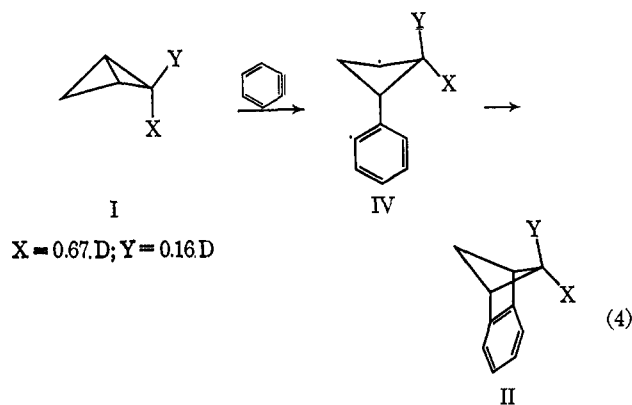


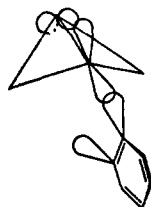
isotope effect is thus expected for the concerted reaction. Alternatively, if attack by benzyne on bicyclobutane is slow and produces diradical IV which, in turn, in a fast step, gives III, no isotope effect (or at most a small one) should be evident. Therefore, the observation of no isotope effect is consistent with both mechanisms.

The formation, by bottomside attack, of benzobicyclo[2.1.1]hex-2-ene (II) is probably best rationalized as a diradical reaction with IV again being the intermediate (eq 4). A concerted cycloaddition would be ruled out on steric grounds since the bottomside of the



bicyclobutane ring is quite hindered and certainly much more hindered than the topside.<sup>11</sup>

Thus the benzyne can come in along the axis of the p orbital of C<sub>1</sub> (which is bonding to C<sub>3</sub>) and in the plane of the 1,3 bond which bisects the C<sub>2</sub>-C<sub>1</sub>-C<sub>4</sub> and C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub> angles. This would allow for a minimum of



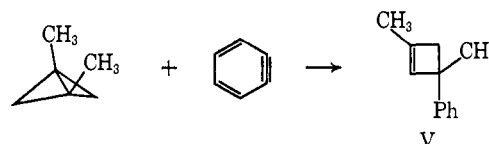
steric interactions and would produce the diradical IV. Any significant twisting of the benzyne out of the plane would mean that the free orbital of the benzyne would be closer to an *endo* hydrogen, and the "ene" synthesis should then result. The same type of diradical intermediate has recently been proposed in the bicyclopentane series.<sup>10,12</sup>

If the cycloadduct is indeed coming about by the mechanism indicated, the substitution of methyl groups for hydrogens on carbons 1 and 3 should produce less cycloadduct as a result of some steric compression between the 3 hydrogen on benzyne and the methyl group. Twisting of the benzyne to alleviate this strain would result in an increased amount of "ene" synthesis product. This prediction has been verified by the observation that, within the limits of nmr analysis, there is no cycloadduct produced by the reaction of 1,3-dimethylbicyclobutane with benzyne.<sup>13</sup> The sole product has been shown to be 1,3-dimethyl-3-phenylcyclobutene (V).

(11) I. Haller and R. Srinivasan, *J. Chem. Phys.*, **41**, 2745 (1964); M. D. Harmony and K. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966).

(12) W. R. Roth and M. Martin, *Tetrahedron Letters*, 4695 (1967).

(13) If it is assumed that the cycloadduct can be separated from the "ene" synthesis product by vpc (7 ft  $\times$  0.25 in. 20% DC 710 silicone oil on 60-80 mesh Chromosorb P column) then there is no (<1%) cycloadduct present.



Structure proof for V consists of its nmr spectrum which shows five aromatic hydrogens at  $\tau$  2.81 ppm, one vinyl hydrogen as a doublet ( $J = 1$  Hz) at  $\tau$  3.89 ppm, two allylic hydrogens at  $\tau$  7.49 ppm, one allylic methyl group as a doublet ( $J = 1$  Hz) at  $\tau$  8.26 ppm, and the second methyl group as a singlet at  $\tau$  8.53 ppm. The infrared spectrum of V showed the double-bond stretch at  $1640\text{ cm}^{-1}$  as compared to  $1641\text{ cm}^{-1}$  for 1-methylcyclobutene.<sup>14</sup> The mass spectrum of V exhibited the parent peak (both high and low ionization potentials) at  $m/e$  158, confirming the C<sub>12</sub>H<sub>14</sub> formula.

