude 3-carboxy-6-phenyl-2-pyrone thus obtained is soluble in bicarbonate solution on gentle warming. On recrystallization from glacial acetic acid there was obtained 0.8 g., 80%, of yellow-orange product, m.p. 218°. Absorption maxima occur at: 1775, 1735, 1675, 1630, 1580, 1545, 1500, 1180, 988, 934, 840, 770 and 687 cm.$^{-1}$ in the infrared and at 240 mμ (log ε 3.73) and 345 mμ (log ε 4.17) in the ultraviolet.

Anal. Calcd. for $C_{12}H_8O_4$: C, 66.67; H, 3.73; neut. equiv., 216. Found: C, 66.88; H, 3.84; neut. equiv., 216.

6-Phenyl-2-pyrone.—A solution of 0.5 g. of 4-phenyl-1-buten-3-yne-1,1-dicarboxylic acid in 20 ml. of 50% sulfuric acid was refluxed for 3 hr. The cooled turbid solution was poured into 200 g. of cracked ice to precipitate the crude 6-phenyl-2-pyrone. Recrystallization from petroleum ether gave 0.2 g., 54%, of light yellow plates, m.p. 68°. Absorption maxima occur at: 1725, 1635, 1580, 1545, 1506, 1460, 1410, 1343, 1118, 1076, 1009, 957, 844, 800, 768 and 687 cm.$^{-1}$ in the infrared and at 235 mμ (log ε 3.92) and 330 mμ (log ε 4.12) in the ultraviolet.

From 3-Carboxy-6-phenyl-2-pyrone.—A solution of 1 g. of 3-carboxy-6-phenyl-2-pyrone in 10 ml. of 50% sulfuric acid was refluxed for 1.5 hr. The cooled reaction mixture was poured into 100 ml. of ice-water to precipitate 0.5 g., 67.5%, of 6-phenyl-2-pyrone.

2,5-Diphenylpenten-2-yne-4-oic Acid.—A solution of 6.0 g. of phenylpropargylaldehyde and 6.0 g. of phenylacetic acid in 25 ml. of acetic anhydride was heated on a boiling water-bath. When temperature equilibrium was attained 3.0 g. of sodium acetate was stirred into the reaction mixture. The reaction was kept at water-bath temperature for 48 hr. The cooled solution was poured onto 300 g. of chipped ice and neutralized with bicarbonate to precipitate the crude product as a yellow brown solid. Recrystallization from ligroin (b.p. 66–75°) gave 9.0 g., 79%, of the product as yellow needles, m.p. 159°. Infrared absorption maxima occur at: 2900, 2200, 1680, 1600, 1580, 1562, 1490, 1440, 1415, 1300, 1280, 1268, 1180, 1070, 1038, 1006, 998, 918, 911, 887, 783, 773, 755, 699 and 687 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87; neut. equiv., 248. Found: C, 82.22, 82.22; H, 5.26, 5.38; neut. equiv., 247.

In the case of *p*-biphenylacetic acid and β-naphthylacetic acid the condensation was complete in 6 hr. Further details of the reaction with other arylacetic acids are given in Table I.

3,6-Diphenyl-2-pyrone.—A catalyst prepared by heating 0.1 g. of yellow mercuric oxide in 5 ml. of concd. sulfuric acid for 15 min. was dissolved in 20 ml. of distilled water. This solution was warmed on a water-bath and 20 ml. of *p*-dioxane containing 1.0 g. of 2-phenyl-5-phenylpenten-2-yne-4-oic acid gradually stirred in. The mixture was heated with agitation for 2.5 hr. The cooled reaction mass was poured onto 200 g. of cracked ice to precipitate the crude yellow product which on recrystallization from ethanol gave 0.4 g., 40%, of yellow needles, m.p. 161° (mixed m.p. with the starting acetylenic acid is 120°). The use of acetone in place of *p*-dioxane in this procedure results in yields of 60%. Absorption maxima occur at: 1712, 1625, 1600, 1575, 1550, 1490, 1450, 1355, 1258, 1110, 1085, 1078, 1046, 1023, 1002, 967, 944, 915, 901, 814, 784, 767, 754, 719, 691 and 685 cm.$^{-1}$ in the infrared and at 245 mμ (log ε 4.25) and 360 mμ (log ε 4.46) in the ultraviolet.

