

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WIS.]

Stereochemistry of the Copper-Salt-Catalyzed Reaction of *t*-Butyl Perbenzoate with Optically Active Bicyclo[3.2.1]octene-2<sup>1,2</sup>

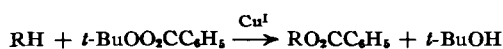
BY HARLAN L. GOERING AND UDO MAYER

RECEIVED APRIL 13, 1964

The cuprous bromide catalyzed reaction of *t*-butyl perbenzoate and bicyclo[3.2.1]octene-2 (I) results in the formation of *exo*(axial)-bicyclo[3.2.1]oct-3-en-2-yl benzoate (IIIa) which contains <1% of the *endo* isomer. Optically active I gives racemic IIIa which means that the allylic carbon atoms (C-2 and C-4) are completely randomized. These results are consistent with the Kochi mechanism (eq. 1-3), *i.e.*, abstraction of an allylic hydrogen atom to give the symmetrical bicyclo[3.2.1]oct-3-en-2-yl radical II which is stereoselectively converted to racemic *exo*-benzoate IIIa.

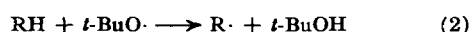
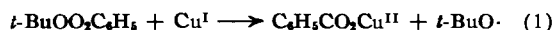
## Introduction

In 1958, Kharasch and co-workers reported the important discovery that the reaction of *t*-butyl perbenzoate and olefins (RH) in the presence of catalytic amounts of cuprous salts results in replacement of an allylic hydrogen atom by a benzoyloxy group in high yield.<sup>3</sup> The over-all reaction is



In the original work<sup>3</sup> 1-alkenes were used as substrates and it appeared that 3-benzoyloxy-1-alkenes were formed exclusively. Because of this apparent specificity it was concluded<sup>3b</sup> that the reaction does not involve allylic radicals or carbonium ions. The claim<sup>4</sup> (since found to be in error<sup>5</sup>) that allylbenzene and propenylbenzene are converted to the corresponding allylic benzoates seemed to support this conclusion.

In sharp contrast to the earlier reports, Kochi<sup>6</sup> observed that the three isomeric normal butenes are converted to similar, if not identical, mixtures of  $\alpha$ -methylallyl (~90%) and crotyl (~10%) benzoate. Moreover, it was found that neither the olefins nor the allylic esters are isomerized under the conditions of the reaction. To accommodate these results, a three-step chain process was proposed<sup>6</sup> which involves (a) reduction of the perester to give *t*-butoxy radicals (eq. 1), (b) hydrogen abstraction to produce intermediate allyl radicals (eq. 2), and (c) conversion (oxidation) of the latter to mixtures of the two corresponding allylic esters (eq. 3). Recent investigations of this and closely related reactions by Kochi<sup>7</sup> and Walling and Zavitsas<sup>8</sup>



have provided convincing supporting evidence for this scheme and it appears that in all cases olefins are converted to products that would be expected from allylic radical intermediates.<sup>5,6,8</sup> A curious feature of allylic radicals common to 1- and 2-alkenes is that they give

(1) Presented before the XIX International Congress of Pure and Applied Chemistry, London, July, 1963.

(2) This work was supported by the Air Force Office of Scientific Research, Grant No. AF-AFOSR-47-63.

(3) (a) M. S. Kharasch and G. Sosnowski, *J. Am. Chem. Soc.*, **80**, 758 (1958); (b) M. S. Kharasch, G. Sosnowsky, and N. C. Yang, *ibid.*, **81**, 5819 (1959).

(4) D. B. Denny, D. Z. Denny, and G. Freig, *Tetrahedron Letters*, No. 15, 19 (1959).

(5) D. Z. Denny, A. Applebaum, and D. B. Denny, *J. Am. Chem. Soc.*, **84**, 4969 (1962).