Thermal rearrangement (160°) of 1,3-dimethyl-3-phenylcyclobutene (V) afforded three products, in the ratio 2:1:8. The major product was identified as 2-methyl-4-phenyl-1,3-pentadiene by the identity of its nmr spectrum with that reported for this compound, of unknown stereochemistry.<sup>15</sup> From mechanistic considerations it seems most likely that this compound is *cis*-2-methyl-4-phenyl-1,3-pentadiene since conrotatory ring opening of the cyclobutene (V) would involve less steric strain in the transition state if the methyl rather than the larger phenyl group rotated inward.

Because reaction of benzyne with bicyclobutane occurs from the bottomside, it is not surprising that attempted reaction of 1,5-dimethyltricyclo[2.1.0.0<sup>2,3</sup>]pentan-3-one (VI)<sup>16</sup> with benzyne (ethylene dichloride solvent, 84°) apparently resulted in no detectable amount of products.<sup>17</sup>



**Acknowledgment.** We wish to thank the National Science Foundation for a grant (GP 7859) in support of this work.

(14) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1967, p 81.

(15) T. L. Jacobs and R. A. Meyers, *J. Am. Chem. Soc.*, **86**, 5244 (1964).

(16) W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, 961 (1964).

(17) Examination of the residual ketone (VI) by vpc using an internal standard indicated only about 85% recovery. A blank reaction (same conditions as the benzyne reaction but lacking *o*-benzenediazonium-carboxylate) showed that approximately the same amount of ketone could be recovered, the loss being due either to evaporation or to decomposition of VI.

Martin Pomerantz, Gerald W. Gruber, Robert N. Wilke  
Department of Chemistry, Case Western Reserve University  
Cleveland, Ohio 44106

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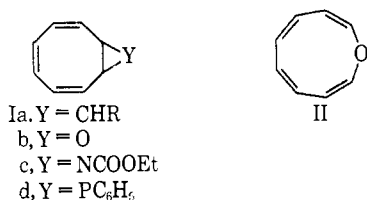
### Photolysis and Photoisomerization of Cyclooctatetraene Oxide

Sir:

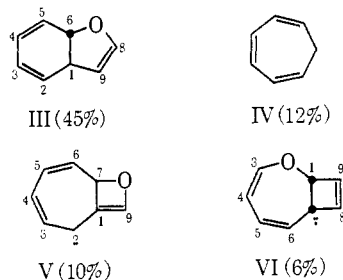
Cyclooctatetraene oxide (Ib) is an interesting member of the bicyclo[6.1.0]nona-2,4,6-triene family (I) as it is

a valence tautomer of the theoretically important oxacyclononatetraene (II). The Ib  $\rightarrow$  II transformation is expected to be a disallowed ground-state electrocyclic process but should be allowed in the excited state if it is governed by symmetry conservation.<sup>1</sup> The results described here stemmed from our interest in II as well as from several interesting but "anomalous" reports on ground-state chemistry of Ia, Ic,<sup>2</sup> and Id.<sup>3</sup> The ground-state<sup>4,5</sup> behavior of Ia, in particular, appears not to be governed by orbital symmetry conservation, and thus the effect of a hetero atom became of interest.

Irradiation of Ib in pentane solution with filtered light<sup>6</sup> ( $\lambda > 3100 \text{ \AA}$ ) afforded III-VI in yields shown along with 26% of polymer.<sup>7</sup> The structure of III ( $\lambda_{\text{max}} 256 \text{ m}\mu$  ( $\epsilon 3600$ )) was established by spectroscopic methods and by catalytic hydrogenation (3 mol equiv) to the known *trans*-7-oxabicyclo[4.3.0]nonane.<sup>8</sup>



The more pertinent signals in the nmr spectrum<sup>9</sup> of III are those due to H<sub>1</sub>, H<sub>6</sub>, H<sub>8</sub>, and H<sub>9</sub> at  $\tau$  6.28, 4.90,



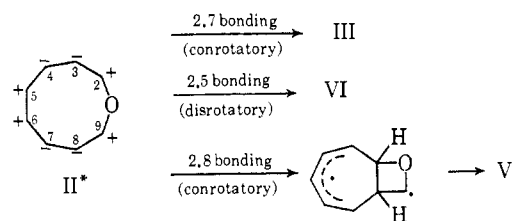
3.65, and 5.18, respectively. The *trans* ring fusion gives rise to a large H-H coupling,  $J_{1,6} = 13.6$  cps. Other significant couplings are  $J_{1,9} = 3.0$  and  $J_{8,9} = 2.8$  cps. Treatment of III with dilute acid gave phenylacetaldehyde instantaneously.

