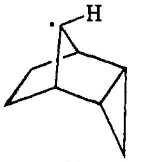
been noted for norbornane[15,16] and norbornene.[17,18] The factors which are responsible for the unique role of the fused cyclopropane unit are presently under investigation.

In sharp contrast to the radical substitution pattern found for *exo*-tricyclooctane **1**, attack of *tert*-butoxy radical on *endo*-tricyclooctane **5** at C-8 occurs to an extent of 93% or greater. Since neither *anti*-8-chloride **6**-Cl nor rearranged **7**-Cl undergoes epimerization or skeletal rearrangement during the reaction conditions or vpc analysis, it seems reasonable to assume that *endo*-**7**-Cl is a primary product, and the question arises as to whether the products are generated *via* a rapid equilibrium of radicals (**10** $\rightleftharpoons$ **11**) or a single delocalized radical **12**. The dilution experiments listed in Table I demonstrate that at high concentrations of chain transfer agent the first formed radical intermediate is trapped before there is much rearrangement to the second radical intermediate, while at low concentrations of *tert*-butyl hypochlorite the reverse is the case. Thus, on this basis, an equilibrium (**10** $\rightleftharpoons$ **11**) is favored over **12**. However, in addition, one must explain the regiospecificity for C-8 abstraction and the stereoselectivity of the radicals leading to C-8 unrearranged (anti:syn ≥ 66:2) and C-2 rearranged (endo:exo > 27:2) products (run 1). It seems clear that the high preference for C-8 abstraction must be due to abstraction of the anti C-8 hydrogen with the generation of a transition state in which the electronegative *tert*-butoxy radical induces some carbonium ion character on the tricyclooctyl moiety. Thus, the evidence suggests trishomocyclopropenyl anchimeric assistance to hydrogen abstraction in the transition state.[19] Once the anti C-8 hydrogen is removed, a localized pyramidal radical similar in structure to **10** might be formed. A combination of competition of chain transfer with inversion and greater steric access to the anti side (LiAlH$_4$ reduction of *endo*-tricyclo[3.2.1.0^{2,4}]octan-8-one gives **6**-OH–**8**-OH in a ratio of 33:67)[8] might explain the stereoselectivity. However, steric access to the C-2 position of radical **11** would be expected to be highly biased toward exo approach (LiAlH$_4$ reduction of tricyclo[3.3.0.0^{4,6}]-octan-2-one yields entirely *endo*-2-alcohol). Thus, intermediate **10** rearranges to a second intermediate, which, although reasonably well represented by structure **11**, might possess some degree of transannular interaction of the cyclopropane bond with the radical center, hence protecting the exo face from attack.

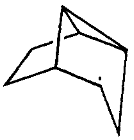
Table I. Reaction of *tert*-Butyl Hypochlorite with **5** in CCl$_4$ at 40°

Run	Concn of **5**, *m*	Concn of *t*-BuOCl, *m*	Product composition, % 6-Cl[a]	7-Cl[a]	A[a]	B[a]
1	1.56	0.68	66	27	5	2
2	1.56	0.49	63	28	6	3
3	1.56	0.26	32	41	11	16
4	0.73	0.18	11	56	15	18

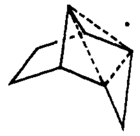
[a] ±2%.



10



11



12

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Received January 27, 1972

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[15] E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

[16] V. R. Koch and G. J. Gleicher, *J. Amer. Chem. Soc.*, **93**, 1657 (1971).

[17] E. Toebler, D. E. Battin, and D. J. Foster, *J. Org. Chem.*, **29**, 2834 (1964).