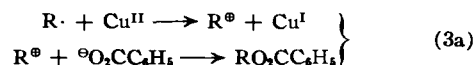
(6) J. K. Kochi, *ibid.*, **83**, 3162 (1961); **84**, 774 (1962).

(7) J. K. Kochi, *ibid.*, **85**, 1958 (1963), and earlier papers in that series.

(8) C. Walling and A. A. Zavitsas, *ibid.*, **85**, 2084 (1963).

preponderant amounts (~90%) of the 1-alken-3-yl ester.<sup>6,8</sup> Evidently this is the reason for the failure of the earlier workers,<sup>3</sup> who investigated only 1-alkenes, to detect the small amount of substitution with allylic rearrangement.

Although production of allylic radicals by steps 1 and 2 seems well established,<sup>7,8</sup> there is some uncertainty concerning details of the transformation (oxidation) of the intermediate radical to product. It is not clear if the reaction is a one-step ligand transfer process<sup>9</sup> (*i.e.*, a modified radical displacement reaction as implied by eq. 3) or a two-step process in which the radical is oxidized to the carbonium ion (electron transfer<sup>9</sup>) which subsequently is converted to product as illustrated by 3a.<sup>8</sup> Kochi<sup>7,9</sup> has proposed that the for-



mer is involved with simple (uncomplexed) cupric salts and that the latter obtains with complex cupric salts (*e.g.*,  $\alpha,\alpha$ -dipyridyl or 1,10-phenanthroline complexes)—the reason for proposing different processes is that the composition of the binary mixture of allylic esters derived from the radical differs substantially for the two cases.<sup>9</sup> On the other hand, Walling and Zavitsas<sup>8</sup> have objectively reviewed the evidence and conclude that available information does not rule out the possibility of electron transfer (eq. 3a) for cases involving oxidation by simple cupric salts.

This paper describes an investigation of the stereochemistry of the reaction of bicyclo[3.2.1]octene-2 (I) and *t*-butyl perbenzoate in the presence of cuprous bromide. In this work we were interested in two stereochemical problems, one of which has to do with a more sensitive test than has heretofore been applied to determine if all of the allylic substitution product is derived from an allylic radical intermediate.

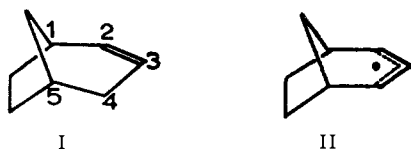
Although the earlier studies<sup>5-8</sup> clearly point to radical intermediates, the systems used are not suitable for determining if all of the product is derived from such intermediates because of the following complications. First, in nearly all cases hydrogen abstraction can give rise to a mixture of radicals of unknown composition. It has been shown by Walling and Thaler<sup>10</sup> that *cis*- and *trans*-2-butene give different radicals (geometric isomers) and that 1-butene gives a mixture of these isomeric *n*-butenyl radicals. Thus even with apparently simple olefins a mixture of radicals of unknown composition is involved. An additional complication is that even if the radical system were well defined the

(9) J. K. Kochi, *ibid.*, **84**, 3271 (1962).

(10) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

composition of the binary mixture of allylic isomers derived from a particular unsymmetrical allylic radical (or carbonium ion) cannot be predicted. If the composition of products derived from radical intermediates cannot be predicted in complete detail, observed compositions cannot be used as proof that all of the product is derived from such intermediates.

