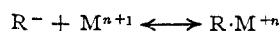
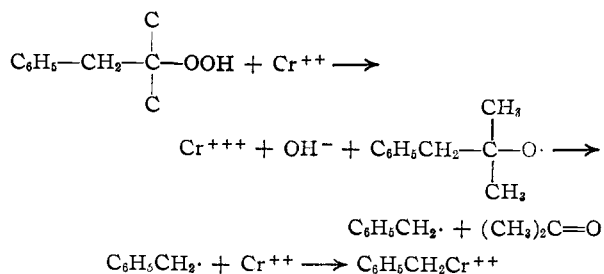


The postulation of a metal ion-free radical complex is not without precedent. Formally, organo-metallics derived via carbanionic processes do possess free radical character.² More directly,



we have observed that chromous sulfate reacts with phenyl-*tert*-butyl hydroperoxide to form an isolable benzyl chromous ion, $C_6H_5CH_2 \cdot Cr^{+2}$, identical to the species isolated by Anet³ from the reaction of benzyl chloride and chromous perchlorate.



This complex ion dimerizes to bibenzyl and reacts with oxygen to form benzaldehyde.

In a subsequent report we shall explore further the oxidation-reduction reactions of these complex ions and intermediates derived from the interaction of free radicals and metal ions.

(2) E. Rochow, P. Hurd and R. Lewis, 'Chemistry of Organometallic Compounds,' John Wiley and Sons, Inc., New York, N. Y., 1957.

(3) F. Anet, *J. Am. Chem. Soc.*, **79**, 2649 (1957).

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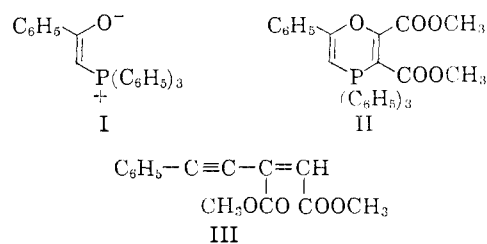
SYNTHESIS OF A PHOSPHORANE HETEROCYCLE

Sir:

The few known phosphoranes with five P-C single bonds¹ have mostly involved benzene rings attached to phosphorus and their formation only from high-energy materials such as phenyl-lithium as well as their easy decomposition has led to a view that such a bonding circumstance is intrinsically unstable. It seemed likely to us that the instability of compounds such as pentaphenylphosphorane was caused largely by steric compression of the phenyl rings. We have now prepared the first monocyclic phosphorane heterocycle, an oxaphosphorin,² by a method which involves no high-energy starting materials and its general stability bears out this qualitative view.

When the phosphonium enolate I³ was boiled for ten minutes with an equivalent of dimethyl acetylene-dicarboxylate in methanol and left overnight, a 35% yield of dimethyl 4,4,4,6-tetraphenyl-

1,4-oxaphosphorin-2,3-dicarboxylate (II), as yellow blocks, m.p. 175-179° (*Anal.* Calcd. for $C_{32}H_{27}PO_5$, C, 73.53; H, 5.22. Found: C, 73.78, 73.42; H, 4.97, 5.21). The infrared spectrum was consistent with this formulation in showing no hydroxyl bands, one carbonyl at 5.82 μ , and double



bond at 6.30 μ . The ultraviolet spectrum exhibited maxima at 222 $m\mu$ ($\log \epsilon$ 4.57), 267 $m\mu$ (3.88), 274 $m\mu$ (3.84), 307 $m\mu$ (3.76), and 367 $m\mu$ (3.77). Vacuum pyrolysis of II at its melting point caused clean sublimation, in virtually quantitative yields, of triphenylphosphine oxide, m.p. 153-155°, and a compound, $C_{14}H_{12}O_4$ (*Anal.* Calcd.: C, 68.84; H, 4.95. Found: C, 68.70; H, 4.97), as colorless needles, m.p. 83.5-85°. The latter was identified as III by its infrared spectrum (4.50, 5.80, 6.22 μ), and its conversion, by three equivalents of hydrogen (over platinum in ethanol) and saponification, to β -phenylethylsuccinic acid, m.p. 134-136° (lit.,⁴ 136°), anhydride, m.p. 55-57° (lit.,⁴ 56°). The proton magnetic resonance spectrum supports the formulation of III, showing only three peaks with τ -values (relative intensities in parentheses): phenyl, 2.70 (5), olefinic hydrogen, 3.72 (1), and methoxyl, 6.27 (6). Inquiries into the mechanistic course of this unusual pyrolytic reaction will be the subject of a future communication, although it may be conjectured safely at present that in general terms the triphenylphosphine moiety is extruded with the transannular oxygen, leaving all the remaining groups to reform into III; consideration of the boat form of the oxaphosphorin⁵ shows the formation of such a P-O bond to be sterically reasonable.

