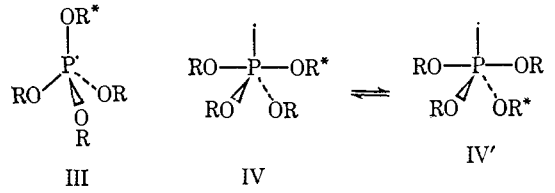

III IV IV′

Previous studies in this laboratory[9] have shown that oxygen transfer from alkoxy radicals to cyclic six-membered ring phosphites and optically active phosphines occurs with retention of configuration at phosphorus. Pseudorotation of phosphoranyl radical intermediates might be expected to lead to some inverted product in these oxidations. The specificity observed could result from reactions involving phosphoranyl intermediates which are either short lived or configurationally stable. The configuration, configurational stability, and lifetime of phosphoranyl radicals probably depend on the nature of the substituents on phosphorus and the configurational requirements imposed by the substituents (*e.g.*, whether the substituents are part of a ring structure). These effects are currently under investigation in our laboratory.

Acknowledgment. This work was supported by a grant from the National Science Foundation (GP-8363) which is gratefully acknowledged. We thank Professor Hans Rilling, Department of Biochemistry, University of Utah, for assistance with the counting experiments.

(9) W. G. Bentrude, J. H. Hargis, and P. E. Rusek, Jr., *Chem. Commun.*, 296 (1969).

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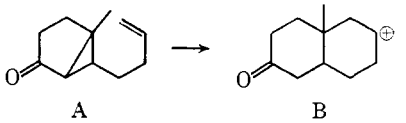
Olefin Participation in the Acid-Catalyzed Opening of Acylcyclopropanes. III. Formation of the Bicyclo[2.2.1]heptane System

Sir:

We have previously shown[1,2] that acylcyclopropanes can undergo acid-catalyzed transformation with participation of a suitably disposed olefinic center and formation of a new ring (*cf.* A → B). The cyclohexyl cation

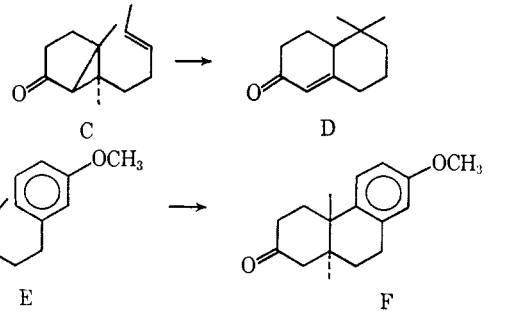


A B

generated in the process has been shown to be capable of rearrangement (C → D)[1] or, in a particularly favorable case, of simple proton loss (E → F).[2] We now report on a case in which the cation is efficiently trapped by the *enol* generated *via* the acylcyclopropane opening.

The *endo*-bicyclo[3.1.0]hexanone I was synthesized from the dienic acetal II[3] by the usual sequence *via* the aldehyde III, R = H [λ (film) 3.65, 5.78 μ; δ ($CDCl_3$) 9.69 (s, 1, H)], acid III, R = OH (silver oxide oxidation)

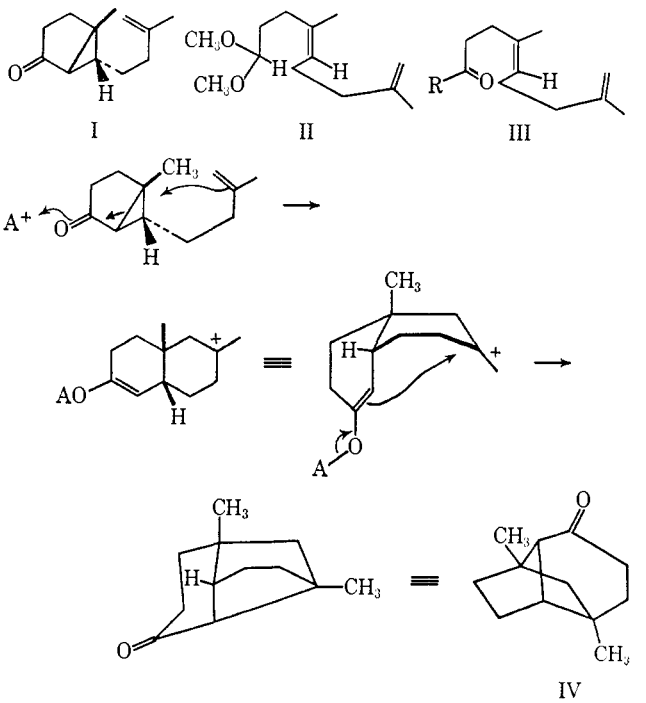
(1) G. Stork and M. Marx, *J. Am. Chem. Soc.*, 91, 2371 (1969).
(2) G. Stork and M. Gregson, *ibid.*, 91, 2373 (1969).
(3) G. Stork, P. A. Grieco, and M. Gregson, *Tetrahedron Letters*, in press.