The oxetene V ( $\lambda_{\text{max}} 244 \text{ m}\mu$  ( $\epsilon 1200$ )) gave an nmr spectrum<sup>9</sup> with pertinent signals at  $\tau$  3.60 (H<sub>9</sub>), 4.76 (H<sub>7</sub>), 5.86 (H<sub>2</sub>), and 6.77 (H<sub>2'</sub>). The more significant H-H couplings are  $J_{7,9} = 2.9$ ,  $J_{2,9} = 0$ ,  $J_{2',9} = 2.8$ , and  $J_{2,2'} = 23.5$  cps. The extraordinarily large geminal coupling observed for H<sub>2</sub>-H<sub>2'</sub> is characteristic of bisal-

lylic methylenes having a distorted geometry.<sup>10,11</sup> It is important to note that the signal due to H<sub>9</sub> has a low-field chemical shift which is very typical of the  $\alpha$ -H of vinyl ethers and that it is significantly coupled with H<sub>2</sub>. Equally important in the interpretation of these data is the conspicuous absence of a signal at  $\tau \sim 5$  where the  $\beta$ -H of vinyl ethers typically resonates. It is thus clear the C<sub>1</sub> is a bridgehead atom and that H<sub>7</sub> and H<sub>9</sub> are rather strongly long range coupled through C<sub>1</sub>. Support for the oxetene assignment (V) was obtained from its hydrogenation product which exhibits infrared absorption at  $985 \text{ cm}^{-1}$  typical of oxetanes.

The nmr spectrum of the cyclobutene (VI,  $\lambda_{\text{max}} 252 \text{ m}\mu$  ( $\epsilon 2600$ )) exhibits signals at  $\tau$  4.76 (H<sub>1</sub>), 3.66 (H<sub>3</sub>), 4.90 (H<sub>4</sub>), 4.44 (H<sub>5</sub>), 4.11 (H<sub>6</sub>), 6.44 (H<sub>7</sub>), 3.73 (H<sub>8</sub>), and 4.00 (H<sub>9</sub>). Spin couplings are  $J_{1,7} = 3.4$ ,  $J_{1,8} = 0.8$ ,  $J_{1,9} = 1.1$ ,  $J_{3,4} = 6.3$ ,  $J_{4,5} = 6.1$ ,  $J_{5,6} = 11.3$ ,  $J_{6,7} = 5.0$ ,  $J_{7,8} = 0$ ,  $J_{8,9} = 2.9$ , and  $J_{7,9} = 1.1$  cps. The bridgehead coupling (3.4 cps) is consistent with values observed for other cyclobutenes *cis* fused to another ring.<sup>12</sup> All couplings are consistent with those observed in model compounds and, with the exception of  $J_{3,4}$ , they comply with the coupling-ring size correlations described by Chapman.<sup>13</sup> It is noteworthy that vinyl couplings of all cyclic vinyl ethers we have examined are lower in magnitude than predicted by these correlations (*cf.*  $J_{8,9}$  in III).

Although we are uncertain about the origin of cycloheptatriene, the formation of III, V, and VI points clearly to oxacyclononatetraene (II) as a common intermediate. Moreover, the stereochemistry of III and VI indicates that they are derived from *excited* II. These transformations are illustrated with the following plane projection of orbital symmetry in excited II. It would thus appear that orbital symmetry is conserved in the photochemistry of Ib and that II\* does not undergo internal conversion before reacting to give products; ground-state II would be expected to give *cis*-III and *trans*-VI. The multiplicity of II\* is not known with certainty, but the failure of piperylene (solvent) to quench the reaction suggests that II reacts in its singlet



excited state. The reaction is photochemically very inefficient, and it has been necessary to use a very high irradiation flux to obtain desired conversions. As a consequence, data from experiments using sensitizers are at present somewhat equivocal, even though they also point to a singlet excited intermediate.

By contrast with these results, in which several symmetry-predicted products are observed, the ground-state behavior<sup>4</sup> of Ia appears not to be symmetry allowed if one assumes that the all-*cis*-cyclononatetraene is an intermediate. It is quite possible that symmetry is

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); *Accounts Chem. Res.*, **1**, 17 (1968).

