p.p.m.) is coupled additionally to at least two unlike hydrogen nuclei.

All the spectroscopic data can be accommodated by formulating the photochemical reaction of cis-2-cyclooctenone as an isomerization to trans-2-cyclooctenone (I). This highly strained α,β-unsaturated ketone is locked into a rigid conformation in which the π-orbital planes of the carbonyl and ethylenic groups are nearly orthogonal. Clearly, this geometry interrupts the conjugative interactions of the two chromophores. Thus, in both the infrared and ultraviolet spectra the carbonyl absorption appears similar to that of a saturated ketone.

I
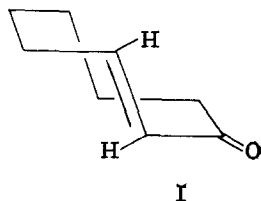
Complete verification of the trans structure can be achieved chemically. The irradiation product is extraordinarily reactive. Whereas cis-2-cyclooctenone reacts only slowly at 90° with 1,1-dimethoxy-2,3,4,5-tetrachlorocyclopentadiene, the photoproduct reacts vigorously at room temperature. The cis ketone forms only a single 1:1 adduct (II, m.p. 118–120°). The photoproduct gives two 1:1 adducts (III and IV); neither of these is identical with the adduct obtained from cis-2-cyclooctenone, but one (III, m.p. 116–118°) is isomerized quantitatively by either active alumina or methanolic base to that adduct. Hence, both the geometry of the double bond and its position in the photoproduct are established.


II III

IV
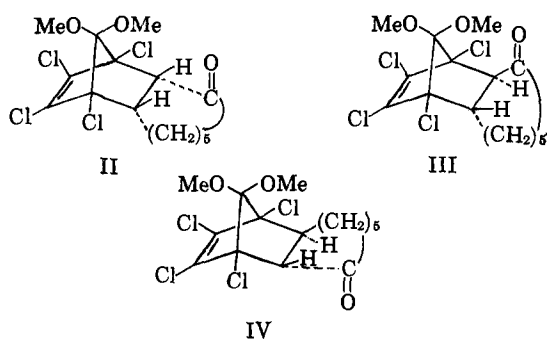
The remarkable ease with which the ethylenic segment of trans-2-cyclooctenone enters into carbon–carbon bond forming reactions[7] is foreign to more prosaic α,β-unsaturated ketones. This reaction is not limited to condensation only with active dienes. Indeed, trans-2-cycylooctenone dimerizes in the dark at room temperature. Of the dimers formed, two have been isolated pure, m.p. 133–134° and 88–90°. Both are saturated diketones. They are taken to be substituted cyclobutanes, stereoisomers of either V or VI.

It is important to note that products such as these are normally obtained only by ultraviolet excitation of cyclic α,β-unsaturated ketones, e.g., 2-cyclopentenone[8a] and 2-cyclohexenone.[8b] Whether or not the thermal dimerization of a strained trans olefinic ketone, itself

(7) Cyclopentadiene and furan react easily with trans-2-cyclooctenone but only with difficulty with the cis isomer, cyclopentenone, or cyclohexenenone. The furan adducts to trans-2-cyclooctenone open on treatment with acid to give 3-(2-furyl)-cyclooctan-1-one.

(8) (a) P. E. Eaton, J. Am. Chem. Soc., 84, 2344 (1962); (b) P. E. Eaton, unpublished work.

V VI
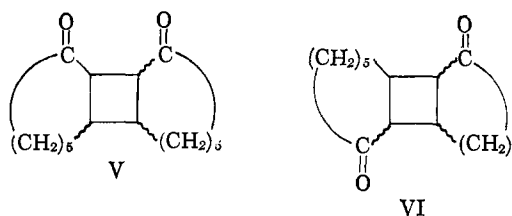
produced photochemically, and the light-induced dimerizations of other unsaturated ketones are related remains the object of our further work.

DEPARTMENT OF CHEMISTRY   PHILIP E. EATON[9]
THE UNIVERSITY OF CHICAGO   KANG LIN
CHICAGO 37, ILLINOIS

The Reaction of Carbethoxycarbene with Biphenylene

Sir:

The selective addition of carbenes to aromatic hydrocarbons is a valuable route to certain nonbenzenoid aromatic systems.[1] Orientation in the addition of carbethoxycarbene to naphthalenes,[2] anthracene,[3] and phenanthrene[4] has been qualitatively correlated with the localization energy of the π-bond undergoing attack.[5] In the case of biphenylene (I), bond-localization energy calculations[6] predict the C-2–C-3 bond as the preferred site of addition, and it is clear that the initial adduct (II) from such addition could lead to novel systems containing a fused cyclobutene ring.

