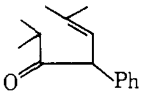
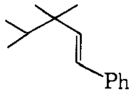
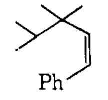
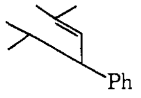
irradiated in ethanol using a mercury source and a Pyrex filter, the isomeric photoproduct IV formed; prolonged irradiation gave the decarbonylation products V–VII.

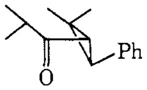

IV


V

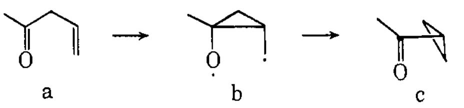

VI


VII

When 1 g of I [I$_c$, $\lambda\lambda_{\max}^{\text{EtOH}}$ 248 nm ($\epsilon$ 9300), 284 nm ($\epsilon$ 47), 292 nm ($\epsilon$ 89); I$_t$, $\lambda\lambda_{\max}^{\text{EtOH}}$ 253 nm ($\epsilon$ 14,950), 285 nm ($\epsilon$ 292), 293 nm ($\epsilon$ 376)] was irradiated in 100 ml of benzene using a Nonex filter ($\lambda$ >310 nm) and 25 ml of acetophenone as a sensitizer ($E_t$ 74), it disappeared at a much slower rate than under direct excitation conditions. After 60 hr all the starting material had been consumed, and a single isomeric photoproduct, *trans*-2,2-dimethyl-3-phenylcyclopropyl isopropyl ketone (VIII), was obtained in 93% yield. Careful monitoring of the course of the photolysis by glpc showed that no other products, such as IV through VII, were ever formed in detectable amounts. The spectral properties of VIII are as follows: nmr ($\delta$, $CCl_4$), 7.00 (5 H, s, phenyl), 2.67 (1 H, sept, $J$ = 7 cps, $-CH-(CH_3)_2$), 2.47 (2 H, q, $\delta_A - \delta_B$ = 0.56 ppm, $J_{AB}$ = 6 cps, *trans*-cyclopropyl), 1.20 (3 H, s, methyl), 1.10 (6 H, $J$ = 7 cps, $-CH-(CH_3)_2$), 1.06 (3 H, s, methyl); ir ($CCl_4$) 1700 cm$^{-1}$; uv max (EtOH) 220 nm ($\epsilon$ 11,700); mass spectrum ($m/e$) 216 (parent ion), 145 (base peak). The rearrangement of I to the cyclopropyl ketone VIII also proceeded when benzophenone ($E_t$ 69) and 1-acetonaphthone ($E_t$ 56) were used as sensitizers.

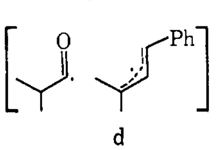

VIII

The direct analogy between the photochemical rearrangement of $\beta,\gamma$-unsaturated ketone I and its 1,4-diene analog II suggests similar mechanisms for the two processes (eq 1 for the ketone): (1) vinyl–carbonyl bridging of a to give biradical b, (2) radical rearrangement and reclosure of b to cyclopropane c.[17]



(1)

It has previously been suggested that rearrangements of $\beta,\gamma$-unsaturated ketones to cyclopropyl-conjugated ketones proceed *via* ketonic $\alpha$ cleavage (see eq 2) to a biradical d which then recloses at the center of the allylic system. From an energetic standpoint, bonding to the central carbon of an allylic system or the rearrangement of an allyl radical to a cyclopropyl radical is the least favorable of the pathways available to radical species d. Closure of this species to give compounds I and IV would be expected to take precedence.[18] The absence of formation of a detectable amount of IV in the sensitized excitation and the effective use of a low energy sensitizer ($E_t$ 56) further indicate that an initial acyl cleavage is not likely and that 2,4 bonding between the carbonyl and vinyl groupings[19] precedes $\alpha$ cleavage.



(2)

The concept of the oxa-di-$\pi$-methane process can be extended to 2,4-cyclohexadien-1-ones which rearrange, photochemically, to a bicyclo[3.1.0]hex-3-en-2-one ring system.[8] Furthermore, initial formation of a 2,4 bond in a variety of 1,4-di-$\pi$ systems appears to be a general phenomenon, a typical example being the ring closure of an acyclic 4,6-heptadien-2-one.[20,20a]

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[17] Normally, all $\beta,\gamma$-unsaturated ketone rearrangements to cyclopropyl ketones stem from the triplet state.[12] Since in any synchronous rearrangement process, the multiplicity of the state should not change, [$\sigma^2 + \pi^2$] cycloaddition mechanisms require that the product be formed in the triplet state. Such is not energetically possible in the rearrangement of I to VIII and thus a stepwise process seems indicated.

