

prepared by deuterioboration of 4-*t*-butylcyclohexene with deuteriodiborane, oxidation with alkaline hydrogen peroxide, separation of axial and equatorial alcohols by elution chromatography and preparative v.p.c., and separation of the desired alcohol by fractional crystallization of the axial *p*-nitrobenzoates. Combustion analyses indicated that the deuterated alcohols were about 98% isotopically pure. The brosylates of the various alcohols were prepared by the usual Tipson procedure.⁵

A determination of the products of the solvolysis of *cis*-4-*t*-butylcyclohexyl brosylate is complicated by insolubility of the substrate and volatility of the olefin fraction of the product. Direct analysis for olefin concentration relative to *cis*-decalin as internal standard was found to be possible at substrate concentrations of ca. $2.5 \times 10^{-3} M$ by v.p.c. with flame ionization detection. Such an analysis on the products of solvolysis of ester I in 60 vol. % aqueous ethanol at 45° in a sealed tube with suspended calcium carbonate indicated the olefin yield to be 86%. Analysis of the products of solvolysis of a more concentrated solution at higher temperature showed the yield of alcohols to be 11% and ethers 3%. The alcohol fraction consisted of 79% *trans*-4-*t*-butylcyclohexanol (inversion) and 21% *cis*-4-*t*-butylcyclohexanol (retention). This pattern of substitution and elimination is similar to that observed by Winstein and Holness³ for the acetylation of *cis*-4-*t*-butylcyclohexyl tosylate and is in accord with a carbonium ion reaction rather than a solvent-assisted bimolecular elimination reaction.

The rate data, collected in Table I, were obtained by a precise conductometric determination⁶ of the first-order solvolysis rate constants of the brosylates at 35° in 50 vol. % aqueous ethanol. The precision of the method, without the determination of conductance parameters, is $\pm 0.1\%$. The sensitivity of the conductometric method is such that we were able to measure the solvolysis rates at a substrate concentration of $5 \times 10^{-4} M$. Thus, the solubility problem which usually requires that solvolysis rates of arenesulfonate esters measured titrimetrically be done in organic acid media at higher temperatures was circumvented.

TABLE I
SOLVOLYSIS RATES OF DEUTERATED *cis*-4-*t*-BUTYLCYCLOHEXYL
BROSYLATES

Deuteration	$k_1 \times 10^4, \text{sec.}^{-1}$	k_H/k_D
None	3.938 ± 0.004	...
α -deuterium, equatorial	3.275 ± 0.004	1.202 ± 0.002
β -deuterium, axial	2.743 ± 0.001	1.436 ± 0.002
β -deuterium, equatorial	3.593 ± 0.003	1.096 ± 0.002

The axial β -deuterium slows the solvolysis rate by a factor of 1.436 which is the largest reported secondary isotope rate effect attributable to a single deuterium atom. Furthermore, it is almost *ten times* larger than the average steric isotope effect per deuterium atom calculated by Bartell⁷ for the *t*-butyl chloride solvolysis. On the other hand, the equatorial β -deuterium atom slows the solvolysis rate by the dramatically reduced factor of 1.096.

Thus, the conformational dependence of the β -deuterium effect, predicted by the hyperconjugation postulate, is confirmed in this reaction.

The possibility exists that the axial isotope effect is due to neighboring hydrogen participation, which in our view is simply an extreme manifestation of a

type of electronic interaction also associated with hyperconjugation. One consequence of hydrogen participation would be a nonequivalence of the 2- and 6-axial hydrogens in the solvolytic transition state. Should this be the case, the solvolytic rate retardation caused by 2,6-diaxial deuteration would exceed the square of 1.436. Although this interesting question remains to be settled, there seems to be no doubt that the present results cannot be explained in terms of the simple steric model proposed by Bartell.⁷

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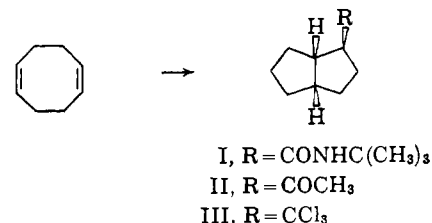
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Free-Radical Cycloadditions to *cis,cis*-1,5-Cyclooctadiene

Sir:

Although ionic reactions in the cyclooctane series¹ frequently lead to transannular rearrangements, and the reactions involving carbene intermediates have also been shown² to result in transannular rearrangements, the corresponding free-radical rearrangements are unknown.³ We provide here the first example of a free-radical cycloaddition in the cyclooctane series.

