degenerate Cope process,[6] renders the individual CH groups in sets of barbaralyl positions (3, 7, 9) and (1, 2, 4, 5, 6, 8) equivalent. Leakage—mixing of these two sets of positions—occurs practically not at all in the experiments described here. Somewhat more leakage was found earlier during solvolysis of labeled 9-barbaralyl tosylate (IV, R = D, X = OTs):[2] 7% in 80% acetone and 26% during acetolysis. Such leakage may involve the intermediacy of the bicyclononatrienyl cation (I), formed slowly from II.

It is tempting to ascribe the apparent instability of the bicyclo[3.2.2]nona-2,6,8-trien-4-yl cation (I) to "antibicycloaromaticity."[3] However, this cation may be destabilized by the ring strain factors present in the covalent ion precursors and also by the adverse electron-withdrawing inductive effect of the two nonallylic double bonds. These factors, coupled with a favorable mechanistic pathway for conversion of V directly to II, may account for the results we have observed. We continue efforts to find unambiguous evidence for "antibicycloaromaticity" in cation I.

Acknowledgments. This work was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the Petroleum Research Fund, administered by the American Chemical Society. We thank Professor J. B. Grutzner for an exchange of information.[8]

(9) National Institutes of Health Postdoctoral Fellow, 1969–1970.

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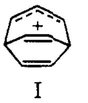
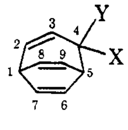
Received December 22, 1969

Bicycloaromaticity. The Stability and Rearrangement of the Bicyclo[3.2.2]nonatrienyl Cation[1]

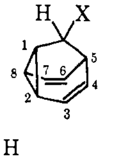
Sir:

According to the theory proposed by Goldstein,[2] the bicyclo[3.2.2]nonatrienyl cation, I, should be "destabilized and antibicycloaromatic." Evidence has been presented[3] that this system undergoes a facile rearrangement to yield barbaralyl products. We now wish to report results to show that this behavior cannot be attributed to the inherent destabilization of I, but is due to the availability of a low-energy route for its conversion to the energetically favored barbaralyl system III. Data will be presented which reveals a new and interesting asymmetric deuterium scrambling reaction. Parallel studies have been undertaken by Schleyer.[4]


I



IIa, X = H, Y = H
b, X, Y = O
c, X = H, Y = OH
d, X = D, Y = OH
e, X = H, Y = OPNB
f, X = D, Y = OPNB

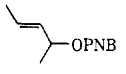
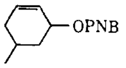
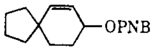


IIIa, X = H
b, X = OH
c, X = OPNB(*p*-nitrobenzoate)

In order to establish the degree of destabilization associated with I, we carried out the solvolysis of the *p*-nitrobenzoate, IIe[5] (mp 95–6°). Any marked rate depression of the [3.2.2] system when compared with suitable model compounds can be attributed to destabilization of the antibicycloaromatic cation. Solvolyses were carried out in 80% aqueous acetone at 100 and 125°. Only a 77 ± 1% infinity was attained at both temperatures, but work-up of the solvolysis products showed that 23% of the initial IIe had isomerized to the barbaralyl *p*-nitrobenzoate, IIIc, which is stable to the reaction conditions.[6] After correction for this competing reaction, the data gave good first-order plots and the results are shown in Table I together with model systems for comparison. After chromatographic purification the remaining solvolysis products were shown to be IIc and IIIb by comparison with authentic samples. The yield of IIc varied with the solvolysis (0–20%), but control experiments showed that IIc could be converted to IIIb under reaction conditions.[7] Thus, the rates and products of the solvolysis indicate that there is little unusual destabilization associated with the [3.2.2] cation, I. The observation of the rearranged internal return product, IIIc, shows that while I is not strongly destabilized relative to other allylic cations, it can readily rearrange to the lower energy barbaralyl cation IV.[8]

In the earlier work,[3] it was reported (without experimental detail) that no bicyclo[3.2.2]nonatriene, IIa, was detected in the $LiAlH_4$–$AlCl_3$ reduction of the

Table I. Solvolysis Data for Allyl *p*-Nitrobenzoates[a]

Compound	Temp, °C	Rate × 10^6 sec^{-1}
IIe	100	11.8 ± 1.0
IIe	125	98 ± 5
	100	12[b]
	100	3.7[b]
	100	3.8[b]

[a] In 80% aqueous acetone. [b] E. C. Friedrich, Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1961.