It is to be expected⁶ that an adjacent phosphorus nucleus, with its spin of 1/2 will couple with a proton and show a splitting of the proton magnetic resonance signal, and initial observations in this laboratory⁷ bear out this prediction. In particular, while triphenyl phosphite shows a clean single peak at 2.80 τ , triphenylphosphine shows a split doublet at 2.83 τ (intensity = 2, J = 2 cps.) and a single peak at 2.93 τ (intensity = 3), indicating splitting of only the ortho-hydrogen signals by adjacent phosphorus. Appropriately, then, the oxaphosphorin II showed four peaks with these τ -values: a complex assemblage similar to that of triphenylphosphine at 2.52 (20) due to the four phenyls, a clean doublet at 4.70 (1) (J = 4 cps.) due to the

(4) J. Thiele and J. Meisenheimer, *Ann.*, **306**, 247 (1899).

(1) G. Wittig and M. Rieber, *Ann.*, **562**, 187 (1949); G. Wittig and G. Geissler, *ibid.*, **580**, 44 (1953); see P. C. Crofts, *Quart. Revs.*, **12**, 341 (1958).

(2) "The Ring Index," no. 183, A. M. Patterson, Reinhold Publ. Corp., New York, N. Y., 1940.

(3) F. Ramirez and S. Dershowitz, *J. Org. Chem.*, **22**, 41 (1957).

(5) The somewhat similar heterocycle, dithiadene, is known to exist in a boat form: W. E. Parham, *et al.*, *J. Am. Chem. Soc.*, **76**, 4957 (1954).

(6) L. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959.

(7) H. D. Kaesz and James B. Hendrickson, in preparation.

olefinic hydrogen adjacent to phosphorus, and two sharp methoxyl peaks at 6.57 (3) and 6.92 (3)

The synthesis of this unique heterocycle promises to be a general one, providing as it does an unusual example of our recent proposal of a general method for heterocycle synthesis.⁸ Further investigations into the properties of this and other pentavalent phosphorus heterocycles are underway.

(8) James B. Hendrickson and R. Rees, *J. Am. Chem. Soc.*, **83**, 1250 (1961).

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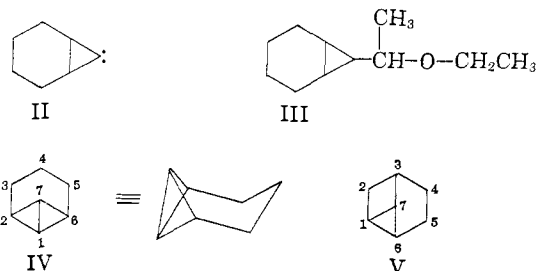
RECEIVED FEBRUARY 28, 1961

THE FORMATION OF HIGHLY-STRAINED SYSTEMS BY THE INTRAMOLECULAR INSERTION OF A CYCLOPROPYLIDENE: TRICYCLO[4.1.0.0^{2,7}]HEPTANE AND TRICYCLO[4.1.0.0^{2,7}]HEPTANE⁸

Sir:

In a recent communication,² we have presented evidence that the reaction of 7,7-dibromobicyclo[4.1.0]heptane, I, with methyllithium gives rise to carbene II, as shown by the isolation of spiro-pentanes in trapping experiments with olefins. Subsequently, the addition of II to olefins has been shown to be stereospecific³ since *cis*-2-butene gives a spiro-pentane isomeric with that obtained from *trans*-2-butene (both reactions are at least 99.6% stereospecific). Remarkably, however, II does not react with tetramethylethylene, presumably due to steric hindrance.

Further evidence for the carbene nature of II has been derived from the isolation of products of insertion reactions. For example, II reacts with the solvent, diethyl ether, to give a saturated ether (20%), C₁₁H₂₀O, assigned structure III (Found: C, 78.44; H, 12.07; mol. wt.,⁴ 168), $\nu_{\max}^{\text{CCl}_4}$ 2990 (tertiary cyclopropane C-H), 1380 (the intensity indicates two C-CH₃), 1100 cm.⁻¹ (C-O-C). Hydrogenation of III (30% Pd/C, propionic acid) proceeded with the slow absorption of two equivalents of hydrogen to give *n*-propylcyclohexane, a result which is entirely consistent with the formulation of III as a cyclopropylcarbinyl ether.