Addition of a mixture of 35.6 g. (0.33 mole) of *cis,cis*-1,5-cyclooctadiene and 5.11 g. (0.035 mole) of di-*t*-butyl peroxide to 1010 g. (10.0 mole) of *t*-butylformamide⁴ at 135–140° and distillation of the reaction mixture gave 35 g. (51%) of a liquid, b.p. 115° (0.08 mm.)–165° (0.25 mm.), which, after solidification, was recrystallized from aqueous methanol, then from petroleum ether (b.p. 45–60°), to give *exo,cis*-N-*t*-butylbicyclo[3.3.0]octane-2-carboxamide⁵ (I), m.p. 134–135°, λ_{max} 3.08, 3.30, 6.11, and 6.48 μ . The amide (I) did not absorb any hydrogen (5% Pd on charcoal,



50 p.s.i.) and was recovered unchanged. All attempts at its saponification, including heating it with potassium hydroxide at 200° and fusing it with a mixture of potassium and sodium hydroxides at 200°, failed to give the acid.⁶ The authentic amide (I) was prepared from *exo,cis*-bicyclo[3.3.0]octane-2-carboxylic acid⁷ (via its acid chloride) and *t*-butylamine. The two compounds were indistinguishable in their infrared spectra and melting points, and the melting point of the mixture was undepressed.

cis,cis-1,5-Cyclooctadiene and acetaldehyde⁸ gave,

(1) E. g., A. C. Cope, J. N. Grisar, and P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 4299 (1960).

(2) L. Friedman and H. Shechter, *ibid.*, **83**, 3159 (1961).

(3) A. N. Nesmeyanov, R. Kh. Freidlina, V. N. Kost, and M. Ya. Khorlina, *Tetrahedron*, **16**, 94 (1961).

(4) L. Friedman and H. Shechter, *Tetrahedron Letters*, 238 (1961).

(5) Satisfactory elemental analyses were obtained for all new compounds reported here.

(6) Compound I may be one of the most difficultly saponifiable amides known.

(7) A. C. Cope and M. Brown, *J. Am. Chem. Soc.*, **80**, 2859 (1958).

(5) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

(6) B. L. Murr, Jr., and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **84**, 4672 (1962).

(7) L. S. Bartell, *ibid.*, **83**, 3567 (1961).

in the presence of benzoyl peroxide, methyl *exo,cis*-2-bicyclo[3.3.0]octyl ketone (II) which, after purification through its semicarbazone, m.p. 180.8–181.8° dec. (lit.⁹ m.p. 181.0–182.4° dec.), and recovery by the action of sodium nitrite in acetic acid,¹⁰ had the following properties: b.p. 93° (5 mm.), n_D^{25} 1.4732, λ_{\max} 5.87 μ , homogeneous in gas chromatography (lit.⁹ b.p. 94–95° (10 mm.), n_D^{25} 1.4655). Its infrared spectrum was indistinguishable from that of the authentic ketone II (prepared by the published⁹ procedure), and the infrared spectra of the semicarbazones as well as their melting points were the same, with no depression in the mixture melting point.

The reaction of *cis,cis*-1,5-cyclooctadiene and chloroform in the presence of benzoyl peroxide resulted in a 37% yield of 2-(trichloromethyl)bicyclo[3.3.0]octane (III), b.p. 110–111° (9 mm.), n_D^{25} 1.5110, no absorption in the infrared at wave length lower than 3.4 μ attributable¹¹ to =CH stretching vibrations, and no signals due to olefinic protons in its n.m.r. spectrum.¹² Compound III was inert to aqueous potassium permanganate and did not absorb hydrogen over a palladium-on-charcoal catalyst. Hydrogenation of III in methanol and triethylamine in the presence of Raney nickel gave *exo,cis*-2-methylbicyclo[3.3.0]octane, b.p. 143–144°, n_D^{25} 1.4538, transparent in the region of 3.6 to 6.8 μ ; and *exo,cis*-2-(dichloromethyl)bicyclo[3.3.0]octane, b.p. 108–112° (15 mm.), further purified by g.l.c., n_D^{25} 1.5005.

Hydrolysis of III by hot phosphoric acid gave 2-(dichloromethylene)bicyclo[3.3.0]octane, b.p. 68° (0.2 mm.), n_D^{24} 1.5191, λ_{\max} 6.13 μ (also prepared by dehydrochlorination of III with potassium hydroxide in ethanol); and *exo,cis*-bicyclo[3.3.0]octane-2-carboxylic acid,⁷ b.p. 93° (0.1 mm.), n_D^{25} 1.4847, λ_{\max} 5.9 μ , which gave an amide, m.p. 178–179° (lit.⁷ m.p. 179°). The infrared spectrum of this amide was indistinguishable from that of the authentic *exo,cis*-bicyclo[3.3.0]octane-2-carboxamide¹³ and the mixture melting point of two compounds was undepressed. This establishes the structure of III.¹⁴

The generality of these 1,5-cycloadditions in *cis,cis*-1,5-cyclooctadiene was established with further addends. Thus, carbon tetrachloride, dimethylformamide, γ -butyrolactone, ethyl chloroacetate, and ethyl trichloroacetate gave derivatives of bicyclo[3.3.0]octane, thus furnishing an easy and convenient entry into the bicyclo[3.3.0]octane system. The reaction mixtures were not examined for the presence of small amounts of *endo* derivatives of bicyclo[3.3.0]octane or of derivatives of bicyclo[4.2.0]octane. The details of this work as well as elaboration of the mechanism will be published at a later date.