[18] O. P. Strausz, P. J. Kozak, G. N. C. Woodall, A. G. Sherwood, and H. E. Gunning, *Can. J. Chem.*, **46**, 1317 (1968).

[19] Formally nonconjugated $\beta,\gamma$-unsaturated ketone systems exhibit remarkable uv, cd, and ord properties, indicating an interaction between the double bond and the carbonyl moiety (see D. E. Bays, R. C. Cookson, and S. MacKenzie, *J. Chem. Soc., B*, 215 (1967), and references cited therein). The concept of 2,4-carbonyl–vinyl bridging in the photochemistry of such systems is in accord with these spectral properties.

[20] J. Meinwald and J. W. Kobzina, *J. Amer. Chem. Soc.*, **91**, 5177 (1969).

[20a] NOTE ADDED IN PROOF. Since the submission of this manuscript, the possibility of vinyl–carbonyl 2,4 bridging has also been suggested by K. Schaffner and coworkers, *Helv. Chim. Acta*, **52**, 2436 (1969).

[21] National Institutes of Health Predoctoral Fellows.

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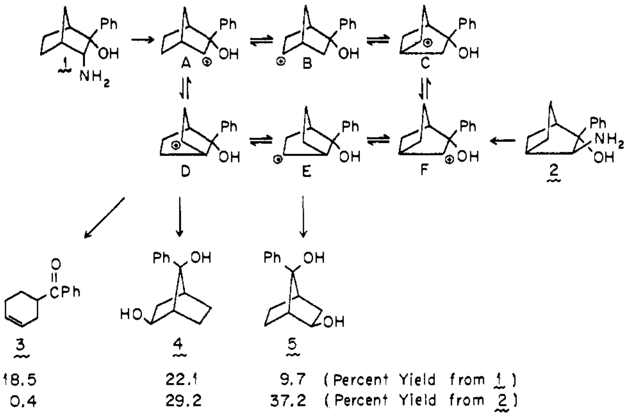
*Received December 22, 1969*

## Anion Control of Stereoselectivity During Deaminations[1]

*Sir:*

We wish to report a striking difference in stereoselectivity exhibited by presumably identical carbonium ions (D in Chart I) which have been indirectly formed during the deaminations of two different reactant amines (**1** and **2**). We tentatively ascribe this stereoselectivity to partial control of product formation by the counter-

**Chart I**



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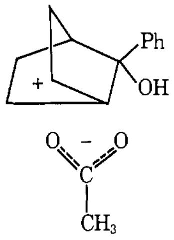
[1] (a) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.; (b) presented in an address to the Gesellschaft Deutscher Chemiker, Ortsverband Süd-Württemberg, Tübingen, May 30, 1969.

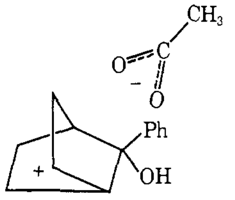
anions which are oriented differently with respect to the carbonium ion.

In 1967 we reported[2] the isolation and identification of eight major products on deamination, in acetic acid–sodium acetate, of 3-*endo*-hydroxy-3-*exo*-phenyl-2-*endo*-bicyclo[2.2.1]heptylamine (**1**). We have now prepared the amine **2** and subjected it to deamination under similar conditions.[3] All of the same products previously isolated[2] except one (the monoacetate of 3-*exo*-phenylbicyclo[2.2.1]heptane-2,3-*cis*-*endo*-diol) were present in the deamination mixture from **2**.[4] The mechanism for the deamination of both amines can be partially described by the loop of carbonium ions depicted in the chart. From the yields of all the products it is clear that whereas products from **1** are formed preferentially through a counterclockwise course, the products from **2** are formed preferentially through a clockwise course (this difference in *direction* of reaction flow is not necessarily important, but could result from the processes A → B and F → C being slow in relation to other processes in the ionic cycle). Experiments with **1** which contained deuterium in the 5,6-*exo* positions and separately in the 2-*exo* position confirm these conclusions, and further demonstrate that ions B and C arise through both clockwise and counterclockwise pathways. There is less than 0.5% recycling of material after one counterclockwise loop. Our experiments with deuterium-containing **1** also tell us that $\Delta^3$-cyclohexenyl phenyl ketone (**3**) comes predominantly from ion D, rather than from the possible precursor (E).[5] In the present communication we report the difference in stereoselectivity exhibited by ion D which, when generated from reactant **1**, yields the monoacetate of **4** and **3** in the ratio of 1.1:1, whereas when formed from **2** it yields these same products in a ratio greater than 70:1. According to current carbonium ion theory[6] the "hot," classical ions A and F on Wagner–Meerwein rearrangement (A → D or F → E) should fall immediately to the nonclassical state, so a difference in potential energy between the two ions D formed from the different reactants can hardly be used to explain these results.