(2) S. Masamune and N. T. Castellucci, *Angew. Chem. Intern. Ed. Engl.*, **3**, 582 (1964).

(3) T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Am. Chem. Soc.*, **88**, 3832 (1966).

(4) E. Vogel, *Angew. Chem.*, **73**, 548 (1961).

(5) K. F. Bangert and V. Bockelheide, *J. Am. Chem. Soc.*, **86**, 905 (1964); T. J. Katz and P. J. Garratt, *ibid.*, **85**, 2852 (1963).

(6) The photoproducts are light sensitive, and short-wavelength irradiation of Ib gives polymeric material: G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **84**, 3104 (1962).

(7) The separation of III was effected by fractional distillation. Pure samples of V and VI were obtained by preparative glpc during which III was destroyed. All three substances are quite unstable.

(8) S. E. Cantor and D. S. Tarbell, *J. Am. Chem. Soc.*, **86**, 2902 (1964). We are indebted to Professor Tarbell for infrared spectra of the *cis* and *trans* isomers.

(9) Spectra and decoupling data were obtained using a Varian HA-100 instrument. Infrared and mass spectral data are consistent with structure assignments. Compounds III, V, and VI all form adducts with maleic anhydride.

(10) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

(11) R. C. Cookson, T. A. Crabb, J. J. Frankel, and H. Hudec, *Tetrahedron Suppl.*, **7**, 355 (1966).

(12) The bridgehead coupling constant in *cis*-2-oxabicyclo[3.2.0]hepta-3,6-diene, for example, is 4.0 cps.

(13) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963).

in fact conserved in the early stages of the reaction coordinate but becomes lost near the energy maximum as a consequence of the combined effects of very bad warping of orbitals and the strain imposed by the developing *trans* double bond. This merely restates the obvious fact that symmetry should be conserved only when it provides the lowest energy reaction path.<sup>1</sup> The observed *cis*-bicyclo[4.3.0]nonane system is the one expected from the symmetry-allowed ground-state bridging of the all-*cis*-cyclononatetraene intermediate. The symmetry conservation observed in the Ib  $\rightarrow$  III + VI conversion indicates that the oxygen atom plays an important role, probably involving mixing of its orbitals with those of the  $\pi$  system. MO calculations of II and II\* are not yet complete, but it would appear that such orbital mixing will not change the orbital symmetry represented for the carbon atoms of II\*.<sup>14</sup>

The photochemistry of Ia is most easily rationalized as proceeding through the excited all-*cis*-cyclononatetraene which then undergoes internal conversion before bridging in the ground state.

**Acknowledgment.** We are indebted to Badische Anilin- & Soda-Fabrik AG for a generous gift of cyclooctatetraene.

(14) Such is the case with furan and thiophene: D. S. Sappenfield and M. Kreevoy, *Tetrahedron Suppl.*, 19, 157 (1963).

J. M. Holovka, P. D. Gardner

Department of Chemistry, University of Utah  
Salt Lake City, Utah

C. B. Strow, M. L. Hill, T. V. Van Auken

Union Carbide Corporation, Chemicals and Plastics  
South Charleston, West Virginia  
Received April 20, 1968

## Resolution of an Alkyl Aryl Ketone with Asymmetry due to Restricted Rotation about the Carbonyl Group

Sir:

In connection with a program of studies on hindered alkyl mesityl ketones<sup>1</sup> we wish to report the first resolution of an alkyl aryl ketone, *t*-butyl 3-carboxy-2,4,6-trimethylphenyl ketone (**1**). **1** was synthesized by the sequence of reactions shown.<sup>2</sup>

Acid **1** was resolved with cinchonine (acetone solvent). A solution of the cinchonine salt (**5**) of the acid (60.7% first crop based on one diastereomer) in pyridine at 0° was poured into a concentrated hydrochloric acid-ice slush at -15°. The precipitated acid **1** was collected by filtration, washed with water, and dried; 46% yield (based on cinchonine salt). **1** (first crop) showed an initial<sup>4</sup> specific rotation of  $[\alpha]^{20.5D} +61^\circ$  (chloroform) which decreased to zero on standing. The half-life was calculated to be 6.2 min under these conditions. The cinchonine salt (**5**) showed mutarotation<sup>5</sup>

(1) A. G. Pinkus, W. C. Servoss, and K. K. Lum, *J. Org. Chem.*, **32**, 2649 (1967).

