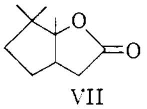
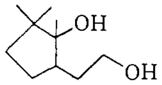

VII


VIII

These results (1) establish the configurations of photolytically generated II and its previously unknown epimer and (2) uncover a novel rearrangement of IIA and B to give VII and an isomeric acid of unknown structure.

[9] Fellow of the Alfred P. Sloan Foundation.

[10] National Science Foundation Cooperative Fellow, 1959–1960.

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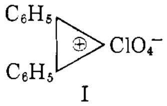
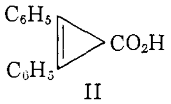
RECEIVED MARCH 24, 1960

THE DIPHENYLCYCLOPROPENIUM ION: PYROLYSIS OF 3,3-BIS-(1,2-DIPHENYLCYCLOPROPENYL) ETHER

Sir:

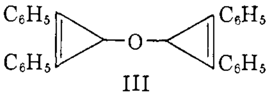
We wish to report a convenient synthesis of diphenylcyclopropenium perchlorate (I).[1] Reaction of 1,2-diphenylcyclopropene-3-carboxylic acid (II)[2] with 10% perchloric acid in acetic anhydride[3] at 0–10° resulted in the evolution of carbon monoxide[4] with concomitant formation of colorless needles of the explosive I, isolated in 70% yield, m.p. 149.5–150.5° (dec.) (from acetonitrile–benzene). Found: C, 61.81; H, 4.25; Cl, 12.23. The presence of perchlorate ion in the product was indicated by a positive test with methylene blue[5] and the presence of strong absorption at 9.1μ characteristic of perchlorate ion in its infrared spectrum. The substance is insoluble in benzene and dichloromethane, but soluble in acetonitrile, dimethylformamide and aqueous sulfuric acid. The spectral properties of I provide interesting confirmation of its ionic nature in that the infrared spectrum exhibits a sharp band at 3.18μ absent from the spectra of the covalent diphenylcyclopropenes encountered in this work, while the ultraviolet spectrum in acetonitrile–10% ethanol exhibits a transition from that characteristic of the covalent diphenylcyclopropenes[6] (λ_m 318, 303, 288, 231, 223 mμ; log ϵ 4.38, 4.50, 4.37, 4.22, 4.31) below *ca.* 0.05 *N* perchloric acid to one very similar (λ_m 305, 292, 246; log ϵ 4.52, 4.50, 4.03) to that of the triphenylcyclopropenium ion[6] in 0.05 to 0.1 *N* perchloric acid. Chemical evidence for the assigned structure was provided by hydrolysis of I in aqueous potassium hydroxide to give α-phenylcinnamaldehyde identical with an authentic sample.[7] The general utility of the preparative method for I is suggested by the similar preparation of dipropylcyclopropenium perchlorate by Breslow and Höver.[8]

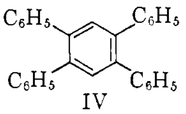

I

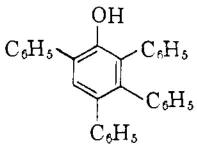

II

Hydrolysis of I in aqueous sodium bicarbonate resulted in the formation of 3,3-bis-(1,2-diphenylcyclopropenyl) ether (III), m.p. 163–165° (dec.). Found: C, 90.37; H, 5.58. The structural assignment follows from the spectroscopic properties of the product; λ_m (CH_3CN) 319, 303, 290, 231, 224; log ϵ 4.63, 4.74, 4.63, 4.54, 4.61; λ_m (0.1 *N* $HClO_4$, CH_3CN) 305, 292, 246; log ϵ 4.82, 4.80, 4.28. Pyrolysis of III at 180° for a short time yielded a mixture of products containing, as the major component, 1,2,4,5-tetraphenylbenzene (IV), m.p. 264.5–267°, identical with an authentic sample.[9] In addition, *2,3,4,6-tetraphenylphenol* (V) m.p. 247–248°, identical with an authentic specimen,[10] was isolated as the only phenolic component detectable by infrared spectroscopy.

The photolysis of III, and the mechanistic implications of its pyrolysis are currently under investigation.


III


IV


V

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[1] Salts of this cation have been prepared independently by R. Breslow and J. Lockhart, unpublished work, by reaction of phenylchlorocarbene with phenylacetylene. We wish to thank Professor Breslow for a pre-publication account of his results.

[2] R. Breslow, R. Winter and M. Battiste, *J. Org. Chem.*, **24**, 415 (1959).

[3] *Cf.* M. J. S. Dewar and C. Ganellin, *J. Chem. Soc.*, 2438 (1959).