We have shown[7] that the $^{14}$C-labeled counterion (acetoxyl) formed upon thermal decomposition, in acetic acid–sodium acetate solution, of optically active N-acetyl-$^{14}$C-N-nitroso-1,2,2-triphenylethylamine preferentially attacks the carbonium ion from the topside with retention, whereas unlabeled acetoxyl from solvent attacks the same ion preferentially from the backside with inversion. We demonstrated[7] further that the ion pair so formed maintains its integrity through repeated phenyl migration. We propose therefore that the different stereoselectivities exhibited by ion D could be caused by the different positions assumed by the counterions in the two different tight ion pairs. The ion pair resulting from the deamination of **1** should be oriented approximately as shown in structure D-I, whereas the ion pair resulting from deamination of **2** should appear approximately as shown in structure D-II.



D-I



D-II

Not only should the charge distribution in the cations of D-I and D-II differ, but in D-II the acetoxyl counterion is already in position for easy collapse to yield the acetate of diol **4**, and ring opening to give **3** cannot successfully compete. The acetoxyl of D-I is unfavorably placed for ion-pair collapse, however, so the reacting anion must come from the solvent, thus allowing ring opening to **3** to successfully compete with the formation of **4**. Goering[8] has demonstrated very recently that the tosylate anion formed on acetolysis of *syn*-7-chloro-2-*exo*-norbornyl tosylate can undergo an apparently facile 6,2 shift before internal return to form *anti*-7-chloro-2-*exo*-norbornyl tosylate, and we have confirmed this result with an isotopic experiment.[9] In our earlier work[7] we observed a similar phenomenon—although to an overall extent of only about 3% of the reaction—and offered an explanation very much like that now given by Goering.[8]

Since the two reactants **1** and **2** seem incapable of producing the type of "twisted" ion proposed by Berson[10] to explain his "Erinnerungseffekte," it now seems clear that "twisted" ions do not satisfactorily explain all such effects.

**Acknowledgment.** We wish to thank Professor Michael Hanack, of the University, Tübingen, for several stimulating discussions of the present work. We also thank Dr. B. M. Benjamin, of Oak Ridge National Laboratory, for assistance with the nmr spectra.

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[2] C. J. Collins, V. F. Raaen, B. M. Benjamin, and I. T. Glover, *J. Amer. Chem. Soc.*, **89**, 3940 (1967); **89**, 5314 (1967).

[3] The method of synthesis was 3-*endo*-phenylbicyclo[2.2.1]heptanone-2 [C. J. Collins, *et al.*, *ibid.*, **86**, 4913 (1964)] through the Biltz reaction [H. Biltz, *Ber.*, **32**, 650 (1899)] to 3-*exo*-hydroxy-3-phenylbicyclo[2.2.1]heptanone-2. The latter compound was converted to the oxime which was reduced with lithium aluminum hydride to give the amine **2**. The overall yield of pure product was very low (about 1%). C and H analyses and nmr spectra of all compounds are consistent with the assigned structures.

[4] The yields previously reported[2] were determined by isolation of each product after liquid column chromatography, and are in good agreement with the new determinations (glpc and isotope dilution measurements).

[5] This conclusion follows since 1, containing a 2-*exo*-deuterium, yields mostly 4-deuterio-$\Delta^3$-cyclohexenyl phenyl ketone, and 5,6-di-*exo*-dideuterio-1 yields ketone 3 containing deuterium only in the 5 and 6 positions of the cyclohexenyl group. From these data a third pathway (see structure B in ref 2) cannot make a major contribution to the production of 3.

[6] P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965. See particularly the commentary on p 463.

[7] C. J. Collins and J. B. Christie, *J. Amer. Chem. Soc.*, **82**, 1255 (1960); C. J. Collins, J. B. Christie, and V. F. Raaen, *ibid.*, **83**, 4267 (1961).

[8] H. J. Goering and M. J. Degani, *ibid.*, **91**, 4506 (1969).

[9] C. E. Harding, unpublished work.

[10] J. A. Berson, *Angew. Chem.*, **80**, 765 (1968).

[11] Predoctoral Fellow from the University of Tennessee. M. D. E. acknowledges financial support of the Oak Ridge Associated Universities. This paper was taken in part from the Ph.D. dissertation of Michael D. Eckart.

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