I II
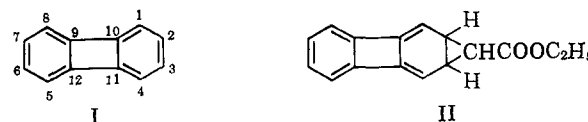
Baker and McOmie have reported that attempted addition of ethyl diazoacetate to biphenylene, followed by saponification, produced only traces of an unidentified carboxylic acid, m.p. 260–268°.[7] In our hands the dropwise addition of excess ethyl diazoacetate to biphenylene at 165° led to the gradual development of a new chromophore in the ultraviolet spectrum at 290–320 mμ. Extraction of the reaction mixture with hot petroleum ether followed by alumina chromatography of the extract produced (in addition to recovered biphenylene) a 15% yield[8] of a colorless crystalline ester, m.p. 80–82°, $\lambda_{max}^{cyclohexane}$ 307, 299, 294, 283, and 272 mμ

(1) E.g., azulenes, tropylium derivatives, cyclononatetraenyl anion [(T. J. Katz and P. J. Garratt, J. Am. Chem. Soc., 85, 2852 (1963); A. E. LaLancette and R. E. Benson, ibid., 85, 2853 (1963)].

(2) R. Huisgen and G. Juppe, Chem. Ber., 94, 2332 (1961); Tetrahedron, 15, 7 (1961).

(3) G. M. Badger, J. W. Cook, and A. R. M. Gibb, J. Chem. Soc., 3456 (1951).

(4) M. J. S. Dewar and C. R. Ganellin, ibid., 3139 (1959).

(5) A general treatment of orientation by "double bond reagents" in terms of bond localization energies is given by R. D. Brown, Quart. Rev. (London), 6, 63 (1952).

(6) The loss in π energy by localizing adjacent positions in biphenylene is given by simple Hückel LCAO theory as follows (positions localized given by subscripts).

$$L_{1,2} = 3.60\beta \qquad L_{1,10} = 3.58\beta$$
$$L_{2,3} = 3.36\beta \qquad L_{10,11} = 4.40\beta$$

(7) W. Baker and J. F. W. McOmie in D. Ginsburg, "Non-Benzenoid Aromatic Compounds," Interscience, New York, N. Y., 1959, p. 79.

(8) Based on biphenylene not recovered.

(log ε 4.54, 4.36, 4.34, 4.43, and 4.33) which gave analytical data consistent with adduct II (*Anal.* Found: C, 80.13; H, 6.05). The proton magnetic resonance spectrum of this ester in CDCl$_3$ showed, in addition to the ethoxyl protons, a two-proton singlet at τ 6.16 and a seven-proton complex of bands in the region τ 1.8 to 2.8. These features immediately excluded any norcaradiene structure (such as II) and were also in disagreement with a tautomeric cyclo-heptatriene formulation (*e.g.*, III), since spin–spin coupling between protons on saturated carbon and the olefinic protons would be expected.[9] However, the unsplit CH$_2$ resonance at τ 6.16 was reminiscent of the CH$_2$ resonance of fluorene, which appears at τ 6.19,[10] and indeed the properties of the ester were consistent with its formulation as ethyl fluorene-2-carboxylate (VI), reported[11] to melt at 83–84°. Synthesis of the authentic ester by oxidation of 2-acetylfluorene[12] left no doubt as to the nature of the carbethoxycarbene product; the mixture melting point, ultraviolet, and n.m.r. spectra were identical.

Although isolation of the fluorene VI from addition of carbethoxycarbene to biphenylene is at first surprising, its formation can be understood in terms of known processes of tropilidene chemistry.[13] Thus the primary adduct II should be in tautomeric equilibrium with cycloheptatriene III, which in turn could undergo thermal 1,5-hydrogen transfer[14] to the isomeric triene IV.
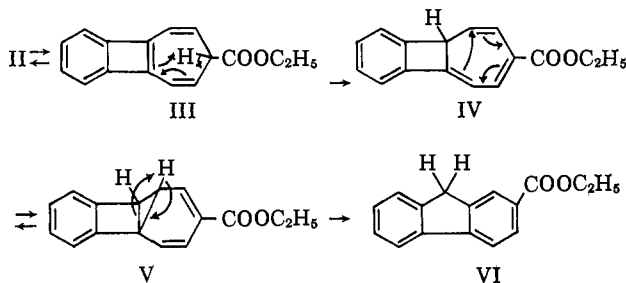
The latter should exist in equilibrium with a second norcaradiene, V, which contains the elements of a *highly strained bicyclopentane system.* Criegee and Rimmelin have observed[15] that bicyclopentane itself undergoes thermal isomerization at 330° to give cyclopentene; the analogous rearrangement of diene V would be expected to proceed even more readily and lead directly to the observed fluorene ester VI.

It is apparent that the remarkable chain of isomerizations represented by the postulated reaction sequence could seriously interfere with syntheses of molecules containing cyclobutenes fused to actual or potential cycloheptatriene rings. We are currently examining the possibility of intercepting some of the proposed

(9) In cycloheptatriene the coupling constant between CH$_2$ and adjacent olefinic CH is *ca.* 7 c.p.s. (NMR Spectra Catalog, Varian Associates, 1962, spectrum 158).