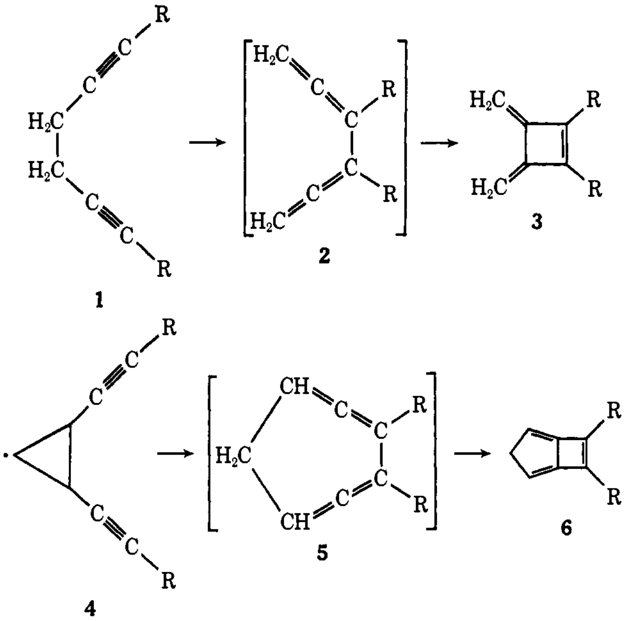
[18] M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965).

[19] An estimate of anchimeric assistance based on the relative rates for hydrogen abstraction in *tert*-butyl hypochlorite chlorination of **5** and norbornane gives $k_{5\text{ at C-8}}/k_{\text{norbornane at C-7}} \geq 110$ at 40°, assuming all the C-8 abstraction on tricyclooctane **5** is anti; T. D. Ziebarth, unpublished observation.

Independent Mechanisms in the Thermal Rearrangement of Mono- and Bicylic 3,4-Bismethylenecyclobutene Derivatives

Sir:

Thermolysis of 1,5-hexadiynes at moderate temperature produces 3,4-bismethylenecyclobutene derivatives.[1,2] For example, compounds **1** and **4** rearrange at 250° to trienes **3** and **6**, presumably *via* intermediate diallenes[3] **2** and **5**.



a, R = H
b, R = D

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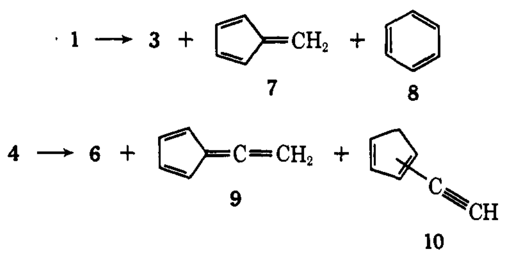
[1] (a) W. D. Huntsman and H. J. Wristers, *J. Amer. Chem. Soc.*, **85**, 3308 (1963); (b) W. D. Huntsman and H. J. Wristers, *ibid.*, **89**, 342 (1967); (c) R. Criegee and R. Huber, *Chem. Ber.*, 103, 1855 (1970); (d) H. A. Brune, *Tetrahedron*, 24, 4861 (1968); (e) H. A. Brune, H. P. Wolff, and H. Huether, *ibid.*, 25, 1089 (1969); (f) H. A. Brune and H. P. Wolff, *ibid.*, 27, 3949 (1971); (g) A. Viola and J. H. MacMillan, Abstracts, 159th National Meeting of the American Chemical Society, Houston, Tex., Feb 1970, No. ORGN 50.

[2] M. B. D'Amore and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 5694 (1969).

[3] (a) H. Hopf, *Chem. Ber.*, **104**, 1499 (1971); (b) H. Hopf, *ibid.*, **104**, 3087 (1971).

At higher temperatures, however, diacetylenes **1** and **4** give rise to more complex product mixtures,[4,5] whose mechanism of formation is not well understood. Vacuum flow pyrolysis of **1a** at 620° produces both fulvene (**7**) and benzene (**8**) as well as **3**; depending upon reaction conditions any of these can be made a major constituent of the product mixture.[4] Similarly, *trans*-**4**, when subjected to pyrolysis at high temperature or converted to vibrationally excited **6** at more moderate temperature, leads[5] to fulvenallene (**9**) and a mixture of ethynylcyclopentadienes (**10**) in addition to **6**.