[4] F. Feigl, "Spot Tests in Organic Analysis," Elsevier, New York, N. Y., 1956, p. 327.

[5] G. Charlot, "Quantitative Inorganic Analysis," John Wiley and Sons, New York, N. Y., (1954) p. 271 (Translation).

[6] R. Breslow and C. Yuan, THIS JOURNAL, **80**, 5991 (1958).

[7] K. Alder, J. Hayden, K. Heimbach, K. Neufang, G. Hansen and W. Gerhard, *Ann.*, **586**, 110 (1954).

[8] R. Breslow and H. Höver, THIS JOURNAL, **82**, 2644 (1960).

[9] W. Dilthey, I. Thewalt and O. Trosken, *Ber.*, **67B**, 2004 (1934).

[10] P. Yates and J. Hyre, unpublished work. The authors affirm their indebtedness to Professor Yates for supplying spectroscopic data and comparison samples of the three isomeric tetraphenylphenols.

DEPARTMENT OF CHEMISTRY
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RECEIVED APRIL 7, 1960

A CARBON-SKELETON REARRANGEMENT DURING THE OXIDATIVE DEPHOSPHORYLATION OF A NEW TYPE OF PHOSPHORUS COMPOUND. REACTION OF MOLECULAR OXYGEN WITH THE CRYSTALLINE 1:1 ADDUCTS DERIVED FROM TERTIARY PHOSPHITE ESTERS AND *alpha*-DIKETONES[1]

Sir:

During our investigations[2] of the reactions of phosphite esters with quinones and with other carbonyl compounds, we have encountered a carbon-skeleton rearrangement which we believe to be new and significant. This rearrangement

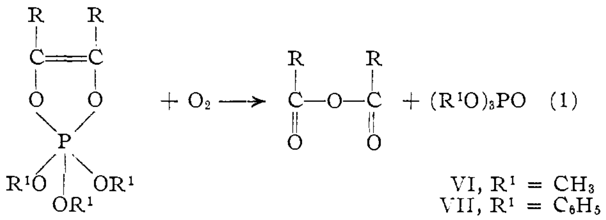
[1] Acknowledgment is made to the Donors of the Petroleum Research Fund Administered by the American Chemical Society for partial support of this Research (Grant 286-A), and to the National Cancer Institute of the National Institutes of Health (Grant CY-4769).

[2] (a) F. Ramirez and N. B. Desai, THIS JOURNAL, **82**, 2652 (1960); (b) F. Ramirez, E. H. Chen and S. Dershowitz, *ibid.*, **81**, 4338 (1959), and reference therein.

takes place when the 1:1 adducts[2,3] formed from tertiary phosphite esters $(R^1O)_3P$ and α-diketones, RCOCOR are allowed to react with dry molecular oxygen, in benzene solution at room temperature.

A stirred solution of the *colorless, crystalline* benziltrimethyl phosphite adduct[2a] I, m.p. 49°, in anhydrous benzene was kept at room temperature for five days under a slight pressure of dry oxygen. The mixture obtained upon removal of the benzene under reduced pressure contained benzoic anhydride (IV, *ca.* 30%), benzil (VIII, *ca.* 67%) and trimethyl phosphate (VI, *ca.* 94%).

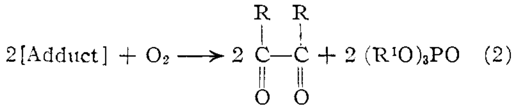
The composition of the reaction mixture was ascertained by examination of its infrared spectrum and by actual isolation of the three substances in the stated yields. The presence of benzoic anhydride was confirmed by the direct formation, from the reaction mixture, of benzanilide and of benzoic acid. These results conform to the equations



(1)

VI, $R^1 = CH_3$
VII, $R^1 = C_6H_5$

I, $R = C_6H_5$; $R^1 = CH_3$ IV, $R = C_6H_5$
II, $R = R^1 = C_6H_5$ V, $R = CH_3$
III, $R = R^1 = CH_3$



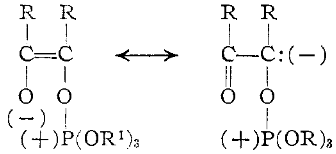
(2)

VIII, $R = C_6H_5$ VI, $R^1 = CH_3$
IX, $R = CH_3$ VII, $R^1 = C_6H_5$

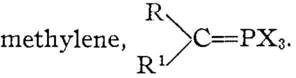
A similar, although faster, reaction was observed between molecular oxygen and the colorless, crystalline benzil-triphenylphosphite adduct,[2a] II, m.p. 99°. Benzoic anhydride (IV, *ca.* 25%), benzil (VIII) and triphenyl phosphate (VII) were isolated after three days.