(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

(3) W. M. Jones, *J. Am. Chem. Soc.*, **82**, 6200 (1960), has reported that 2,2-diphenylcyclopropylidene, generated from the diazocyclopropane, reacts stereospecifically with *cis* and *trans*-2-butene.

(4) Obtained by mass spectrometry. We thank Professor K. Biemann and his co-workers for measuring mass spectra.

Of greater interest is the fact that cyclopropylidene II can undergo intramolecular insertion⁵ to produce certain highly-strained systems. Thus the reaction of I⁶ with methyllithium in ether (-80 to 0°) gives about 40% of a hydrocarbon fraction, b.p. 110°, separable by gas chromatography⁷ into three isomers (C₇H₁₀), IV (93%), V (4%) and VI (3%).⁸

Compound IV, obtained as a colorless liquid, has been shown to be a bicyclobutane derivative, tricyclo[4.1.0.0^{2,7}]heptane, formed by intramolecular insertion of II in the 2-position (Found: C, 89.10; H, 10.76; mol. wt.,⁴ 94), n_D^{25} 1.4660, $\nu_{\max}^{\text{CCl}_4}$ 3080m, 2995s cm.⁻¹. In heptane it exhibits only weak end absorption in the far ultraviolet, λ_{μ} (log ϵ), 210 (2.81), 200 (3.28), 190 (3.54), 186 (3.58). The n.m.r. spectrum (pure liquid, 56.4 mc.) consists of three peaks with area ratios of 6:2:2 at 8.55 (m), 8.33 (t) and 7.58 (m) τ . The triplet at 8.33 is due to the C-1 and C-7 protons coupled with the C-2 and C-6 protons. The latter appear as the multiplet at 7.58 and the band at 8.55 arises from the methylene protons (C-3, C-4, and C-5).

Hydrogenation of IV (Pd/C, ethanol) proceeds fairly rapidly to give chiefly methylcyclohexane accompanied by small amounts of other compounds, among which cycloheptane and norcarane have been identified. In the absence of acids, IV is quite stable.⁹ Brief contact with acids, e.g., a trace of aluminum chloride in ether, results in isomerization to 2-norcarane, VII (Found: C, 88.81; H, 10.82; mol. wt.,⁴ 94), $t_{\text{VII}} = 3.54$,⁷ $\nu_{\max}^{\text{CCl}_4}$ 3077 and 3005 (cyclopropane C-H), 3035 (olefin C-H), 1643 (C=C) cm.⁻¹; $\lambda_{\max}^{\text{pentane}}$ 207.5 μ (log ϵ 3.65, ν -C=C); n.m.r., two non-equivalent olefin protons, 4.08 (q) and 4.60 (m) τ . Hydrogenation of VII (Pd/C, ethanol) has given chiefly methylcyclohexane accompanied by varying amounts of norcarane and cycloheptane.

The isomerization of IV to VII must involve addition of a proton to C-1 of IV. Formally, the 1,7-bond could cleave to give a cyclobutyl cation or one of the 1,2-bonds could cleave to give a cyclopropylcarbinyl cation (which would afford VII by loss of a proton from C-3). However, it is clear that the geometry of bicyclobutane IV is such that if cyclobutyl-cyclopropylcarbinyl cations can ever be described in terms of a single non-classical ion the present example must be such a case.¹⁰

Isomer V (mol. wt.,⁴ 94; $\nu_{\max}^{\text{CCl}_4}$ 3068w, 3039w, 2971m cm.⁻¹; no ultraviolet maxima, λ_{gas} 186

(5) L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); W. Kirmse and W. von E. Doering, *Tetrahedron*, **11**, 266 (1960); G. L. Closs, Abstracts of Papers, 138th Meeting of the American Chemical Society, New York, Sept., 1960, p. 9-P; L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **83**, 501 (1961).

(6) 7,7-Dichlorobicyclo[4.1.0]heptane reacts with butyllithium in ether at 0° in a similar manner.

(7) Relative retention times on tetraethylene glycol at 27°: $t_{\text{IV}} = 2.35$, $t_{\text{V}} = 1.78$, $t_{\text{VI}} = 1.00$.

(8) The structure of VI will be discussed in the future.

(9) This stability contrasts with that reported for ethyl bicyclobutane-1-carboxylate (apparently the only prior authentic bicyclobutane), K. Wiberg and R. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).

(10) For a discussion of non-classical ions see J. D. Roberts, *et al.*, *ibid.*, **81**, 4390 (1959), and references therein.