Anal. Calcd. for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87. Found: C, 82.12; H, 5.03.

3-(ε-Naphthyl)-6-phenyl-2-pyrone.—A catalyst prepared by heating 0.2 g. of yellow mercuric oxide in 10 ml. of concd. sulfuric acid for 15 minutes was dissolved in 20 ml. of distilled water and brought to 60°. To the hot mixture 0.5 g. of 2-(β-naphthyl)-5-phenylpenten-2-yne-4-oic acid in 75 ml. of acetone was added in a dropwise manner. Refluxing commenced immediately and was continued for 12 hr. The brown reaction mixture was filtered and upon cooling precipitated the crudely crystalline pyrone. Crystallization two times from benzene gave 0.2 g., 40%, of yellow plates, m.p. 197°. Absorption maxima occur at: 1695, 1620, 1598, 1540, 1490, 1450, 1363, 1325, 1273, 1117, 1145, 1023, 986, 917, 896, 863, 847, 824, 767, 750, 646 and 685 cm.$^{-1}$ in the infrared and at 250 mμ (log ε 4.24) and 365 mμ (log ε 4.31) in the ultraviolet.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.54; H, 4.85.

3-(*p*-Biphenylyl)-6-phenyl-2-pyrone.—A catalyst prepared by heating 1.0 g. of yellow mercuric oxide with 10 ml. of concd. sulfuric acid for 0.5 hr. was dissolved in 20 ml. of distilled water. To this was added 0.5 g. of 2-(*p*-biphenylyl)-5-phenylpenten-2-yne-4-oic acid in 50 ml. of acetone. The mixture was refluxed for 24 hr., cooled to room temperature and filtered. The dried precipitate was extracted with

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(11) Analyses by Micro Tech Laboratories, Skokie, Ill.

(12) E. Schwenk and D. Papa, *J. Org. Chem.*, **11**, 799 (1946).

toluene in a Soxhlet apparatus for 2 hr. The product was precipitated by the addition of ligroin to the extracts and crystallized twice from toluene to give 0.1 g., 20%, of yellow needles, m.p. 268°. Absorption maxima occur at: 1705, 1650, 1600, 1550, 1487, 1448, 1355, 1110, 1142, 1120, 1103, 963, 890, 838, 813, 778, 753, 724 and 683 cm.$^{-1}$ in the infrared and at 265 mμ (log ε 4.27) and 365 mμ (log ε 4.56) in the ultraviolet.

Anal. Calcd. for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97. Found: C, 85.46; H, 4.96.

3-(*p*-Methoxyphenyl)-6-phenyl-2-pyrone.—A catalyst mixture was prepared in the same manner as that used in the synthesis of 3,6-diphenyl-2-pyrone and diluted to 100 ml. with distilled water; 5 ml. of this catalyst was added to a solution of 0.5 g. of 2-(*p*-methoxyphenyl)-5-phenylpenten-2-yne-4-oic acid in 50 ml. of methanol. The reaction was kept at 45–50° for 48 hr. and the methanol evaporated. The precipitate was filtered, washed with distilled water and crystallized two times from ethanol to give 0.1 g., 20%, of yellow plates, m.p. 170°. Absorption maxima occur at: 1700, 1625, 1610, 1575, 1550, 1510, 1490, 1450, 1358, 1305, 1290, 1250, 1175, 1110, 1083, 1047, 1027, 965, 900, 840, 806, 777, 763 and 683 cm.$^{-1}$ in the infrared and occur at 250 mμ (log ε 4.00) and 370 mμ (log ε 4.10) in the ultraviolet.

Anal. Calcd. for $C_{18}H_{14}O_3$: C, 77.68; H, 5.07. Found: C, 77.50; H, 5.10.

Infrared absorption spectra were obtained on potassium bromide pellets using a Baird Associates double beam recording infrared spectrophotometer with sodium chloride optics. Ultraviolet absorption spectra were obtained using 1.00-cm. silica cells in a Beckman DU spectrophotometer. Absolute methanol was used as solvent except as noted.

