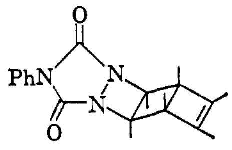
ticularly in the direction of hexamethylbenzene; hence unimolecular decomposition of the prismane may proceed significantly slower than the reported rate and may well yield exclusively the Dewar benzene. Hexamethylprismane is immediately isomerized to **2** and **3** by boron trifluoride etherate in carbon tetrachloride, and more slowly by Lindlar catalyst in benzene[4] to **2**, **3**, and yet another valence tautomer, hexamethylbenzvalene.

Dienophiles such as 4-phenyl-1,2,4-triazoline-3,5-dione (**4**) and tetracyanoethylene attack the prismane extremely rapidly at room temperature. The major product from the azo compound and **1** is a 1:1 adduct (*Anal.* Calcd: C, 71.19; H, 6.87; N, 12.45. Found: C, 71.18; H, 6.84; N, 12.46) whose pmr spectrum ($CDCl_3$) consists of a narrow five-proton multiplet centered at δ 7.43 and three needle-like six-proton singlets at δ 1.72, 1.46, and 0.84. Structures **5**, **6**, and **7** are all consistent with the pmr and other spectral data for the adduct, and all are mechanistically feasible candidates. When this compound is treated with osmium tetroxide and pyridine in deuteriochloroform, the methyl region of its pmr spectrum undergoes a sudden change: as the original three signals disappear, four narrow singlets emerge at δ 2.19, 1.76, 1.30, and 1.12 (area ratio, 1:1:2:2). This result eliminates from consideration structures **5** and **6**, as either osmate ester from either isomer should show three methyl signals of equal area. Structure **7**, however, is fully consistent with the new pmr pattern since formation of the pyridine-complexed osmate ester **8** destroys the equivalence of one of the pairs of methyls.



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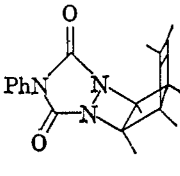

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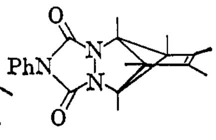
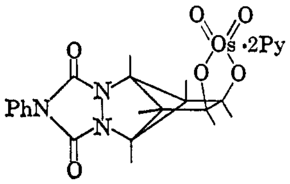
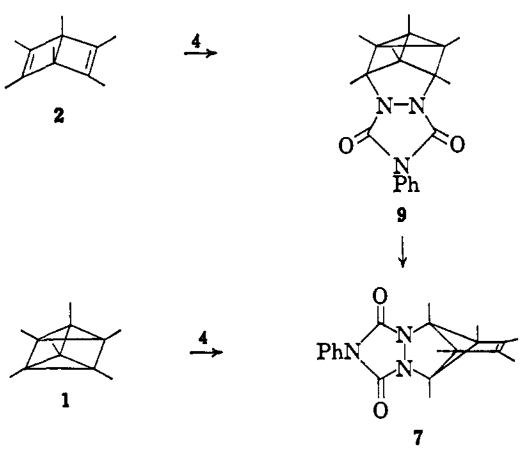


7



8

Interestingly, the same stable adduct (**7**) is generated more slowly but in good yield from **4** and Dewar benzene (**2**) in acetone. A pmr study has revealed the formation of a labile intermediate adduct on the pathway to **7**. This compound is tentatively formulated as **9** on the basis of its pmr spectrum (which features methyl resonances in $CDCl_3$ at δ 1.79, 1.50, 1.36, and 0.80, relative areas 2:1:1:2) and analogy to homoconjugate addition of dienophiles to norbornadiene.[5] With chloroform instead of the more polar acetone as reaction solvent, the intermediate adduct is far stabler; thus the rearrangement to **7** is probably an ionic process.



The Dewar benzene is produced, often in major amounts, in virtually all of the presently known reactions of hexamethylprismane, regardless of the nature of the reagent or the gentleness of the experimental conditions.[6] This fact suggests that catalysis of the valence tautomerization may require only complexation, not formation of a full-fledged σ bond between hydrocarbon and catalyst. Possibly the key function of the catalyst is to reduce the symmetry of the reacting system, thus weakening the symmetry prohibition[7] against concerted ring opening.