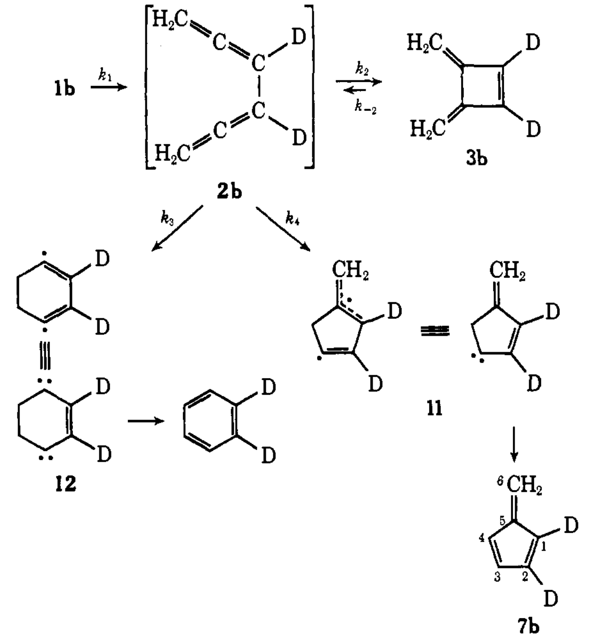


We have now carried out product distribution and labeling studies which provide some insight into the mechanisms of these reactions. Despite the superficial structural similarities implicit in the **1** → **7** and **4** → **9** rearrangements, they take place by strikingly different pathways.

When subjected to flow pyrolysis at 620°, bismethylenecyclobutene (**3**) gave rise to benzene and fulvene[6] in about the same ratio (1:2) as that found on pyrolysis of **1**. However, fulvene required much higher temperatures to rearrange to benzene (>800°). It therefore seems most reasonable that **3** is the only primary product from **1** and both **7** and **8** are formed *via* **3**. We have also subjected dideuterated **1b**[4b] to pyrolysis. Nmr analysis of the product fulvene showed that the 1-H and 2-H resonances were reduced by 50% compared with the perprotio material, while mass spectral analysis showed that the compound contained >95% d_2 species. The product is therefore almost certainly **7b** (Scheme I). Analysis of the dideuterated benzenes was more difficult.[7] We therefore prepared the ortho, meta, and para isomers in pure form[8] and compared gas-phase ir spectra of synthetic mixtures with that of the thermolysis product. By so doing, we were able to show that the material produced from **1b** is a mixture of 93% *o*-, 5% *m*-, and 2% *p*-dideuteriobenzene.

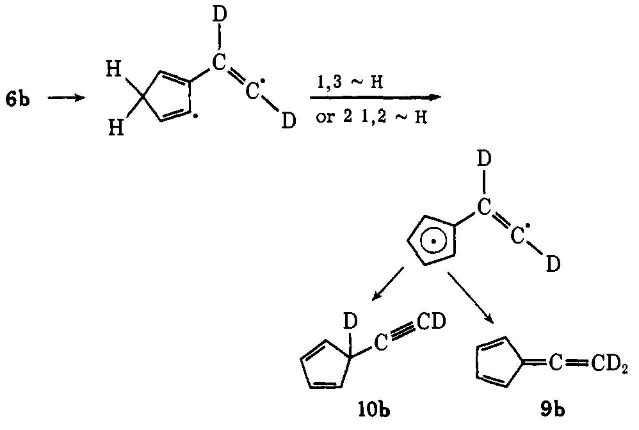
A major pathway consistent with these data is outlined in Scheme I. Allene **2** seems a likely candidate[9] for eventual production of **7** and **8**;[10] k_2 must be greater than k_3 and k_4 at 250°.