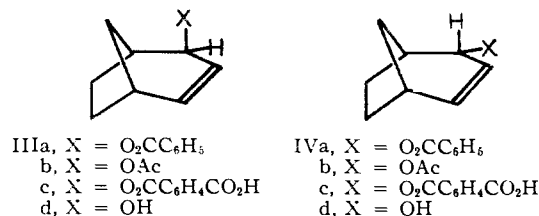
The unique features of the present system are that (a) hydrogen abstraction would be expected to give a single radical and (b) the relative amounts of bonding at the two allylic positions (*i.e.*, ratio of allylic isomers) cannot only be predicted but is known with certainty. Moreover, the composition of the allylic isomers can be measured with high precision. It can be seen that hydrogen abstraction at C<sub>4</sub>—abstraction at the bridgehead would not be expected<sup>11</sup>—results in the formation of the symmetrical bicyclo[3.2.1]oct-3-en-2-yl radical (II). Because of its symmetry, bonding at the two allylic carbon atoms (C-2 and C-4) must be equal. Or to put it another way, if II is an intermediate C-2 and C-4 will be completely randomized. The extent of randomization of these carbon atoms can be determined with high precision by using optically active I—the product derived from II must be racemic. In an earlier investigation<sup>12</sup> it was shown that bicyclo[3.2.1]oct-3-en-2-yl derivatives (the only expected substitution product) have very high optical rotations. Thus by using nearly optically pure I, as was done in the present work, as little as 0.5% substitution without randomization of the allylic carbon atoms can be detected with ease.



Recently Denny and co-workers<sup>5</sup> investigated the reaction of *t*-butyl peracetate and optically active  $\Delta^1$ -*p*-menthene, an olefin with the same symmetry properties as I. In this case hydrogen abstraction can give three radicals, one of which is the symmetrical 5-isopropyl-2-methyl-2-cyclohexenyl radical. These in turn can give rise to nine isomeric acetates. The mixture of acetates was saponified and the resulting alcohol fraction oxidized with potassium dichromate in 15% aqueous acid. Optically inactive solid semicarbazone and 2,4-dinitrophenylhydrazone derivatives of 5-isopropyl-2-methyl-2-cyclohexenone were obtained from the ketone fraction. From this it was concluded that the 5-isopropyl-2-methyl-2-cyclohexenyl acetate (product corresponding to the symmetrical radical) was racemic. For the following reasons the validity of this conclusion seems questionable. Evidently no experiments were carried out to determine if the substrate and acetate of interest are optically stable under the conditions of the experiment. Moreover, the method used to oxidize the alcohol would be expected<sup>13</sup> to result in extensive if not complete racemization of the symmetrical allylic alcohol<sup>14</sup>—oxidation of active *exo*-

bicyclo[3.2.1]oct-3-en-2-ol (IIIId) by this method results in over 60% racemization. Finally, as was recognized,<sup>5</sup> recrystallization involved in purification of the solid derivatives might result in optical fractionation which could obscure partial preservation of optical configuration.

The second stereochemical problem of interest concerns the stereoselectivity of the conversion of the intermediate to substitution product, *i.e.*, the ratio of *exo* (quasi-axial) isomer III to *endo* (quasi-equatorial) isomer IV. In an earlier paper<sup>15</sup> it was suggested that for cyclohexenyl carbonium ions, radicals, and carbonions, quasi-axial bond formation is stereoelectronically favored over quasi-equatorial bond formation. Evidence consistent with this view has been presented for carbonium ion reactions in the 5-methyl-2-cyclohexenyl system<sup>15</sup> and it has been found that the bicyclo[3.2.1]oct-3-en-2-yl carbonium ion (the ion corresponding to II) is converted to the *exo* (quasi-axial) substitution product almost exclusively.<sup>12,16</sup> In this connection it was of interest to determine the stereoselectivity of a substitution reaction involving an intermediate cyclohexenyl radical.