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(1) Supported by the National Science Foundation.

(2) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

(3) M. J. Goldstein and B. G. Odell, *ibid.*, **89**, 6356 (1967).

(4) J. C. Barborak and P. von R. Schleyer, *ibid.*, **92**, 3184 (1970). We thank Professor Schleyer for informing us of his results prior to publication and for agreeing to simultaneous publication.

(5) All new compounds gave satisfactory analyses and spectral properties. IIe was prepared from the corresponding alcohol IIc by conventional methods.

(6) J. C. Barborak, J. Daub, D. M. Follweiler, and P. von R. Schleyer, *ibid.*, **91**, 7760 (1969).

(7) These reactions were monitored by nmr spectroscopy on the crude solvolysis products both before and after separation by column chromatography into ester and alcohol components. Chromatography of each compound individually showed no evidence of rearrangement or decomposition on the column.

(8) We recognize that our conclusions regarding the destabilization of I rest heavily on the observation of IIc in the solvolysis product and the assumption that this material does not arise from direct solvent displacement on IIe. However, comparison with other solvolytic studies involving *p*-nitrobenzoates in these laboratories suggests that this is unlikely. The extent of deuterium scrambling observed in IIc derived from IIf should provide at least partial justification of this point. Unfortunately, in the reaction in which the deuterated products were examined, no IIc was detected by nmr.

ketone IIb and this observation was used as part of the argument against any unusual stability in I. We have studied this reduction and, in contrast to the earlier report, found that IIa[9] was present in the reaction product. The ratio of barbaralane, IIIa, to IIa was dependent on the $LiAlH_4:AlCl_3$ ratio, indicating that rearrangement to the barbaralyl system is probably acid catalyzed. The results are shown in Table II.

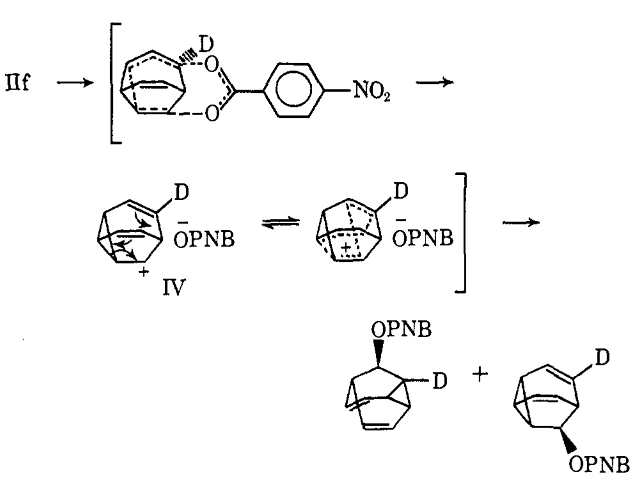
Table II. Reduction of IIb with $LiAlH_4$–$AlCl_3$[a]

	Isolated yields, %			
	Alcohols		Hydrocarbons	
$AlCl_3/LAlH_4$	IIc	IIIb	IIa	IIIa
1.2	30	30	1.5	21.5
0.28	0.5	62	5	6

[a] Reduction was carried to completion (2 hr) at −78° in diethyl ether with a $LiAlH_4$ to ketone ratio of 1.0:0.008 in both cases.

In an attempt to elucidate the mechanism of the solvolytic rearrangement, the solvolysis was repeated with the deuterio-*p*-nitrobenzoate, IIf.[11] Nmr analysis showed that in both the barbaralyl products, IIIb and IIIc, deuterium had been scrambled selectively, within experimental error (±5%), into the 1 and 5 (33% D) and 2, 4, 6, and 8 positions (67% D).[12] No deuterium was found in the 3, 7, or 9 position. This is in accord with the results obtained by Schleyer[6] for the solvolysis of the parent barbaralyl system. In these compounds, the multiplets assigned to H-3 and H-7[13] each consisted of a superimposed doublet (vicinal coupling to one H and one D) and triplet (vicinal coupling to two H's). Careful integration of the relative intensities within these multiplets revealed that the deuterium substitution at positions 2, 4, 6, and 8 in the *p*-nitrobenzoate was asymmetric. Deuterium was found preferentially at the positions *syn* to the *p*-nitrobenzoate group in the ratio 2:1. Within experimental error, the monodeuterio alcohol showed deuterium present equally at positions 2, 4, 6, and 8. These results indicate that in the initially formed barbaralyl cation, the ion pair at least is asymmetric, but that solvent capture is a symmetric process.