As a consequence of the remarkably efficient aluminum chloride catalyzed trimerization of 2-butyne to Dewar benzene **2**,[8] hexamethylprismane is a readily accessible chemical. We are continuing our investigation of this compound and exploring the scope of the Dewar benzene–prismane photoisomerization.

Acknowledgment. The authors wish to thank Dr. G. O. Dudek of Harvard University for determining the mass spectrum of hexamethylprismane, the Danforth Foundation for a fellowship for J. P. L., and the National Science Foundation for financial support of the project.

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[4] It reacts instantly with iodine, but sluggishly with dry methanol; in neither case have the products been adequately characterized.

[5] See, for example, R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *Tetrahedron Letters*, 615 (1962), and references contained therein.

[6] The facile catalyzed isomerization of **1** to **2** finds an earlier counterpart in the ring opening of quadricyclanone ketals to norbornadienone ketals at room temperature (D. M. Lemal, R. A. Lovald, and R. W. Harrington, *Tetrahedron Letters*, 2779 (1965)).

[7] R. Hoffmann and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 2046 (1965).

[8] W. Schäfer, *Angew. Chem.*, **78**, 716 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 669 (1966).

[9] Danforth Foundation Fellow, 1962–1966.

[10] This work will comprise a portion of the Ph.D. dissertation o J. P. Lokensgard, University of Wisconsin.

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Received November 7, 1966

The Photoaddition of 2-Cyclohexenone and Norbornadiene.[1] Studies in Photochemistry. I

Sir:

The usual course of the photochemical reaction of unsaturated ketones,[2] esters,[3] or nitro compounds[4]

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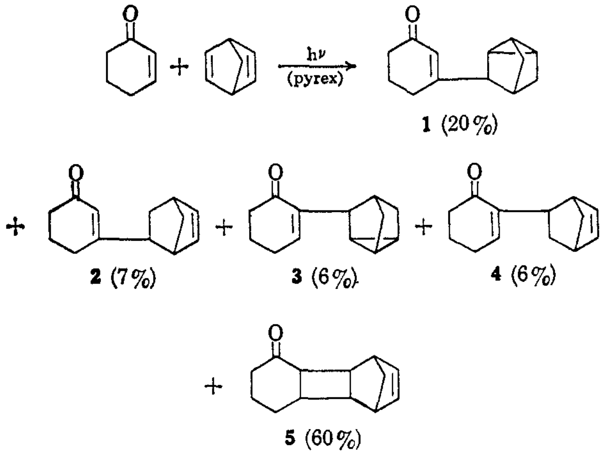
[1] Presented to the Chemical Institute of Canada at the Symposium on Synthesis, Banff, Alberta, Aug 1966.

[2] (a) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964); (b) Y. Yamada, H. Uda, and K. Nakanishi, *Chem. Commun.*, 423 (1966); M. Brown, *ibid.*, 340 (1965).

with alkenes leads to the formation of cyclobutane derivatives. We wish to report that the photoaddition of 2-cyclohexenone and bicyclo[2.2.1]heptadiene gives rise to alkylated cyclohexenones, together with the usual cyclobutane adducts. The former have been identified as 3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone (**1**), 3-(5-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (**2**), 2-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone (**3**), and 2-(5-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (**4**); the numbers in parentheses refer to Chart I.

Chart I



The initial formation of one new carbon–carbon bond followed by a 1,3- or 1,4-hydrogen shift which must occur, leading to the alkylated cyclohexenones, seems to be without precedent in photoaddition reactions.

Irradiation[5a] of 2-cyclohexenone (4.0 g, 0.0416 mole) and norbornadiene (40.0 g, 0.434 mole) in hexane or *t*-butyl alcohol (400 ml) for 2 hr[5b] resulted in the disappearance of 2-cyclohexenone and the formation of products, as was shown by vapor phase[6] and thin layer chromatography and by changes in the infrared spectrum of the mixture. Compounds **1**–**5** (Chart I) were separated by preparative scale gas chromatography and column chromatography on silica gel.