### Results and Discussions

Optically active bicyclo[3.2.1]octene-2 (I) was derived from active *exo*(quasi-axial)-bicyclo[3.2.1]oct-3-en-2-yl acid phthalate (IIIc), of known optical purity,<sup>12</sup> as follows. The optically active acid phthalate IIIc was converted to the corresponding acetate IIIb by a method known to preserve optical purity.<sup>12</sup> Reduction of active IIIb gave the active saturated analog, Va, which was converted to active I in 66% yield by pyrolysis<sup>17</sup> at 540°. Optically active Va prepared by this route was converted to the corresponding saturated acid phthalate derivative Vb which had the same rotation as material obtained by direct hydrogenation of IIIc. Thus hydrogenation evidently does not result in loss of optical purity. It appears that optical purity is also largely, if not completely, preserved in the pyrolysis step. In one experiment (+)-IIIb, [ $\alpha$ ]<sub>25D</sub> 225°,<sup>18</sup> (*ca.* 94% optically pure) was converted in two steps (hydrogenation followed by pyrolysis) to (-)-I, [ $\alpha$ ]<sub>25D</sub> -80.4°. In a similar experiment (-)-IIIb, [ $\alpha$ ]<sub>25D</sub> -143°, gave (+)-I, [ $\alpha$ ]<sub>25D</sub> +56.7°. The agreement in the change in rotation accompanying the conversion of IIIb to I suggests that there is little, if any, loss of optical configuration.

Capillary gas chromatography (g.c.) showed that the olefin obtained by this method contained 3.6% bicyclo[2.2.2]octene as the only contaminant. This resulted

(14) It has been shown that optically active alcohols of this type can be oxidized to the corresponding ketones with manganese dioxide without loss of configuration; H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 5172 (1955).

(15) H. L. Goering and R. R. Josephson, *ibid.*, **84**, 2779 (1962).

(16) R. Anderson, unpublished results.

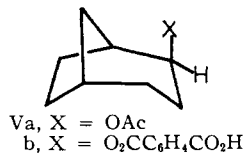
(17) W. L. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(18) All specific rotations are for acetone solutions. In this solvent optically pure isomers (ref. 12) have the following rotations: 111a, 105°; 111b, 240°; 111c, 224°; 111d, 230°; Va, 0.4°; Vb, 33°.

(11) J. D. Roberts and E. R. Trumbull, *J. Am. Chem. Soc.*, **71**, 1630 (1949); A. Reybenbach and M. Szwarc, *Proc. Chem. Soc.*, 347 (1958).

(12) H. L. Goering and D. L. Towns, *J. Am. Chem. Soc.*, **85**, 2295 (1963).

(13) For examples of rapid acid-catalyzed racemizations of symmetrical allylic alcohols, see H. L. Goering and E. F. Silversmith, *ibid.*, **79**, 348 (1957), and ref. 15.



from a corresponding amount of the [2.2.2] isomer in the acid phthalate IIIc from which it was derived. Since the contaminant is symmetrical, it cannot contribute to the rotation of the olefin or give optically active products. Thus its presence in no way disturbs the stereochemical studies but does introduce a small uncertainty in the optical purities of the starting material IIIc and intermediates IIIb and Va involved in the synthesis.<sup>18</sup>

Reaction of (–)-I,  $[\alpha]^{25}_D -80.4^{\circ}$  ( $>90\%$  optically pure), with *t*-butyl perbenzoate in refluxing benzene in the presence of cuprous bromide gave bicyclo[3.2.1]oct-3-en-2-yl benzoate which was completely inactive. The benzoate, isolated in such a way as to avoid fractionation of isomers, was saponified by a method that does not result in change of optical purity.<sup>12</sup> The alcohol obtained by saponification of the benzoate was also completely inactive and consisted of  $>99\%$  *exo*-(quasi-axial)-bicyclo[3.2.1]oct-3-en-2-ol (IIIId). The only contaminant detected (g.c.) was  $<1\%$  of the *endo* isomer IVd. Optical rotations were taken in such a manner that if the product IIIa were as optically pure as the substrate I the expected observed rotations would have been  $>2^{\circ}$  for the benzoate and  $>4^{\circ}$  for the alcohol. Thus as little as 0.5% preservation of optical configuration would have been detected.

