

indicated by the marked (nitrophenolate anion) bathochromic shift which the spectrum of VIb ( $1.47 \times 10^{-5} M$ ) undergoes in alkaline (0.022 *N* in NaOH) 95% ethanol solution,  $m\mu$  ( $\log \epsilon$ ): 243 (infl, 4.28), 285 (4.03), 315 (4.07), and 415 (b, 4.08).

Refluxing a solution of Ia (0.0090 mole) with phenylpropionic acid (VIII, 0.0137 mole) in xylene (40 ml.) for 3.25 hr. gave a crystalline precipitate, which increased in amount upon cooling. Filtration removed white crystals (IX, 38%), m.p. 319–321°. Concentration of the filtrate gave additional IX (10%; total 48%; average yield 45%). Three recrystallizations of the combined IX from ethanol and two from chloroform–1-butanol, with slow cooling, gave 2-benzoyl-3-phenyl-4-quinolinol (IX) as small white needles, m.p. 326–327°;  $\lambda_{\max} m\mu$  ( $\log \epsilon$ ) in 95% ethanol: 255 (4.50), 288 (d infl, 3.98), 328 (infl, 3.89), and 335 (3.90);  $\nu_{C=O} \text{ cm.}^{-1}$  in Nujol: 1678 (s).

*Anal.* Calcd. for  $C_{22}H_{15}NO_2$  (mol. wt. 325.35): C, 81.21; H, 4.65; N, 4.31. Found: C, 80.85; H, 4.91; N, 4.12.

The structure of IX was proved by Wolff–Kishner reduction in refluxing ethylene glycol to the known<sup>8</sup> 2-benzyl-3-phenyl-4-quinolinol (X, 87%), small white needles (from ethanol), m.p. 320–322° (turn yellow), identical, as shown by mixture melting point, ultraviolet, and infrared comparison in Nujol and halo-carbon oil, with samples of m.p. 320–323° prepared by the Conrad–Limpach method<sup>5</sup> in 12% yield from aniline and ethyl 2,4-diphenylacetoacetate, and also by heating of anthranilic acid with dibenzyl ketone<sup>8a</sup> (34%);  $\lambda_{\max} m\mu$  ( $\log \epsilon$ ) in 95% ethanol: 249 (4.44), 298 (infl, 3.6), 323 (4.02), and 335 (4.04).

That IX is not an intermediate in the formation of VIa from Ia and V is shown by recovery of unchanged IX in 92% yield from refluxing xylene containing propionic acid, conditions under which VIa was formed.

The generality of the ring expansion reactions of isotogens with acetylenes is currently under investigation.

(8) (a) H. P. W. Huggill and S. G. P. Plant, *J. Chem. Soc.*, 784 (1939); (b) J. von Braun and A. Heymons, *Chem. Ber.*, **63B**, 3191 (1930).

(9) National Science Foundation Graduate Fellow, June 16, 1962, to the present.

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### *trans*-2-Cyclooctenone

Sir:

The ethylenic portion of the triplet state of an  $\alpha,\beta$ -unsaturated ketone can be treated, in useful simplification, rather like the triplet state of an unconjugated olefin. The antagonistic interactions of unpaired electronic spins should induce a torsional distortion about the  $\alpha,\beta$ -bond.<sup>1</sup> A 90° twist places the unpaired electrons in noninteracting orthogonal orbitals. In flexible acyclic systems such an orthogonal triplet can return either to a *cis* or *trans* ground state configuration.<sup>2</sup> The geometric constraint imposed on the  $\alpha,\beta$ -bond in small, cyclic,  $\alpha,\beta$ -unsaturated ketones pre-

vents full relief of electronic repulsions in the triplet states of these less flexible systems.<sup>3</sup> A Drieding model of triplet 2-cyclopentenone permits under maximum stress a twist of only about 20° in the  $\alpha,\beta$ -dihedral angle; a similar model of 2-cyclohexenone allows a 60° twist. These are maximal figures and are most certainly reduced by the strain concomitantly imposed on the ring and by the loss in overlap energy with the carbonyl group. 2-Cyclooctenone is the lowest homolog of the cyclic  $\alpha,\beta$ -unsaturated ketones in which twisting about the  $\alpha,\beta$ -bond is nearly unrestricted in the triplet. Thus, ultraviolet excitation of *cis*-2-cyclooctenone might induce isomerization to the *trans* isomer. We have in this way succeeded in the preparation of *trans*-2-cyclooctenone, an  $\alpha,\beta$ -unsaturated ketone of exceptional properties.

Irradiation of a cyclohexane solution of *cis*-2-cyclooctenone with light of wave lengths above 300  $m\mu$ <sup>4</sup> leads to a rapid decrease in the concentration of the *cis* ketone. The reaction is best followed spectroscopically. In the ultraviolet spectrum the strong  $\pi-\pi^*$  absorption of *cis*-2-cyclooctenone ( $\lambda_{\max}$  223  $m\mu$ ,  $\epsilon$  7600) is lost; the  $n-\pi^*$  maximum of the conjugated ketone ( $\lambda_{\max}$  321  $m\mu$ ,  $\epsilon \sim 70$ ) gives way to an absorption at lower wave length appropriate to an unconjugated ketone ( $\lambda_{\max}$  283  $m\mu$ ,  $\epsilon \sim 60$ ). Equivalent changes occur in the infrared spectrum. The strong absorption of the conjugated carbonyl group of the starting material (5.97  $\mu$ ) is replaced by a band at lower wave length (5.79  $\mu$ ) more common to unconjugated ketones. Distinct new absorptions appear at 6.12, 8.61, and 10.12  $\mu$ ; significantly, similar bands are present in the infrared spectrum of *trans*-cyclooctene but not in the spectrum of the *cis* isomer.<sup>5</sup>

Under the irradiation conditions described only about 80% conversion of *cis*-2-cyclooctenone can be obtained; apparently the reaction product and the starting material are in photoequilibrium. The tail of the  $n-\pi^*$  absorption of the photoproduct extends above 300  $m\mu$  and allows the light-induced back reaction. In the dark the back reaction is negligible. The smallest trace of mineral acid, however, triggers the nearly instantaneous regeneration of *cis*-2-cyclooctenone.

