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 pentacovalent phosphorus heterocycles are underway.

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

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA JAMES B. HENDRICKSON
LOS ANGELES 24, CALIFORNIA

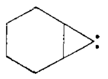
RECEIVED FEBRUARY 28, 1961

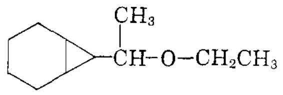
THE FORMATION OF HIGHLY-STRAINED SYSTEMS BY THE INTRAMOLECULAR INSERTION OF A CYCLOPROPYLIDENE: TRICYCLO[4.1.0.0^{2,7}]-HEPTANE AND TRICYCLO[4.1.0.0^{3,7}]HEPTANE[1]

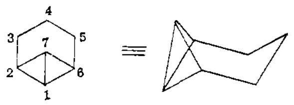
Sir:

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 spiropentanes in trapping experiments with olefins. Subsequently, the addition of II to olefins has been shown to be stereospecific[3] since *cis*-2-butene gives a spiropentane 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.

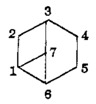
Further evidence for the carbene nature of II has been derived from the isolation of products of insertion reactions. For example, II reacts with the solvent, diethyl ether, to give a saturated ether (20%), $C_{11}H_{20}O$, assigned structure III (Found: C, 78.44; H, 12.07; mol. wt.,[4] 168), $\nu_{\max}^{CCl_4}$ 2990 (tertiary cyclopropane C-H), 1380 (the intensity indicates *two* C-CH$_3$), 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.


II


III



IV



V

Of greater interest is the fact that *cyclopropylidene II can undergo intramolecular insertion*[5] *to produce certain highly-strained systems.* Thus the reaction of I[6] with methyllithium in ether (−80 to 0°) gives about 40% of a hydrocarbon fraction, b.p. 110°, separable by gas chromatography[7] into three isomers (C_7H_{10}), 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), $n^{25}D$ 1.4660, $\nu_{\max}^{CCl_4}$ 3080m, 2995s cm.$^{-1}$. In heptane it exhibits only weak end absorption in the far ultraviolet, $\lambda m\mu$ (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-norcarene, VII (Found: C, 88.81; H, 10.82; mol. wt.,[4] 94), t_{VII} = 3.54,[7] $\nu_{\max}^{CCl}$ 3077 and 3005 (cyclopropane C-H), 3035 (olefin C-H), 1643 (C=C) cm.$^{-1}$; $\lambda_{\max}^{\text{pentane}}$ 207.5 mμ (log ϵ 3.65, $\triangleright$-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; $\nu_{\max}^{CCl_4}$ 3068w, 3039w, 2971m cm.$^{-1}$; no ultraviolet maxima, λ^{gas} 186

---

(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.

(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_{IV} = 2.35, t_V = 1.78, t_{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.

mμ, log ε ~ 3.1) absorbed one equivalent of hydrogen (Pd/C, ethanol) to give norbornane (92%) plus three unidentified compounds (8%).[11] The formation of norbornane greatly restricts the possible structures for V. Since V is neither nortricyclene nor norbornylene, we believe that the assigned structure, tricyclo[4.1.0.0^{3,7}]heptane, must be correct and that V is derived from II by insertion in the 3-position.

The formation of IV and V by self-insertion has encouraged us to attempt extensions of this reaction. In effect, one has at hand a two-step synthesis: addition of a dihalocarbene[12] to an appropriate olefin followed by generation of the cyclopropylidene with an organometallic reagent. Currently, we are trying to define the scope of this approach. Preliminary results suggest that it will be possible to form a number of new highly-strained systems.[13]

[11] Hydrogenation of bicyclo[2.1.0]pentane gives cyclopentane, R. Criegee and A. Rimmelin, *Ber.*, **90**, 414 (1957).

[12] W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **76**, 6162 (1954), and later papers; P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956), and later papers.

[13] For example, 8,8-dibromobicyclo[5.1.0]octane appears to undergo similar reactions.

[14] National Science Foundation Summer Fellow, 1959.

[15] National Institutes of Health Predoctoral Fellow, 1960–1961.