(8) For free-radical initiated additions of aldehydes to olefins, see M. S. Kharasch, W. H. Urry, and B. M. Kuderna [J. Org. Chem., **14**, 248 (1949)], and T. M. Patrick, Jr. [ibid., **17**, 1009 (1952)].

(9) A. C. Cope, M. Brown, and H. E. Petree, J. Am. Chem. Soc., **80**, 2853 (1958).

(10) S. Goldschmidt and W. L. C. Veer, Rec. trav. chim., **65**, 796 (1946).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen Co., Ltd., London, 1954, p. 38.

(12) Obtained by Mr. F. E. Dickson of the Mellon Institute, Pittsburgh, Pa., on a Varian A-60 NMR Spectrometer.

(13) The author is grateful to Professor A. C. Cope for his kindness in furnishing a sample of this amide.

(14) Although it is conceivable that *exo,cis*-bicyclo[3.3.0]octane-2-carboxylic acid could result from rearrangement of III, and not from the simple hydrolysis of the trichloromethyl group, the analogous transannular cycloadditions described here as well as other evidence seem to establish clearly the structure of the chloroform adduct as III.

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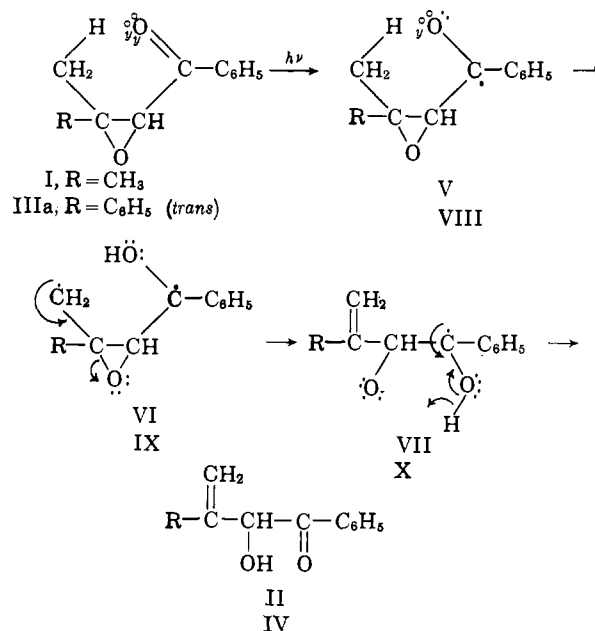
A General Theory of Photochemical Reactions. VII. Mechanisms of Epoxy Ketone Reactions

Sir:

In our previous publications on organic photochemistry,^{1,2} we presented a mechanistic treatment which allows discussion of the electronic details of photochemical transformations. As noted therein, our goals are exploration of the extent to which our hypothesis is correct, modification where necessary, and delineation of mechanistic subtleties. Presently we report two examples of a new photochemical rearrangement and an unusual case of a known photochemical rearrangement. We note (a) a unique difference in photochemical behavior of phenyl *vs.* alkyl ketones, (b) unusual migratory aptitude behavior, and (c) evidence in favor of our excited state description.^{1,2} In the first photochemical reaction, dimethylacrylophenone oxide (I) was observed to afford 1-phenyl-3-methyl-3-buten-2-ol-1-one (II) in 64% yield. Similarly *trans*-dypnone oxide (IIIa) afforded 1,3-diphenyl-3-buten-2-ol-1-one (IV) in 25% yield as the major product. In contrast the structurally related 3,4-epoxy-4-phenyl-2-pentanone (XV) led to 1-phenyl-2-methyl-1,3-butanedione (XVI) as the major product (25%).³

Aside from the synthetic utility of the new reaction described in Chart I, this transformation is of mechanis-

CHART I



tic interest, providing support for our concept of the excited state.^{1,2} Thus we have noted^{1,2,4} that because the single p_y (*i.e.*, n) electron not promoted in the $n-\pi^*$ excitation is localized in this oxygen orbital, the orbital will exhibit chemical behavior characteristic of reactive alkoxy radicals, one example being hydrogen abstraction.^{5,6} In the present instance reactants I and IIIa

(1) This approach was presented by H. E. Zimmerman at the 17th National Organic Symposium of the American Chemical Society, 1961; cf. Abstracts, p. 31.

(2) (a) For extended discussions, cf. paper IV: H. E. Zimmerman and D. I. Schuster, J. Am. Chem. Soc., **84**, 4527 (1962); (b) H. E. Zimmerman, Tetrahedron, Suppl. 2, **19**, 393 (1963).

(3) Reactant syntheses and stereochemistry, photolysis details, degradative and other evidence for product structures, and nature of by-products—all will be detailed in our full paper where space permits.

(4) Note H. E. Zimmerman, H. G. Dürr, R. G. Lewis, and S. Bram, J. Am. Chem. Soc., **84**, 4149 (1962), for an example of p_y orbital reactivity toward a π -system.

(5) We have suggested (ref. 1, 2) that examples of p_y orbital hydrogen abstraction include the Norrish type II cleavage (R. G. W. Norrish, Trans.