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[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Pyrolysis of Alkyl Phosphates

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The preparation of amyl dimethyl, dimethyl hexyl, dimethyl octyl, dioctyl methyl and cyclohexyl dimethyl phosphates is described. These five alkyl phosphates and three others have been pyrolyzed to give olefins in high yield. The pyrolyses were accompanied by extensive rearrangement of the olefinic double bond.

In the preparation of olefins by the pyrolysis of esters, it is becoming increasingly apparent that a considerable variation in the nature of the acid moiety is allowable. A recent review[2] has cited numerous examples of olefin formation by pyrolysis in the liquid and vapor phases of esters of many different organic acids, and to these examples may be added the pyrolyses of esters of the inorganic acids, boric acid[3] and sulfurous acid.[4–6] Although no systematic study of the pyrolysis of the esters of phosphorus acids has been reported, isolated examples of the thermal decomposition of such substances to olefins have been described. For example, Gerrard[7] reported that *n*-octyl phosphorodichloridite decomposed to give octylene at 150°. Arbuzov and Valitova[8] obtained olefinic products by heating tertiary alkyl phosphites with methyl iodide in a sealed tube at 200°. Cronje[9] reported that the pyrolysis of dihydrogen dialkyl pyrophosphates at 180° yielded olefins. Other workers have reported obtaining olefinic by-products during the preparation or reaction of various organophosphorus esters but, in most instances, the immediate precursor of the olefin has not been identified and in many may not have been an organophosphorus compound. The present communication describes the preparation and pyrolysis of a number of alkyl phosphates and is the first of a series to be devoted to the pyrolysis of various phosphorus derivatives.

From the many possible simple and mixed alkyl and aryl phosphates three types were selected for study: alkyl dimethyl phosphates (I), dialkyl methyl phosphates (II) and trialkyl phosphates (III).

$$\underset{\text{I}}{RCH_2CH_2OP(O)(OCH_3)_2} \longrightarrow RCH{=}CH_2 + HOP(O)(OCH_3)_2$$

$$\underset{\text{II}}{(RCH_2CH_2O)_2P(O)OCH_3} \longrightarrow 2RCH{=}CH_2 + (HO)_2P(O)OCH_3$$

$$\underset{\text{III}}{(RCH_2CH_2O)_3PO} \longrightarrow 3RCH{=}CH_2 + (HO)_3PO$$

Preparation of the mixed phosphates (I) was effected by treatment of the appropriate alcohol (IV) with phosphorus oxychloride in the presence of dimethylaniline followed by reaction of the intermediate alkyl phosphorodichloridate (V) with sodium methoxide.

$$\underset{\text{IV}}{RCH_2CH_2OH} + POCl_3 \xrightarrow{C_6H_5NMe_2} \underset{\text{V}}{RCH_2CH_2OP(O)Cl_2} \xrightarrow{CH_3ONa} \underset{\text{I}}{RCH_2CH_2OP(O)(OCH_3)_2}$$

The phosphates thus prepared are described in Table I. This procedure was more effective in our hands than the alternative treatment of dimethyl phosphorochloridate with the alkoxide of IV or with IV and a tertiary amine.[10]

Dioctyl methyl phosphate (II, R = C_6H_{13}) was prepared by treating the commercially available dioctyl phosphorochloridate with sodium methoxide in ether or, preferably, with methanol and tri-

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[1] Minnesota Mining and Manufacturing Co. Fellow, 1955–1956.

[2] W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

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[8] A. E. Arbuzov and F. G. Valitova, *Izvest. Akad. Nauk, U.S.S.R. Otdel. Khim. Nauk*, 801 (1952); *C. A.*, **47**, 10462 (1953).

[9] J. H. Cronje, *J. S. African Chem. Inst.* [*N.S.*], **2**, 15 (1949).

[10] The choice of the procedure selected was based on a relatively small number of orienting experiments. In view of the results of G. M. Steinburg (*J. Org. Chem.*, **15**, 637 (1950)) the reaction of IV with dimethyl phosphorochloridate (or its precursors, dimethyl phosphite, carbon tetrachloride and triethylamine) could prove to be superior to the method chosen.