Any proposal concerning the mechanism of this rearrangement must be speculative at this time. Schleyer[4,6] has discussed the reasonable alternatives. The mechanism we favor at present for the asymmetric component of the ion pair capture process is[15]



We have chosen this mechanism by consideration of the symmetry properties of cyclopropane ring openings and closures.[16,17] Note that geometric limitations require that all such openings and closures must be disrotatory. The possibilities are: (a) ring opening with involvement of the cationic center (*e.g.*, breaking the 1,2 bond to form I), an allowed two-electron process,[16] but energetically unfavorable; (b) ring opening and closure with involvement of the cationic center and one double bond (*e.g.*, breaking the 1,2 bond and forming the 4,9 bond), a symmetry forbidden four-electron process;[16] (c) ring opening and closure with involvement of the cationic center and both double bonds (*e.g.*, the above mechanism). This is a six-electron process and will be allowed if it involves an even number of negative overlap integrals.[17] This requirement is met in the scheme outlined above, since the transition state involves two negative overlap integrals. This explanation must await further experimental facts for its justification.

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[9] The structure was confirmed by the nmr spectrum and vpc retention time, which were identical with those of an authentic sample.[10]

[10] J. B. Grutzner and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6562 (1968).

[11] Obtained from the deuterated alcohol, IId, prepared previously.[10]

[12] Note that positions 1 and 5, 2 and 4, and 6 and 8 cannot be differentiated because of the rapid degenerate Cope rearrangement.[6]

[13] The spectrum is similar to that reported by Doering.[14] The assignment of the more downfield multiplet to H-3 rather than H-7 was based on the chemical shift and line width. The anisotropic deshielding of the *p*-nitrobenzoate group should shift the *syn* proton H-3 downfield of H-7. Further, in all spectra of the alcohols and *p*-nitrobenzoates, both deuterated and undeuterated, the downfield multiplet was slightly, but reproducibly, broader. This is presumably due to a small (<0.3 Hz) coupling with the *anti* hydrogen H-9 *via* a back lobe overlap mechanism. Unpublished observations by Dr. D. Harris of this department on related compounds have confirmed this assignment.

[14] W. von E. Doering, B. M. Ferrier, E. D. Fossel, J. H. Hartenstein, M. Jones, G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

[15] Note that the deuterium scrambling results show that ~40% of the ion-pair capture process is asymmetric and that the remainder is proceeding *via* symmetrical intermediates (which may include I).

[16] H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966).

[17] J. J. C. Mulder and L. J. Oosterhoff, *Chem. Commun.*, 305 (1970).

[18] To whom correspondence should be addressed, at the Department of Chemistry, Purdue University, Lafayette, Ind. 47907.

[19] Deceased Nov 23, 1969.

[20] We wish to thank Drs. P. Ahlberg, J. Dirlam, and D. Harris of this department for helpful discussions.

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Received February 9, 1970

Organocopper Intermediates *via* Decarboxylation of Cuprous Carboxylates

Sir:

Earlier we[1] and several other groups reported that arylcoppers couple with aryl halides to give unsymmetrical biaryls,[2] pyrolyze[3] or oxidize[4] to symmetrical

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[1] A. Cairncross and W. A. Sheppard, *J. Amer. Chem. Soc.*, **90**, 2186 (1968).

[2] (a) M. Nilsson, *Tetrahedron Lett.*, 679 (1966); (b) M. Nilsson and O. Wennerström, *ibid.*, 3307 (1968); (c) G. M. Whitesides, W. F. Fischer, Jr., J. SanFilippo, Jr., R. W. Bashe, and H. O. House, *J. Amer. Chem. Soc.*, **91**, 4871 (1969); (d) R. J. DePasquale and C. Tamborski, *J. Org. Chem.*, **34**, 1736 (1969).

[3] (a) H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pays-Bas*, **55**, 821 (1936); (b) H. Hashimoto and T. Nakano, *J. Org. Chem.*, **31**, 891