C D E F

[λ (film) 5.84 μ; δ ($CDCl_3$) 11.20 (s, 1 H)], acid chloride III, R = Cl (sodium salt and oxalyl chloride) [bp 78–84° (~0.3 mm); (film) 5.53 μ], and diazo ketone III, R = CHN_2 [λ (film) 3.28, 4.74, 6.08 μ]. The latter then (5-hr reflux with copper bronze in cyclohexane) gave the desired I.[4] This was homogeneous by glpc (DEGS, 180°) and had λ (film) 3.28, 5.80, 6.08, 11.3 μ; δ ($CDCl_3$) 1.35 (s, 1 H) and 4.76 (s, broad, 2 H). A pure sample of 300 mg of I, obtained by preparative glpc (FFAP, 210°), was cyclized by keeping its solution in 8 ml of benzene and 2 ml of stannic chloride for 12 hr at room temperature. The major product (70% yield) was isolated by preparative glpc (DEGS, 150°). The new ketone IV, 2,4-dinitrophenylhydrazone mp 160–161° (*Anal.* Found: C, 60.07; H, 6.27), had properties in agreement with the assigned structure: λ (film) 5.85 μ; δ 1.05 (s, 3 H), 1.13 (s, 3 H), no olefinic protons; molecular ion at *m/e* 178.

It is clear that the *concerted*[5] participation of the terminal olefin of I leads to a geometry in which the enol is in a position to trap the resulting carbonium ion, as shown below. The possibility that ketonization might have intervened, and that a different system could have resulted *via* the other enol, was ruled out by show-



I II III IV

(4) The same sequence starting with the other geometric isomer of II gave a different cyclopropyl ketone, with an *exo* substituent, as expected (*cf.* ref 2).
(5) The concerted nature of the cyclization follows from unpublished experiments by Gregson which show that the *exo* isomer of I gives no IV under these cyclization conditions.

ing that the mass spectrum of the cyclic dioxolane from IV showed, in addition to the molecular ion at *m/e* 222, the base peak at *m/e* 99 which demonstrates the presence of the $CH_2CH_2C{=}O$ unit in the ketone IV.[6]

This efficient cyclization should be a fairly general route to various 7-acylbicyclo[2.2.1]heptanes.

Acknowledgment. The support of this work by the National Science Foundation is gratefully acknowledged.

(6) *Cf.* H. Budzikiewicz, C. Djerassi, and D. H. Williams "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 54.

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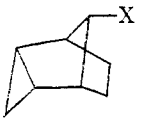
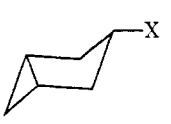
Remote Participation of a Cyclopropyl Ring in Solvolysis of β-(Tricyclo[3.2.1.0^{2,4}]oct-*syn*-8-yl)ethyl *p*-Bromobenzenesulfonate

Sir:

Much attention has been focused on the stereoelectronic effect of a remote cyclopropyl ring on a developing electron-deficient center because of the widely ranging efficiency in assistance.[1] An example of the high efficiency is perhaps our observation that the *endo-anti*-tricyclo[3.2.1.0^{2,4}]octan-8-yl derivative **1** solvolyzes 10^8 times faster than a model, *cis*-3-bicyclo[3.1.0]hexyl **2**.[1j,k] Another study by us, the solvolysis of β-(*syn*-9-



1



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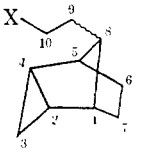
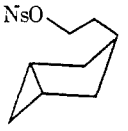


3a, *syn*, X = OBs
b, *syn*, X = OH
4a, *anti*, X = OBs
b, *anti*, X = OH



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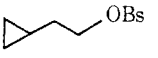
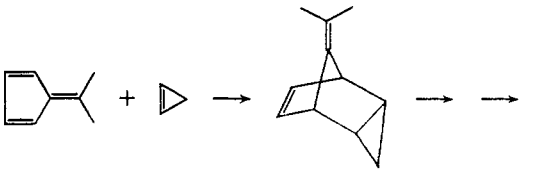