DEPARTMENT OF CHEMISTRY
MASSACHUSETTS INSTITUTE OF TECH.
CAMBRIDGE 39, MASSACHUSETTS

WILLIAM R. MOORE
HAROLD R. WARD[14]
RICHARD F. MERRITT[15]

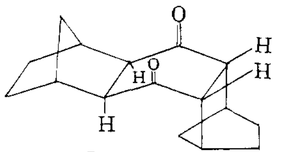
RECEIVED MARCH 2, 1961

INTERACTIONS OF HOMOCONJUGATED 1,4-CHROMOPHORES IN BOAT CYCLOHEXANE DERIVATIVES[1]

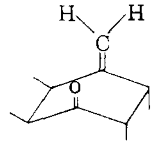
Sir:

The alteration of characteristic ultraviolet spectra by interactions between non-adjacent chromophores is of considerable theoretical interest.[2] In the case of unsaturated ketones,[2–6] these interactions are even more intriguing because of the analogy[2b,3,4] with anchimeric effects of the olefinic group in solvolysis of the toluenesulfonates of the related alcohols. We now have completed the preparation of an instructive series of unsaturated ketones which have 1,4-olefinic and carbonyl groups across from each other in a boat cyclohexane ring, and we report in the present Communication the striking ultraviolet spectra which these ketones display.

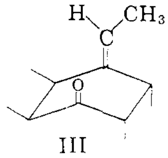
The new ketones are derived from diketone[7] I, m.p. 165°, obtained from hydrogenation of the bis-cyclopentadiene–benzoquinone adduct and subsequent isomerization. The alcohol,[8] m.p. 175–176°, from addition of isopropyllithium to the diketone gives rise to a mixture of unsaturated ketones on treatment with thionyl chloride in pyridine. From this mixture the γ,δ-unsaturated ketone[7,8] IV, m.p. 155–157°, can be isolated in pure condition. Osmium tetroxide oxidation of ketone IV, then lead tetraacetate cleavage of the resulting glycol, regenerates diketone I in high yield. Analogs of ketone IV, the γ-ethylidene ketone[8] III, m.p. 53–55°, and the γ-methylene ketone[8] II, m.p. 66–67°, were prepared by the action of the appropriate Wittig reagent on diketone I. In the case of III, the structure was confirmed by oxidation back to diketone I, as was done for IV.



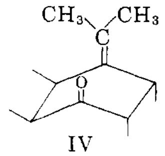
I



II



III



IV

Besides the low[9] and high wave length absorptions at *ca.* 187 and 300 mμ shown by the monoketone[7c] V, all three unsaturated ketones display new absorption bands at intermediate wave lengths. As summarized in Table I, the new bands for the three ketones occur at 210–239 mμ with ε values of 3,000–4,000 in heptane, and at 214–

TABLE I

ULTRAVIOLET SPECTRA OF SEVERAL KETONES[a]

V mμ	V ε	II mμ	II ε	III mμ	III ε	IV mμ	IV ε
				Heptane			
185.2[b]	2800	185[b]	10,700	185.9[b]	11,000	188	8500
						194(sh)	8220
		209.5	3,110	219	2,720	239	3940
300.6	29	298.4	32	301.6	27	306	31
				95% EtOH			
187.3[c]	3600	187.6[c]	11,240	187.6[c]	11,450	192[c]	9000
						199(sh)	8500
		214(sh)	1,810	224.5	1,455	244	2530
297	34	297	43	297	33	302(sh)	50

[a] Cary 14 Recording Spectrophotometer, 0.01 cm. cell and dry nitrogen flush employed for far ultraviolet region. [b] Not a maximum. [c] Doubtful maximum.

---

[1] Research sponsored by the Office of Ordnance Research, U. S. Army.

[2] *E.g.*, (a) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); (b) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960).

[3] P. D. Bartlett and B. E. Tate, *ibid.*, **78**, 2473 (1956).

[4] (a) S. Winstein, M. Brown, K. C. Schreiber and A. H. Schlesinger, *ibid.*, **74**, 1140 (1952); (b) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954).

[5] (a) R. C. Cookson and N. S. Wariyar, *J. Chem. Soc.*, 2302 (1956); (b) R. C. Cookson and N. Lewin, *Chemistry and Industry*, 984 (1956).

[6] (a) C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **43**, 1390 (1960); (b) C. A. Grob and A. Gagneux, unpublished work quoted by Labhart and Wagnière.[2a]

[7] (a) S. Winstein, *Experientia Supplementum II*, 137 (1955); (b) S. Winstein, page 29 of Abstracts of 15th National Organic Chemistry Symposium of the American Chemical Society, Rochester, New York, June 17–20, 1957; (c) L. de Vries, R. Heck, R. Piccolini and S. Winstein, *Chemistry and Industry*, 1416 (1959).

[8] Satisfactory carbon and hydrogen analyses were obtained for the new compounds here mentioned.

[9] The much more intense low wave length absorption of the unsaturated ketones II → IV compared to the mono-ketone V must involve the olefinic as well as the carbonyl group.