(10) Value given by G. V. D. Tiers, in "Characteristic NMR Shielding Values," Vol. II, Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958, p. 12.

(11) D. C. Morrison, *J. Org. Chem.*, **23**, 1772 (1958).

(12) M. D. Barnett, G. H. Daub, F. N. Hayes, and G. D. Ott, *J. Am. Chem. Soc.*, **82**, 2282 (1960). The intermediate fluorene-2-carboxylic acid melts with decomposition at 275° and is thus probably the acid isolated by Baker and McOmie.[7]

(13) Tautomerism in the cycloheptatriene–norcaradiene system has been reviewed by E. Vogel, *Angew. Chem.*, **72**, 6 (1960); **74**, 829 (1962).

(14) A. P. ter Borg, H. Kloosterziel, and N. von Meurs, *Proc. Chem. Soc.*, 359 (1962).

(15) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

tropilidene intermediates by effecting the addition of the appropriate carbenes to biphenylene derivatives at lower temperatures.

ORGANIC CHEMICAL RESEARCH SECTION　　ANDREW S. KENDE
LEDERLE LABORATORIES DIVISION　　PAUL T. MACGREGOR
AMERICAN CYANAMID COMPANY
PEARL RIVER, NEW YORK

Trichloromethyllithium, an Electrophilic Reagent

Sir:

We wish to report the preparation of trichloromethyl-lithium and its reaction with cyclohexene at low temperature to produce 7,7-dichloronorcarane in high yield.[1] Our results point to α-halogenated[3] organometallic compounds of the alkali metals as highly reactive electrophilic reaction intermediates which are distinguishable from the carbenes. The accessibility of such substances for study and as specific reagents is demonstrated.[4]

Experimental results are summarized in Table I. Trichloromethyllithium was prepared by adding CBrCl$_3$ to CH$_3$Li slurry in ether at −115°. Reaction with

TABLE I[a]

	CH$_3$Br	CHCl$_3$	CH-BrCl$_2$	CH$_3$-CCl$_3$	CCl$_2$=CCl$_2$	Other products
A	87	65	11	6	5	
B[b,c]	82	3	0	7	1	77
C[b]	88	56	16	8	5	
D[d]	88	30	6	5	4	{ 13 CHCl$_2$CF$_3$ / 24 CCl$_2$=CF$_2$
E	81					{ 67 CHCl$_2$CF$_3$ / 12 CCl$_2$=CF$_2$ / 4 CH$_3$Cl

[a] The values given are percentages based on CH$_3$Li. In each case *ca.* 0.04 mole of CCl$_3$Li (CF$_3$CCl$_2$Li) was prepared in 150 ml. of ether by adding 5% excess CBrCl$_3$ (CF$_3$CBrCl$_2$) to CH$_3$Li at −115° during 2 hr. All analyses are by g.l.c. on fractions separated after treatment with ethereal HCl. Other identified products such as CH$_3$Cl, CCl$_4$, CH$_2$=CHCl, CCl$_2$=CBrCl, CH$_3$CBrCl$_2$, and CH$_3$CH=CH$_2$ total less than 5% per reaction. [b] Warmed (10 min.) to −100° for 1 hr., recooled to −115°, and HCl added. [c] Partial reaction to form dichloronorcarane was observed at −115°. [d] Six hours at −115° with 0.05 mole CF$_3$CBrCl$_2$.

ethereal HCl yielded 65% CHCl$_3$ and 11% CHBrCl$_2$ (A). With 2 equiv. of cyclohexene present and warming to −100°, 77% dichloronorcarane was formed (B). Under the same conditions (1 hr. at− 100°), CCl$_3$Li was thermally stable but yielded additional CBrCl$_2$Li by exchange with LiBr (C).[7] On warming to −80° the CCl$_3$Li reagent decomposed exothermally to form a mixture of tetrahaloethylenes. With CF$_3$CBrCl$_2$ at −115° partial exchange took place to

(1) The intermediate formation of dichlorocarbene was originally postulated for this synthesis. Initial attempts to demonstrate the formation of CCl$_3$Li were unsuccessful.[2]

(2) W. T. Miller, Jr., and C. S. Y. Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959).

(3) Excluding fluorine.

(4) Nucleophilic reactions of α-chloro alkali metal compounds as transient intermediates[5,11] and as reagents of the type (*p*-R—C$_6$H$_4$)$_2$C=CClLi[6] have been shown.

(5) D. F. Hoeg and D. I. Lusk, *J. Am. Chem. Soc.*, **86**, 928 (1964); C. R. Hauser, W. R. Braser, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *ibid.*, **78**, 1653 (1956); M. S. Kharasch, W. Nudenberg, and E. K. Fields, *ibid.*, **66**, 1276 (1944); W. T. Miller, Jr., and R. Becker, Abstracts, 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963, p. 14M.

(6) G. Kölbrich and H. Trapp, *Z. Naturforsch.*, **18b**, 1125 (1963).

(7) The CH$_3$Li was prepared from CH$_3$Br and lithium metal.