Scheme I



High-pressure pyrolysis[5] of *trans*-**4b** at 480° produced **6b**. In contrast to the situation with **1**, rearrangement of **6b** at 580° led to fulvenallene with deuterium predominantly (87%) in the *terminal methylene* position rather than in the ring.[11] This is accounted for by the mechanism outlined in Scheme II. Apparently high strain energy both promotes cyclobutene ring cleavage in **6** and makes return of **6** to cyclic diallene **5** more difficult. However, a minor pathway still exists

Scheme II



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(4) (a) M. L. Heffernan and A. J. Jones, *J. Chem. Soc. D*, 120 (1966); (b) B. A. W. Coller, M. C. Heffernan, and A. J. Jones, *Aust. J. Chem.*, 21, 1807 (1968); (c) J. E. Kent and A. J. Jones, *ibid.*, 23, 1059 (1970).

(5) M. B. D'Amore, R. G. Bergman, M. E. Kent, and E. Hedaya, *J. Chem. Soc., Chem. Commun.*, 49 (1972).

(6) (a) Pyrolysis was carried out in both the flow apparatus[5] and static system[6b] described earlier; (b) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, 91, 7411 (1969); (c) benzene–fulvene ratios were somewhat variable in the flow system at high temperatures but appeared to be essentially independent of surface effects (determined by carrying out pyrolyses in systems both empty and packed with short quartz tubes).

(7) (a) F. A. Miller, *J. Chem. Phys.*, 14, 292 (1946); (b) C. R. Bailey, S. C. Carson, R. R. Gordon, and C. K. Ingold, *J. Chem. Soc.*, 288 (1946); (c) H. Spedding and D. H. Whiffen, *Proc. Roy. Soc. (London), Ser. A*, 238, 245 (1956); (d) S. Brodersen and A. Langseth, *Mat. Fys. Dan. Vid. Selsk.*, 1 (7), 1 (1959).

(8) Synthesis of each isomer was accomplished by preparing the mono-Grignard reagent of the approprirate dibromobenzene, quenching with D_2O, and then repeating the process on the monodeuteriomonobromobenzene so produced; *cf.* L. H. P. Weldon and C. L. Wilson, *J. Chem. Soc.*, 235 (1946).

(9) (a) It is of course possible that carbene diradical **11** is generated directly from **3b**. However, we have calculated the heats of formation of both **3** and **2** using group equivalent techniques;[9b] this calculation indicates that **2** is only 23 kcal/mol higher in enthalpy than **3**. Thus, **2** can be generated repeatedly during the pyrolysis of **3**, making it a likely intermediate in the formation of benzene and fulvene. (b) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

(10) (a) At present we have no information concerning the mechanism of formation of smaller amounts of *m*- and *p*-dideuteriobenzenes in this reaction. One possibility is that intermediate **12** undergoes some double 1,3-hydrogen insertion to give benzvalene,[10b] which could then undergo a degenerate vinylcyclopropane-type deuterium-scrambling rearrangement before ring opening to benzene. (b) T. J. Katz, T. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, 93, 3782 (1971).

(11) (a) Determined by nmr analysis of both fulvenallene itself and its tetracyanoethylene cycloadduct.[11b] (b) E. Hedaya and M. E. Kent, *J. Amer. Chem. Soc.*, 92, 2147 (1970); for trimethylfulvene adducts, *cf.* W. B. Smith, S. Biesemeier, and D. L. Deavenport, *J. Org. Chem.*, 36, 2853 (1971).

which ultimately produces 13% ring-deuterated fulvenallene. Most interestingly, pyrolysis of **4b** at moderate temperature (480°) and low pressure (0.02 Torr) gave **9b** with a decreased amount (77%) of deuterium in the methylene position.[12] This decrease in selectivity between the two pathways for rearrangement provides additional evidence[5] that under such conditions **6** is formed initially with vibrational energy greatly in excess of both its own ground state and the threshold for rearrangement to **9**.

Acknowledgments. We are grateful for financial support of this work from the Petroleum Research Fund of the American Chemical Society and from the National Science Foundation.