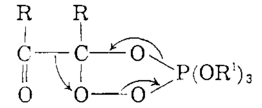
Oxygen reacted also with the colorless, liquid biacetyl-trimethyl phosphite adduct[2a], III. The reaction appeared to be slower and gave acetic anhydride (V, at least 10–15%), biacetyl (IX, over 61%) and trimethyl phosphate (VI, *ca.* 80%) after nine days. A fourth substance, not yet identified, also was formed in *ca.* 15% yield.

In another communication[2a] we have summarized the evidence bearing on the structure of the α-diketone-tertiary phosphite adducts and of the *o*-quinone-tertiary phosphite adducts. The proton and phosphorus nuclear magnetic resonance spectra, the dipole moments and the infrared spectra are consistent only with cyclic structures I, II, III, for these adducts.[2a,3a] The results of the reactions of the adducts with anhydrous hydrogen chloride in ether solution and with bromine in carbon tetrachloride solution at low temperatures were also described.[2a] These reactions could be interpreted as attacks on the cyclic pentacovalent structures or on open dipolar forms such as Ia, IIa, IIIa. The latter could conceivably be present in small amounts in solutions of the adducts.



Ia, IIa, IIIa etc.

It seems possible that the oxygen-induced carbon-skeleton rearrangement, and the oxidative dephosphorylation observed with the adducts in benzene solution at room temperature, proceed via an intermediate such as X. X is essentially an "ozonide" derived from a phosphinemethylene,  $\genfrac{}{}{0pt}{}{R}{R^1}\!>\!C{=}PX_3$. It could decompose to the anhydride (IV or V) or could react with more adduct to give the original α-diketone (VIII or IX). These and other hypotheses are under investigation.



X

DEPARTMENT OF CHEMISTRY OF STATE UNIVERSITY OF NEW YORK COLLEGE ON LONG ISLAND OYSTER BAY, NEW YORK
FAUSTO RAMIREZ
R. B. MITRA
N. B. DESAI

RECEIVED MARCH 23, 1960

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[3] For other reports on "liquid" α-diketone-*trialkyl* phosphite adducts see: (a) G. H. Birum and J. L. Dever, Abstracts, Div. of Org. Chem., A.C.S. Meeting, Chicago, Ill., Sept. 1958, p. 101-P; (b) V. A. Kukhtin, *Doklady Akad. Nauk, S.S.S.R.*, **121**, 466 (1958); *C. A.*, **53**, 1105b (1959).

CRYSTALLINE 1:1 ADDUCTS FROM THE REACTION OF TERTIARY PHOSPHITE ESTERS WITH *ortho*-QUINONES AND WITH *alpha*-DIKETONES. NEW ROUTES TO QUINOL-MONOPHOSPHATES AND TO KETOL-MONOPHOSPHATES[1]

Sir:

Extending our investigations[2] on the reactions of trivalent phosphorus compounds with quinones and with other carbonyl compounds (OAO), we have made observations which have a bearing on the problem of the pentacovalency of phosphorus, and which introduce new methods for the preparation of quinol-monophosphates.

(1) Trialkyl and triaryl phosphites react with *o*-quinones and with α-diketones[3] to form colorless, 1:1 adducts, $[(OAO{\cdot}P(OR)_3]$. Some of these adducts can be obtained in crystalline form and are stable in the absence of both air and moisture. Information derived from proton and phosphorus

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[1] Acknowledgment is made to the Donors of the Petroleum Research Fund Administered by the American Chemical Society for partial support of this Research (Grant 286-A), and to the National Cancer Institute of the National Institutes of Health (Grant CY-4769).

[2] (a) F. Ramirez and S. Dershowitz, THIS JOURNAL, **78**, 5614 (1956); (b) *J. Org. Chem.*, **22**, 856 (1957); (c) **22**, 1282 (1957); (d) **23**, 778 (1958); (e) THIS JOURNAL, **81**, 587 (1959); (f) F. Ramirez, E. H. Chen and S. Dershowitz, *ibid.*, **81**, 4338 (1959); (g) F. Ramirez, H. Yamanaka and O. H. Basedow, *J. Org. Chem.*, **24**, 1838 (1959).

[3] Other recent reports on the reaction of trialkyl phosphites with *α-diketones:* (a) G. H. Birum and J. L. Dever, Abstracts, Div. of Org. Chem., A.C.S. Meeting, Chicago, Ill., Sept., 1958, p. 101-P; (b) V. A. Kukhtin, *Doklady Akad. Nauk, S.S.S.R.*, **121**, 466 (1958); *C. A.*, **53**, 1105b (1959). The latter two mention "liquid" adducts only.