(2) Satisfactory elemental analyses were obtained for the new compounds **1** and **3**; the nmr and ir spectra are in accord with the structures shown. Compound **4** was previously prepared<sup>3</sup> by a Friedel-Crafts reaction of mesitylene and the acid chloride. Further proof of structure included the decarboxylation of **1** to the known<sup>3</sup> *t*-butyl mesityl ketone (**4**).

(3) D. V. Nightingale, R. L. Sublett, R. A. Carpenter, and H. D. Radford, *J. Org. Chem.*, **16**, 655 (1951).

(4) Obtained by extrapolation to zero time (of solution).

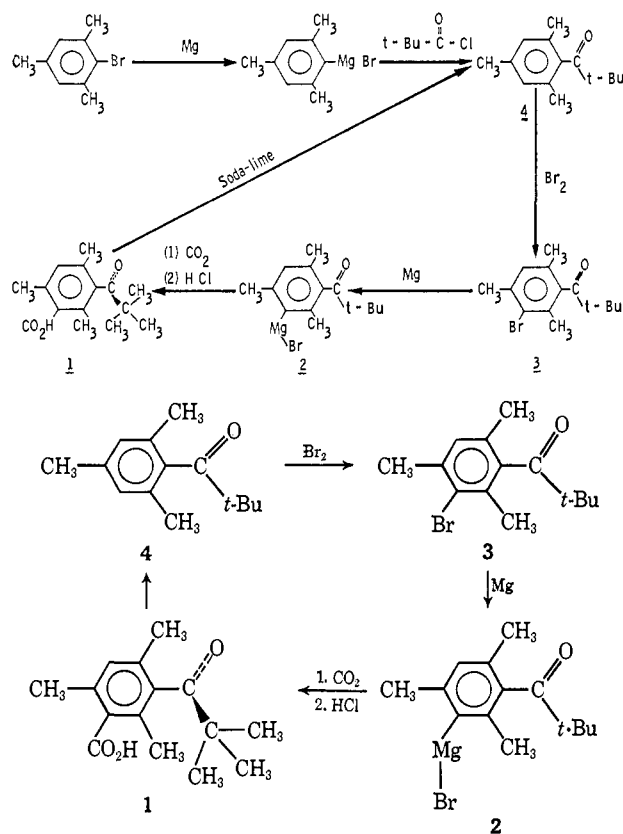
(5) The second crop of cinchonine salt (**5**) was used. A more detailed study will be reported in a more complete account of this work.

on being dissolved in chloroform, the specific rotation increasing from an initial<sup>4</sup> value of +114° to a final constant value of +136° at 20.5°.

An interesting problem arises in considering possible explanations of the racemization. Scale models indicate that interference between the *t*-butyl group and the *o*-methyls prevents transformation into the enantiomer and either the aryl-carbonyl bond or the alkyl-carbonyl bond (of the model) must be broken in order to effect the conversion. This possibility does not appear likely for a racemization mechanism because of the high energy requirements involved in bond breaking. A more likely possibility would involve a low-energy bending of the *t*-butyl group away from the aryl group, thus increasing the C<sub>aryl</sub>-CO-C<sub>*t*-Bu</sub> angle. Studies to investigate this are under way, as well as the investigation of restricted rotation about related types of groupings.

Compound **2** is of interest in that this is the first molecule to our knowledge in which a keto carbonyl and a Grignard function exist simultaneously.

The first published attempts to resolve asymmetrically



substituted benzophenones were by Adams and his coworkers.<sup>6</sup> More recently,<sup>7</sup> Narayanan, Selvarajan, and Swaminathan<sup>8</sup> claimed the first resolution<sup>9</sup> of a compound of this type. They suggested that interconversion of the antipodal benzophenones occurred

(6) J. F. Hyde and R. Adams, *J. Am. Chem. Soc.*, **50**, 2499 (1928); M. E. Maclean and R. Adams, *ibid.*, **55**, 4683 (1933).

(7) The work reported in the present paper was complete when their paper<sup>8</sup> was submitted: J. I. Riggs, Jr., Ph.D. dissertation, Baylor University, Aug 1966, and further unpublished work by A. G. Pinkus and S. M. Broughton.

(8) K. V. Narayanan, R. Selvarajan, and S. Swaminathan, *J. Chem. Soc.*, **C**, 540 (1968).

(9) They observed  $[\alpha]_D -2.2^\circ$  for a sample which was obtained after five quick crystallizations of the crude acid having  $[\alpha]_D -1.79^\circ$ . The racemization behavior of the compound was not reported.