(12) (a) Nmr analysis of recovered **6b** from a pyrolysis of **6b** at 590° showed no detectable hydrogen at C_6 and C_7, under conditions where >5% would have been readily observed; (b) integration of the nmr spectra of **9b** before and after thermolysis at 590° showed no significant decrease in deuterium content in the terminal methylene position.

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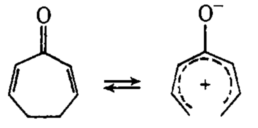
Photochemistry of 2,6-Cycloheptadienones in Strong Acid. A Protonated Version of Cycloheptadienone–Oxyheptatrienyl Transformation

Sir:

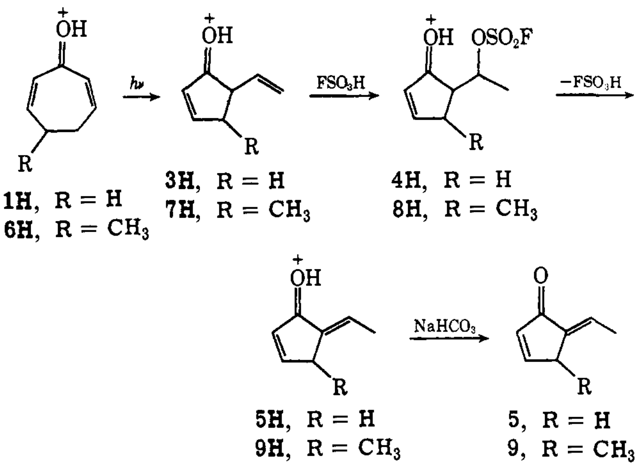
The interconversion of the cyclic dienone **1** and the open-chain dipolar ion **2** (eq 1), although without precedent, has been of theoretical interest in connection with the cyclopropanone–oxyallyl relationship.[1] This paper describes a new photochemical rearrangement of **1** in strong acid medium, which involves the protonated version of eq 1 as the key step.

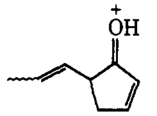


1 **2** (1)

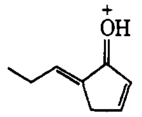
Extraction of **1** with FSO_3H from CCl_4 solution gave the protonated species **1H**,[2,3] which was stable below room temperature and remained unchanged after standing in the dark for extended periods. When the solution, placed in a Pyrex nmr tube, was irradiated at −78° with a 200-W high-pressure Hg arc, a clean rearrangement took place, and after 24-hr irradiation **3H** was produced as the sole species observable by nmr (Scheme I).[4] Warming the photolysate slowly to room temperature led to the formation of the more stable isomer **5H** in addition to some polymeric substances. The isomerization proved to occur, at least mainly, *via* the fluorosulfonate **4H**, which showed characteristic nmr signals at δ 2.10 (d, J = 6.5 Hz, CH_3) and 5.8–6.2 (m, $CHOSO_2F$). Careful neutralization of the acid solution containing **3H** or **5H** with $NaHCO_3$–ether at 0° gave the unprotonated ketone **5**, which upon dissolving in FSO_3H regenerated **5H**.[5] Catalytic hydrogenation of **5** over 10% Pd/C (in C_2H_5OH, 25°) gave 2-ethylcyclopentanone. Photolysis of the methylated derivative **6H** under comparable conditions led to the selective formation of **7H**. Subsequent thermal isomerization afforded **9H**.[6] No signs of the production of the isomer **10H** or **11H** were observed.

Scheme I





10H



11H

The course of the photoreaction was unaffected by the wavelength of incident light (Pyrex (>280 nm), aqueous $CuSO_4$ (>350 nm), or I_2 in CCl_4 (>370 nm) as filter) or reaction temperature (−78 to 0° range).[7]

The photoinduced rearrangement could be rationalized by a stepwise mechanism involving as the key step a protonated version of eq 1 (Scheme II). The protonated dienone **12H** is considered to be in resonance

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(1) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(2) The symbol **H** in the formula number refers to an oxygen-protonated ketone throughout this paper.