The reactivity of the photoproduct (*vide infra*) prevents the isolation of a pure sample. The nuclear magnetic resonance spectrum of the reaction product admixed with the photoequilibrium amount of starting material is still useful. Although the vinyl proton absorptions of product and *cis*-2-cyclooctenone overlap confusingly, it is possible to achieve a partial analysis of this area of the spectrum. It appears that the irradiation product contains two coupled vinyl protons with  $J = 18$  c.p.s., a value appropriate to the coupling of *trans* vinyl hydrogens in an octene ring.<sup>6</sup> One of the vinyl protons (center at *ca.*  $\tau$  3.5 p.p.m.) is not coupled significantly with the nonolefinic protons. On the other hand, the second vinyl proton (center at *ca.*  $\tau$  4.3

(3) The full significance of these differences in angular deformation and the corresponding differences in triplet state energies will be developed in a later paper considering the photocondensation reactions of unsaturated ketones.

(4) The light source is a 450-w. Hanovia mercury arc lamp surrounded by water-cooled Pyrex filters.

(5) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

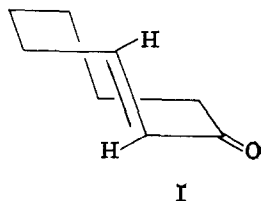
(6) O. L. Chapman, *ibid.*, **85**, 2014 (1963), and L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959, p. 85.

(1) Mulliken has pointed out that the energies of the parallel and orthogonal states of triplet ethylene differ substantially. The orthogonal state is the more stable by about 20 kcal./mole [R. S. Mulliken and C. C. J. Roothaan, *Chem. Rev.*, **41**, 219 (1947)].

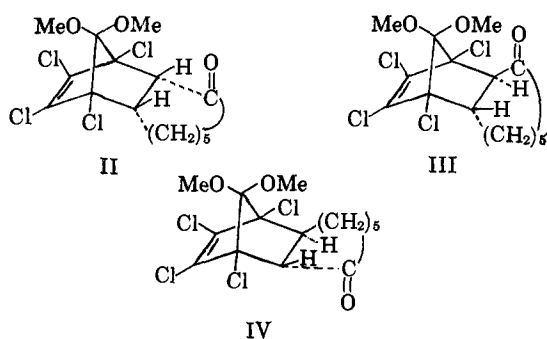
(2) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4983 (1962).

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  $\alpha,\beta$ -unsaturated ketone is locked into a rigid conformation in which the  $\pi$ -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.



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.

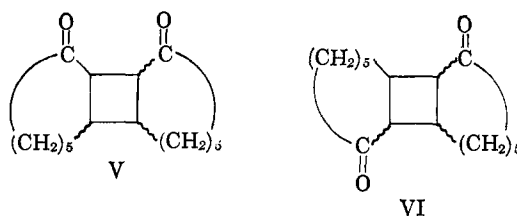


The remarkable ease with which the ethylenic segment of *trans*-2-cyclooctenone enters into carbon-carbon bond forming reactions<sup>7</sup> is foreign to more prosaic  $\alpha,\beta$ -unsaturated ketones. This reaction is not limited to condensation only with active dienes. Indeed, *trans*-2-cyclooctenone 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  $\alpha,\beta$ -unsaturated ketones, e.g., 2-cyclopentenone<sup>8a</sup> and 2-cyclohexenone.<sup>8b</sup> 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 cyclohexenone. 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.



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

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(9) Alfred P. Sloan Foundation Fellow.

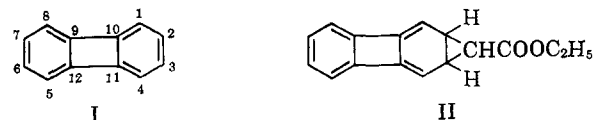
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### The Reaction of Carboethoxycarbene with Biphenylene Sir:

The selective addition of carbenes to aromatic hydrocarbons is a valuable route to certain nonbenzenoid aromatic systems.<sup>1</sup> Orientation in the addition of carboethoxycarbene to naphthalenes,<sup>2</sup> anthracene,<sup>3</sup> and phenanthrene<sup>4</sup> has been qualitatively correlated with the localization energy of the  $\pi$ -bond undergoing attack.<sup>5</sup> In the case of biphenylene (I), bond-localization energy calculations<sup>6</sup> 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.



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°.<sup>7</sup> 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 m $\mu$ . 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<sup>8</sup> of a colorless crystalline ester, m.p. 80–82°,  $\lambda_{\text{max}}^{\text{cyclohexane}}$  307, 299, 294, 283, and 272 m $\mu$

(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*, **18**, 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  $\pi$  energy by localizing adjacent positions in biphenylene is given by simple Hückel LCAO theory as follows (positions localized given by subscripts).

$$\begin{array}{ll} L_{1,2} = 3.60\beta & L_{1,10} = 3.58\beta \\ L_{2,3} = 3.36\beta & L_{10,11} = 4.40\beta \end{array}$$

(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.