Structures **1**–**4** were assigned on the basis of the following evidence. The compounds were all shown to be 1:1 adducts of norbornadiene and cyclohexenone by their mass spectra, which had parent peaks at *m/e* 188. 3-Nortricyclylcyclohexenone (**1**) had $\lambda_{\max}^{\text{hexane}}$ 229 mμ (log ϵ 4.19); n–π* maxima at 338, 352, and 368 mμ (log ϵ 1.53, 1.38, and 0.95, respectively); strong infrared bands at 6.00, 6.15, and 12.35 μ (doublet), the last showing that the nortricyclene system was present.[7] The nmr spectrum[8] showed a signal at δ 5.81 (1 H, vinyl, α to carbonyl) and a sharp signal at δ 1.16, apparently due to the nortricyclyl group. Structure **1** was confirmed by synthesis[9] from 3-ethoxycyclohexenone and nortricyclylmagnesium bromide by the method of Woods, *et al.*[10]

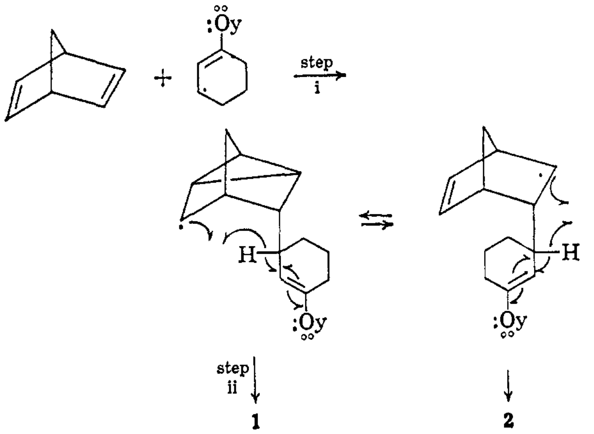
The norbornenyl structure (**2**) had ultraviolet absorption very similar to **1**; the infrared also had strong bands at 6.00 and 6.15 μ, but showed strong absorption due to the norbornene double bond at 14.20 μ.[11] The nmr spectrum showed peaks at δ 5.70 (1 H, singlet, vinyl, α to carbonyl) and 6.11 (2 H, triplet, norbornene vinyl). It was not possible to determine from the nmr spectrum whether this compound had the *exo* or *endo* configuration.[12]

The 2-substituted isomers are difficult to isolate,[13] but infrared spectra characterized **3** as the nortricyclene derivative (12.40 μ) and **4** as a norbornene (14.20 μ). In the nmr the vinyl proton of the enone system appeared at δ 6.63 (1 H, singlet, β to carbonyl), showing that the cyclohexenone was 2-substituted.

It is reasonable to consider the formation of these alkylated cyclohexenones as occurring in two steps: (i) attack of excited cyclohexenone on ground-state diene, with formation of a carbon–carbon bond, and (ii) a hydrogen-transfer process.

Such a mechanism is depicted in electronic detail[14] in Chart II. Evidence has been produced that the first excited state of 2,5-cyclohexadienones and enones has odd electron character[15,16] and that this state is very probably the n–π* triplet.[17] We are considering step i as resembling a free-radical addition;[18] the predomi-

Chart II



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(3) (a) A. Cox, P. deMayo, and R. W. Yip, *J. Am. Chem. Soc.*, 88, 1043 (1966); H. D. Scharf and F. Korte, *Ber.*, **99**, 1299 (1966).

(4) O. L. Chapman, A. A. Griswold, E. Hoganson, G. Lenz, and J. Reasoner, *Pure Appl. Chem.*, **9**, 585 (1964).

(5) (a) The photolysis was carried out in a conventional quartz immersion well, under purified nitrogen, using a Hanovia Type L, 450-w lamp fitted with a Pyrex sleeve. (b) The product distribution was the same in both solvents, and did not change markedly as the reaction proceeded.

(6) Gas chromatography was carried out on a Varian Aerograph Model 200 instrument; columns used were (i) 0.25 in. × 5 ft 15% FFAP on Chromosorb W; (ii) 0.25 in. × 15 ft 15% FS 1265 on Chromosorb W; these columns gave similar separations at 200°.

(7) G. E. Pollard, *Spectrochim. Acta*, **18**, 837 (1962).