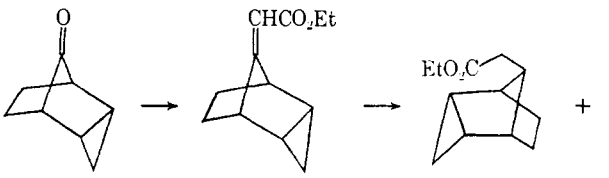
6

benzonorbornenyl)ethyl brosylate, has provided important evidence for remote aryl participation.[2] As an extension of the related studies, we report here the solvolyses of β-(tricyclo[3.2.1.0^{2,4}]oct-*syn*-8-yl)ethyl brosylate (**3a**) and its *anti* isomer (**4a**). While our investigation was in progress, the solvolyses of related systems **5** and **6** were reported and unimportant participation of the cyclopropyl ring was suggested.[1m-o] Nonetheless, the present results indicate definitely participation for a far reaction center.

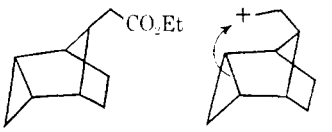
Introduction of gaseous cyclopropene into a solution of 6,6-dimethylfulvene in *n*-pentane led to the *endo* adduct **7**, bp 194–198°, $n^{23.0}$D 1.5121.[3,4] Catalytic hydrogenation of **7** with 1 equiv of hydrogen followed by ozonolysis afforded the saturated ketone **8** which was identical with that obtained previously from cyclopentadienone diethyl ketal and cyclopropene.[1j] The



7



8 9 10



11 12

Wittig reaction of **8** with carbethoxymethylenetriphenylphosphorane under forced conditions[5] afforded **9**, bp 86–88° (1 mm), $n^{23.0}$D 1.5070, which was converted into a 6:4 mixture of the *syn* ester **10** and the *anti* ester **11** by catalytic hydrogenation. By preparative vpc separtion, **10**, bp 90° (1 mm), $n^{24.0}$D 1.4790, and **11**, bp 91–92° (1 mm), $n^{24.0}$D 1.4796, were obtained in the pure states. These two isomers were transformed by $LiAlH_4$ reduction into the corresponding alcohols **3b** and **4b**. Assignments of the *anti* and *syn* configuration are determined by the fact that the C-9 methylene protons in **3b** (centered at τ 8.06) are markedly deshielded compared to those in **4b** (centered at τ 8.62). The measurements were performed by decoupling of the C-10 methylene protons (for **3b**, τ 6.38, triplet, J = 6.7 Hz; for **4b**, τ 6.51, triplet, J = 7.0 Hz).[6] The brosylates **3a**, $n^{26.5}$D 1.5605, and **4a**, $n^{26.5}$D 1.5629, were obtained by the usual manner and solvolyzed in 70% aqueous dioxane, acetic acid, and 2,2,2-trifluoroethanol.

The first-order rate constants are set forth in Table I. The acetolysis rate of **4a** is nearly the same as the "unassisted" rate observed for primary brosylates[7] in buffered acetic acid, indicating the unimportance of an inductive effect due to the cyclopropyl in **4a**. The rate ratios of **3a** and **4a** by the factors of 1.08–1.23 in

(1) For examples, (a) S. Winstein, "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 5; (b) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, 30, 2278 (1965); (c) A. K. Colter and R. C. Musso, *ibid.*, 30, 2462 (1965); (d) M. Hanack and H. M. Ensslin, *Tetrahedron Lett.*, 4445 (1965); (e) R. R. Sauers and R. W. Ubersax, *J. Org. Chem.*, 31, 495 (1966); (f) J. Haywood-Farmer, R. E. Pincock, and J. I. Wells, *Tetrahedron*, 22, 2007 (1966); (g) R. R. Sanors, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, 32, 569 (1967); (h) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967); (i) C. F. Wilcox and R. G. Jesaitis, *ibid.*, 2567 (1967); (j) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, 89, 1953 (1967); (k) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, 89, 1954 (1967); (l) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 955 (1967); (m) G. D. Sargent, *Tetrahedron Lett.*, 2275 (1968); (n) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, 90, 4468 (1968); (o) Y. E. Rhodes and T. Takino, *ibid.*, 90, 4469 (1968).

(2) R. Muneyuki and H. Tanida, *ibid.*, 90, 656 (1968).

(3) This is the first example of cycloaddition of cyclopropene to a fulvene system.

(4) Satisfactory analyses were obtained for all compounds described.

(5) G. Fodor and I. Tomoskozi, *Tetrahedron Lett.*, 579 (1961).

(6) Varian Model HA-100 in CCl_4.

(7) Some examples of the rate are found in ref 2.