In a control experiment with (+)-I it was found that if less than an equivalent amount of *t*-butyl perbenzoate is used the unreacted olefin retains its optical purity fully. It was also found that reaction of cyclohexene with *t*-butyl perbenzoate in the presence of (–)-*exo*-bicyclo[3.2.1]oct-3-en-2-yl benzoate ((–)-IIIa) does not result in racemization of the bicyclic ester. These experiments show that both the olefin and the substitution product IIIa are optically stable under the conditions of the reaction. Thus the reaction of I with *t*-butyl perbenzoate is highly stereoselective, the *exo*-benzoate IIIa is formed almost exclusively, and the product derived from active I is completely racemic. Or to put it another way, there is no detectable substitution without randomization of the two allylic carbon atoms (C-2 and C-4). These results are consistent with the Kochi mechanism and show that all of the product is derived from a symmetrical intermediate, *i.e.*, II or the corresponding carbonium ion.

The stereoselectivity of this reaction is greater than that of reactions involving the 2-norbornyl radical<sup>19</sup> and about the same as that of reactions involving the bicyclo[3.2.1]oct-3-en-2-yl carbonium ion (the cation corresponding to II).<sup>12,16</sup> As mentioned before, it is not known if the intermediate radical II is converted directly to product (eq. 3) or if it is oxidized to the carbonium ion (eq. 3a). In any event it seems likely that the high stereoselectivity results from a combination of two factors, both of which favor formation of the *exo* (quasi-axial) isomer. The first of these is a steric factor; as in the case of the norbornyl system,<sup>19</sup> approach to C-2 from the *exo* side is favored. The second is a stereoelectronic factor. For reasons outlined else-

(19) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

where<sup>12,15</sup> it appears that in cyclohexenyl systems the transition state for formation and cleavage of a quasi-axial bond is favored over that involving a quasi-equatorial bond. In the present system, which is conformationally rigid, formation of a quasi-axial bond gives rise to the *exo* isomer.

## Experimental

**Materials.**—(+)-*exo*-Bicyclo[3.2.1]oct-3-en-2-yl acid phthalate ((+)-IIIc),  $[\alpha]^{25}_D +224^{\circ}$ ,<sup>18</sup> was prepared and resolved by a method shown earlier<sup>12</sup> to give optically pure material. The acid phthalate derivative was converted<sup>12</sup> to the corresponding acetate IIIb, which had  $[\alpha]^{25}_D +225^{\circ}$  (*c* 1.6).<sup>18</sup> Capillary gas chromatography (g.c.), Ucon-polar column, showed the acetate to be a mixture of isomers consisting of 89% IIIb, 7.7% of the *endo* (quasi-equatorial) isomer IVb, and 3.3% *endo*-bicyclo[2.2.2]oct-5-en-2-yl acetate.<sup>12</sup> Work-up of the mother liquors from the resolution gave (–)-IIIc which was converted to (–)-IIIb,  $[\alpha]^{25}_D -143^{\circ}$  (*c* 1.4). The composition of the levorotatory acetate (g.c.) was similar to that of the dextrorotatory acetate.

(+)-*exo*(axial)-Bicyclo[3.2.1]octan-2-yl Acetate (Va).—In a typical preparation a solution of 2.6 g. of the above-described (+)-IIIb in 30 ml. of acetic acid containing 0.3 g. of sodium acetate was hydrogenated at atmospheric pressure using a palladium-on-charcoal catalyst. After the uptake of 1 equivalent of hydrogen the catalyst was removed and the solution diluted with 1 l. of water. The product was isolated by continuous extraction with pentane. After removal of the pentane the residual (+)-Va was distilled, b.p. 112–114° (14 mm.),  $n^{25}_D$  1.4695,  $[\alpha]^{25}_D +0.4^{\circ}$  (*c* 1).

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>: C, 71.39; H, 9.59. Found: C, 71.55; H, 9.63.