(3) Chemical shifts of nmr are expressed in parts per million downfield from TMS as external standard in FSO_3H and internal standard in CCl_4: nmr of **1H** δ 3.17 (br s, CH_2), 7.05 (d, J = 12 Hz, COC*H*=CH), and 8.17 (br d, COCH=C*H*); uv (FSO_3H) 267 (log ϵ 3.95) and 335 sh nm (3.55).

(4) Nmr δ 3.5–4.7 (m, allylic CH_2 and CH), 5.90 (br s, vinyl), 7.30 (br d, COC*H*=CH), and 9.50 (br d, COCH=C*H*).

(5) Nmr of **5H** δ 2.61 (d, J = 7.5 Hz, CH_3), 4.00 (br s, CH_2), 7.29 (d of t, J = 5.2 and 2.1 Hz, COC*H*=CH), 8.22 (q, =C*H*CH_3), and 8.98 (m, COCH=C*H*). Ketone **5**: ir (CCl_4) 1700 (C=O) and 1660 cm^{-1} (C=C); uv (C_2H_5OH) 244 nm (log ϵ 3.93); mass (70 eV) *m/e* 108 (M^+); nmr (CCl_4) δ 1.86 (d, J = 7.5 Hz, CH_3), 3.15 (br s, CH_2), 6.25 (d of t, J = 6 and 2 Hz, COC*H*=CH), 6.50 (q, J = 7.5 Hz, =C*H*CH_3), and 7.45 (m, COCH=C*H*). The stereochemical assignment of the =$CHCH_3$ moiety rested on the chemical shift of the signal due to the olefinic proton: the trans olefinic proton was reported to give a signal at δ ~6.6 and the cis olefinic proton at δ ~5.7 [J. E. Dubois and M. Dubois, *C. R. Acad. Sci., Ser. C*, **256**, 715 (1963); see also, R. A. J. Smith and T. A. Spencer, *J. Org. Chem.*, **35**, 3220 (1970)].

(6) Nmr of **6H** δ 1.57 (d, J = 7.5 Hz, CH_3), 2.9–3.6 (m, allylic CH_2 and CH), 6.8–7.2 (m, COC*H*=CH), and 7.8–8.4 (m, COCH=C*H*). Nmr of **7H** (stereochemistry unknown) δ 1.50 (br d, CH_3), 3.7–4.5 (m, allylic CH), 5.82 (br s, vinyl), 7.20 (br d, COC*H*=CH), and 9.30 (br d, COCH=C*H*). Nmr of **9H** δ 1.73 (d, J = 7.5 Hz, >CHC*H*$_3$), 2.61 (d, J = 7.5 Hz, =CHC*H*$_3$), 4.25 (br q, >C*H*CH_3), 7.21 (d of d, J = 5.2 and 1.5 Hz, COC*H*=CH), 8.19 (q, J = 7.5 Hz, =C*H*CH_3), 8.92 (br d, COCH=C*H*). Ketone **9** showed the following spectral characteristics: ir (CCl_4) 1703 (C=O) and 1655 cm^{-1} (C=C); uv (C_2H_5OH) 244 nm (log ϵ 3.92); mass (70 eV) *m/e* 122 (M^+); nmr (CCl_4) δ 1.29 (d, J = 7.5 Hz, >CHC*H*$_3$), 1.90 (d, J = 7.5 Hz, =CHC*H*$_3$), 3.2–3.7 (m, >C*H*CH_3), 6.17 (d of d, J = 6.0 and 1.5 Hz, COC*H*=CH), 6.48 (q, J = 7.5 Hz, =C*H*CH_3), and 7.33 (d of d, J = 6.0 and 2.5 Hz, COCH=C*H*).

(7) The mode of the present reaction exhibits a striking contrast to those of the previously discovered photoreactions of **1** [H. Nozaki, M. Kurita, and R. Noyori, *Tetrahedron Lett.*, 3635 (1968)].