(8) Nmr spectra were measured on a Varian Associates A-60 instrument, in carbon tetrachloride solution, using hexamethyldisiloxane (δ 0.05) as internal standard.

(9) A satisfactory carbon and hydrogen analysis was obtained on this compound.

(10) G. F. Woods, P. H. Griswold, Jr., B. H. Armbrecht, D. I. Blumenthal, and R. Plapinger, *J. Am. Chem. Soc.*, 71, 2028 (1949).

(11) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 48; (b) L. Kaplan, H. Kwart, and P. von R. Schleyer, *J. Am. Chem. Soc.*, **82**, 2341 (1960).

(12) The spectrum was complicated by the cyclohexenone moiety; we are conducting chemical experiments to allow an assignment of stereochemistry.

(13) Separation was achieved by gas chromatography on a SE 30, 0.25 in. × 5 ft column at 150°.

(14) The ·, °, y notation is explained by H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(15) H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *J. Am. Chem. Soc.*, **87**, 1138, (1965).

(16) D. I. Schuster and D. J. Patel, *ibid.*, **87**, 2515 (1965).

(17) H. E. Zimmerman, J. J. McCullough, and G. A. Zimmerman, unpublished results, quoted in H. E. Zimmerman, *Pure Appl. Chem.*, **9**, 493, (1964).

(18) It is possible that a complex between ground-state diene and excited cyclohexenone is formed prior to σ-bond formation; such a species was postulated by Corey and co-workers in ref 2a.

nance of 3-alkylated products can then be understood, since the n-π^* state has greatest odd electron density at the 3 position.[19] The major pathway for step ii involves a 1,4-hydrogen transfer leading to **1**, a process which has been reported for diradical systems.[20,21] The ratio of **1** to **2** is explicable in terms of strain in the transition state for hydrogen transfer, a 1,4 process being more rapid than the corresponding 1,3.[22]

We are presently investigating mechanistic aspects of this alkylation reaction.

Acknowledgment. We wish to thank the National Research Council of Canada for financial support of this work.

(19) The coefficient of π_3^* (HMO) at C_3 is at least three times that at C_2 for acrolein-like systems. See, *e.g.*, C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965, p 227.

(20) (a) A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, **31**, 853 (1959); **33**, 1882 (1960); (b) 1,4-hydrogen shifts occur in the photolysis of cyclopentanone: R. Srinivasan, *J. Am. Chem. Soc.*, **81**, 1546 (1959).

(21) A referee has pointed out that since 1,4 ionic hydrogen shifts have not been reported, this argues against a zwitterionic intermediate undergoing step ii.

(22) The 1:1 ratio of **3** and **4** may be a result of their formation from a highly reactive intermediate, with corresponding loss in selectivity.

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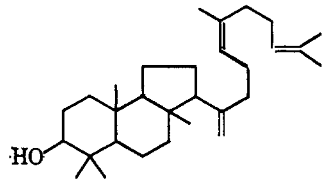
Received September 24, 1966

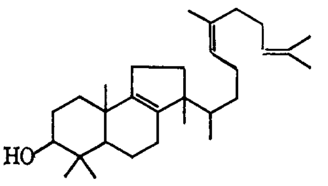
Nonenzymic Laboratory Cyclization of Squalene 2,3-Oxide

Sir:

In view of the utilization of squalene 2,3-oxide (I) in the biosynthesis of lanosterol and cholesterol,[1] the behavior of this new transformation product in nonenzymic cyclizations becomes of more than routine interest, particularly since such chemistry may help identify the molecular areas of enzymatic importance. Herein we describe the preparation and characterization of the tricyclic substances IIa and IIb, produced from epoxide I under mildly acidic, laboratory conditions.



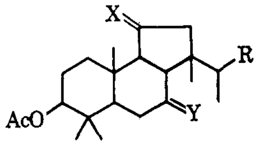
IIa



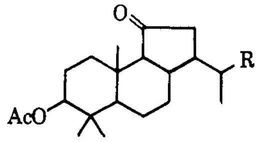
IIb

Squalene 2,3-oxide was obtained from squalene[2] by the selective terminal oxidation method, as previously described.[1,3] Cyclization of I was carried out by means of 0.2 mole of stannic chloride in benzene at 10° for 5 min. In addition to hydrocarbon, some ketonic material, and a product apparently of the previously observed bicyclic type,[4] there were generated in comparatively major amounts two tricyclic components, separated from congeners by chromatography over silica gel–silver nitrate and silica gel–water.