The saturated acetate (+)-Va was converted to the corresponding acid phthalate derivative (+)-Vb as follows. A solution of 0.273 g. of (+)-Va and 4 g. of potassium hydroxide in 15 ml. of methanol was refluxed for 2 hr. The mixture was then diluted with 250 ml. of water and continuously extracted with 30 ml. of pentane. After removal of the pentane, the residual alcohol was converted to the acid phthalate derivative (+)-Vb, n.p. 109–110° (pentane),  $[\alpha]^{25}_D +30.5^{\circ}$  (*c* 1.2).<sup>18</sup>

*Anal.* Calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>4</sub>: C, 70.05; H, 6.61. Found: C, 69.93; H, 6.49.

Direct reduction of the above-described unsaturated acid phthalate (+)-IIIc gave (+)-Vb having  $[\alpha]^{25}_D +30.8^{\circ}$  (*c* 1). Thus the optical purity of Vb is the same when prepared directly from IIIc as when prepared by the sequence IIIc → IIIId → IIIb → Va → Vb. This shows that all of the steps in this sequence proceed with complete preservation of optical configuration.

**Optically Active Bicyclo[3.2.1]octene-2 (I).**—Optically active I was obtained by pyrolysis of active saturated acetate Va using an apparatus similar to that described earlier.<sup>17</sup> In a typical experiment 2.3 g. of (+)-Va,  $[\alpha]^{25}_D +0.4^{\circ}$ , was mixed with 2 ml. of pentane and the resulting solution added dropwise to the pyrolysis tube which was maintained at 540°. The yellow pyrolysis was collected in a trap containing 10 ml. of cold (–20°) pentane. The pentane solution was washed with water and aqueous sodium carbonate and then dried (MgSO<sub>4</sub>). After removal of the solvent with an efficient column the residual bicyclo[3.2.1]octene-2 (I) was purified by distillation (66% yield), b.p. 132–134°, m.p. 42–44°,  $[\alpha]^{25}_D -80.4^{\circ}$  (*c* 1.1).<sup>15,20</sup>

*Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>: C, 88.82; H, 11.18. Found: C, 88.64; H, 11.25.

The (–)-I obtained by this route contained 3.6% bicyclo[2.2.2]octene-2 as the only contaminant. The latter was prepared for comparison purposes by pyrolysis (540°) of bicyclo[2.2.2]octan-2-yl acetate.<sup>21</sup>

Pyrolysis (520°) of (–)-Va, derived from (–)-IIIb,  $[\alpha]^{25}_D -143^{\circ}$ , gave (+)-I,  $[\alpha]^{25}_D +56.7^{\circ}$  (*c* 1.4). The infrared spectrum of this material was indistinguishable from those of its enantiomer and racemic material.<sup>20</sup>

**Reaction of (–)-Bicyclo[3.2.1]octene-2 ((–)-I) with *t*-Butyl Perbenzoate.**—To a solution of 0.511 g. (4.73 mmoles) of (–)-I,

(20) Racemic bicyclo[3.2.1]octene-2, prepared by different routes, has been reported previously. K. Alder, H. Krieger, and H. Weiss, *Chem. Ber.*, **88**, 144 (1955); W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963); R. C. DeSels and C. M. Coombs, *ibid.*, **28**, 2206 (1963).

(21) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1397 (1961).

$[\alpha]^{25}_D - 80.4^\circ$ , and 0.897 g. (4.63 mmoles) of *t*-butyl perbenzoate in 5 ml. of benzene was added 5 mg. of cuprous bromide. The solution was refluxed for 30 min. during which time it turned blue. The reaction mixture was added to 500 ml. of water and the product was isolated by continuous extraction with pentane. The residual bicyclo[3.2.1]oct-3-en-2-yl benzoate was completely inactive.<sup>18</sup>

Saponification of the residual benzoate (methanolic KOH) gave 0.337 g. (57%) of bicyclo[3.2.1]oct-3-en-2-ol which was also completely racemic.<sup>18</sup> This product was shown to be >99.1% *exo* (quasi-axial)-bicyclo[3.2.1]oct-3-en-2-ol (IIIId) and <0.9% of the *endo* isomer IVd by g.c. analysis. No other components were detected.