Although in itself an oil, the alcohol IIb formed a crystalline 3,5-dinitrobenzoate (mp 151–153°). On catalytic reduction the acetate of alcohol IIb provided, after chromatography, pure (tlc) tetrahydroacetate (IIIa, X = Y = H_2).[5] Chromium trioxide–acetic acid[6] oxidation of the latter gave rise to ketones IIIb (X = O, Y = H_2)[5] and IIIc (X = H_2, Y = O),[5] separable by chromatography. Lithium–ammonia reduction of IIIb yielded saturated keto acetate IV. The ultraviolet and infrared spectral behavior of the ketonic functions in IIIb ($\nu_{max}^{CCl_4}$ 1690 cm^{-1}; λ_{max}^{EtOH} 240 mμ (ϵ 10,000)), IIIc ($\nu_{max}^{CCl_4}$ 1665 cm^{-1}; λ_{max}^{EtOH} 253 mμ (ϵ 7000)), and IV ($\nu_{max}^{CCl_4}$ 1725 cm^{-1}; λ_{max}^{EtOH} 240 mμ (ϵ 100)) denoted the designated size of the ketonic rings.



III



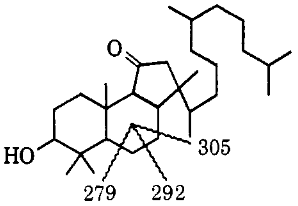
IV

R = $(CH_2)_3CH(CH_3)(CH_2)_3CH(CH_3)_2$

Conclusive evidence for the assigned structures was found by mass spectral means. The mass spectrum of IIIa shows the expected molecular ion at *m/e* 472 (mol wt 472.77). Loss of the side chain gives rise to the major fragment at *m/e* 289. The loss of acetic acid, followed by the retro-Diels–Alder fragmentation in the A ring, results in two major ions at *m/e* 229 and 147.

The two unsaturated ketones IIIb and IIIc have molecular ions at *m/e* 486, the molecular ion of IIIb being more intense than that of IIIa. Cleavage of the side chain leads to major fragmentation in both cases. In IIIb this occurs at *m/e* 304, while in IIIc a hydrogen migration takes place, giving an ion at *m/e* 303. Loss of acetic acid from the major fragment occurs in both cases giving ions at *m/e* 244 and 243, respectively.

The saturated ketone IV has the expected molecular ion at *m/e* 446. It shows the fragmentation pattern characteristic of 11-keto steroids[7] and gives rise to three major fragments at *m/e* 305, 292, and 279. Cleavage of the side chain, followed by loss of water, accounts for the remaining major fragments at *m/e* 263 and 245. These mass spectral data are completely consistent with the assigned structures and are incompatible with all other possibilities. The second tricyclic alcohol, IIa, has been studied less thoroughly, but by similar spectral means its constitution was clarified. For example,



(1) E. E. van Tamelen, J. D. Willett, R. B. Clayton, and K. E. Lord, *J. Am. Chem. Soc.*, **88**, 4752 (1966).

(2) Squalene was purified by sequential (a) chromatography on active silica gel, (b) chromatography on alumina, (c) distillation through a Vigreaux column, and (d) conversion to the thiourea complex, followed by regeneration with aqueous petroleum ether.

(3) E. E. van Tamelen and T. J. Curphey, *Tetrahedron Letters*, No. 3, 121 (1962).

(4) E. E. van Tamelen, A. Storni, E. J. Hessler, and M. Schwartz, *J. Am. Chem. Soc.*, **85**, 3295 (1963).

(5) Nmr spectral data are consistent with the assigned structure.

(6) L. Ruzicka, E. Rey, and A. C. Muler, *Helv. Chim. Acta*, **27**, 472 (1944).

(7) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. II, Holden-Day Inc., San Francisco, Calif., 1964, p 81.