The bicyclic alcohol was converted to *dl*-*exo*-bicyclo[3.2.1]oct-3-en-2-yl *p*-nitrobenzoate, m.p. 84–85° (lit.<sup>22</sup> 86.2–86.6°). The infrared spectrum was indistinguishable from that of an authentic sample and the melting point was not depressed when mixed with authentic material.<sup>22</sup>

**Control Experiments.**—(–)-*exo*-Bicyclo[3.2.1]oct-3-en-2-ol ((–)-IIIId),  $[\alpha]^{25}_D - 143^\circ$ , was converted to the benzoate derivative (–)-IIIa which had  $[\alpha]^{25}_D - 66.5^\circ$ .<sup>18</sup>

(22) H. L. Goering, R. W. Greiner, and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961).

To a solution of 0.615 g. (3.17 mmoles) of *t*-butyl perbenzoate, 1 g. (12.2 mmoles) of cyclohexene, and 5 mg. of cuprous bromide in 3 ml. of benzene was added 0.412 g. of the above (–)-IIIa. After refluxing for 30 min. the mixture was diluted with ether and shaken with cold dilute aqueous acid to remove the copper salts. The ether was removed and the residue diluted to exactly 10 ml. with acetone. The expected observed rotation for a 4-dm. tube is  $-10.962^\circ$  if the (–)-IIIa retains its activity. The observed rotation was  $-10.982^\circ$ . This shows that IIIa is completely optically stable under the conditions of the copper-salt-catalyzed reaction of *t*-butyl perbenzoate with olefins.

In a second control experiment a solution of 0.124 g. (1.15 mmoles) of (+)-I,  $[\alpha]^{25}_D + 57.1^\circ$  (*c* 1.1, pentane), 0.043 g. (0.22 mmole) of *t*-butyl perbenzoate, and 5 mg. of cuprous bromide in 2 ml. of benzene was refluxed for 30 min. The reaction mixture was diluted with 4 ml. of pentane and shaken with cold dilute aqueous acid to remove the copper salts. The organic layer was dried ( $\text{Na}_2\text{SO}_4$ ) and diluted to exactly 10 ml. with pentane. If the excess (+)-I retains its activity completely the expected observed rotation for a 4-dm. tube is  $2.293^\circ$ . The observed rotation was  $2.237^\circ$ . This experiment shows that I is optically stable under the conditions of the reaction with *t*-butyl perbenzoate in the presence of copper salts.

[CONTRIBUTION FROM THE IBM WATSON RESEARCH CENTER, YORKTOWN HEIGHTS, N. Y.]

## Thermal Decomposition Processes in the System Tricyclo[3.3.0.0<sup>2,6</sup>]octane–1,5-Cyclooctadiene<sup>1</sup>

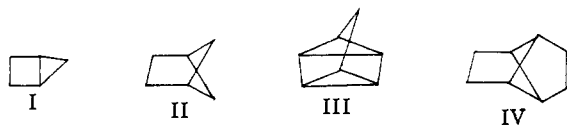
BY R. SRINIVASAN AND A. A. LEVI

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The thermal isomerization of tricyclo[3.3.0.0<sup>2,6</sup>]octane in the gas phase at 1.5-mm. pressure in the temperature range from 327 to 366° is a homogeneous, first-order reaction. The rate of the reaction fitted the equation  $K = 3.22 \times 10^{15} \exp(-55,900 \pm 1400/RT)$ . The addition of propylene had no effect on the kinetics. The products that were observed (in the order of decreasing yield) were 4-vinylcyclohexene, 1,3-butadiene, and 1,5-cyclooctadiene. From separate studies of the pyrolysis of 1,5-cyclooctadiene and 4-vinylcyclohexene, it was concluded that tricyclooctane isomerized to 1,5-cyclooctadiene which in turn isomerized rapidly to 4-vinylcyclohexene. While 1,3-butadiene is a product of the pyrolysis of 1,5-cyclooctadiene, it is not certain that this is the only path by which it is formed from tricyclooctane. The kinetics of the pyrolysis of 1,5-cyclooctadiene was studied over the temperature range from 299.5 to 358.1° at 1.2-mm. pressure. From 299.5 to 327.3° the reaction seemed to be first order, homogeneous, and unaffected by the addition of propylene. Above this range the reaction was complex, although the products remained qualitatively the same.

### Introduction

The thermal decomposition of a great variety of alkyl-substituted cyclobutanes has been investigated by Walters and his co-workers.<sup>2</sup> These reactions, which in every case have been found to be homogeneous, first order, and unimolecular, have activation energies which are affected very little by one or even two alkyl substituents. In view of this fact, it seems reasonable to attribute the diminution in activation energy in going from cyclobutane itself to bridged cyclobutane systems such as bicyclo[2.1.0]pentane (I),<sup>3</sup> bicyclo[2.1.1]hexane (II),<sup>4</sup> and quadricyclene (III)<sup>5</sup> to the



strain energy that the presence of one or more additional ring systems contributes to the energy required

(1) Presented at the Third Annual Metropolitan Regional Meeting of the American Chemical Society New York, N. Y., Jan., 1964.

(2) C. T. Genaux, F. Kern, and W. D. Walters, *J. Am. Chem. Soc.*, **75**, 6196 (1953); M. N. Das and W. D. Walters, *Z. physik. Chem.*, **15**, 22 (1958); R. E. Wellman and W. D. Walters, *J. Am. Chem. Soc.*, **79**, 1542 (1957); S. M. E. Kellner and W. D. Walters, *J. Phys. Chem.*, **65**, 466 (1961); H. R. Gerberich and W. D. Walters, *J. Am. Chem. Soc.*, **83**, 3935, 4884 (1961).

(3) M. L. Halberstadt and J. P. Chesick, *ibid.*, **84**, 2688 (1962).

(4) R. Srinivasan and A. A. Levi, *ibid.*, **85**, 3363 (1963).

(5) H. M. Frey, *J. Chem. Soc.*, 365 (1964).

to break the cyclobutane ring. Whether the decrease in activation energy is exactly equal to the strain energy (as it is in the case of I) can be determined only when data on the heats of formation of these strained hydrocarbons become available.

The present study was undertaken to extend these kinetic data to tricyclo[3.3.0.0<sup>2,6</sup>]octane (IV) which is a cyclobutane with two bridges of two carbon atoms each. The formation of this molecule by a photochemical route<sup>6</sup> makes it especially interesting to know the position of the equilibrium in the thermal and photochemical systems.

### Experimental

**Materials.**—Tricyclooctane was prepared by the photochemical isomerization of 1,5-cyclooctadiene in the presence of cuprous chloride.<sup>7</sup> The crude mixture of tricyclooctane and cyclooctadiene that was obtained by a simple distillation after stripping off the ether was fractionated on a spinning-band column. A fraction rich in tricyclooctane was collected. Further purification was carried out on a gas chromatographic column using small samples (0.05 ml.) and conditions of high resolution. The sample that was collected was dried, degassed, and stored at  $-20^\circ$ . The final sample had a refractive index of 1.4709 at  $23.0^\circ$  and contained no detectable impurity when analyzed by gas chromatography. This refractive index agreed with that of a sample that had been prepared by the mercury-sensitized isomerization of 1,5-cyclooctadiene in the gas phase.<sup>6</sup>

(6) R. Srinivasan, *J. Am. Chem. Soc.*, **85**, 819 (1963).

(7) R. Srinivasan, *ibid.*, **85**, 3048 (1963).