Table IV. Dipole Moments of Phthalide and of Its Sulfur and Selenium Isologs (Benzene, D)

	B =	A = O	A = S	A = Se
	O	4.75	4.86	4.98
	S	4.31	4.53	4.61
	Se	4.09	4.24	Unstable

moments of phthalide, thiolphthalide, and selenolphthalide are higher than those of the corresponding γ-butyrolactone analogs. Obviously, there is resonance interaction with the benzene ring, this interaction being similar for all the benzbutyrolactone analogs. The decreases in dipole moment induced by the replacement of the noncarbonyl oxygen by sulfur and selenium are similar to the decreases induced by analogous substitution in the γ-butyrolactone series.

When the carbonyl oxygen of phthalide (or its thiol ester and selenol ester analogs) is replaced with sulfur and selenium a slight but meaningful increase in dipole moment is observed. However, this increase is much smaller than that noted when the carbonyl oxygen of amides is replaced by sulfur and by selenium.[31,43] The relatively high dipole moments of thioamides and selenamides, relative to those of their oxygen isologs, had been attributed to the progressively increasing contribution of charge-separated forms of the type $-NH^+=C(-B)$ as the carbonyl oxygen was replaced with sulfur and selenium, atoms in which octet expansion is possible. This postulate could be confirmed, when it was found that in isologous amides, thioamides, and selenamides the bond orders of the C=O, C=S, and C=Se bonds decreased in the order stated, while the bond orders of the vicinal C–N bonds increased.[17] Furthermore, acidity increases in passing from carbamyl to thiocarbamyl to selenocarbamyl compounds. Such interactions are, of course, less likely in esters than in amides and, thus, the relatively small increases in the dipole moments of the phthalide isologs induced by replacing their carbonyl oxygens with sulfur and selenium are not surprising.

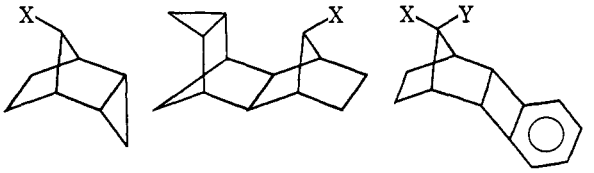
(43) M. H. Krackov, C. M. Lee, and H. G. Mautner, *ibid.*, 87, 892 (1965).

Communications to the Editor

Edge Participation by Cyclobutane in a Bridged Homocyclobutylcarbinyl System

Sir:

Extensive edge participation at a developing carbonium ion center by a cyclopropane ring structurally if not spatially removed from the reaction site has been amply demonstrated in the 7-norbornyl systems **1**[1] and **2**.[2] Although the literature records no relevant

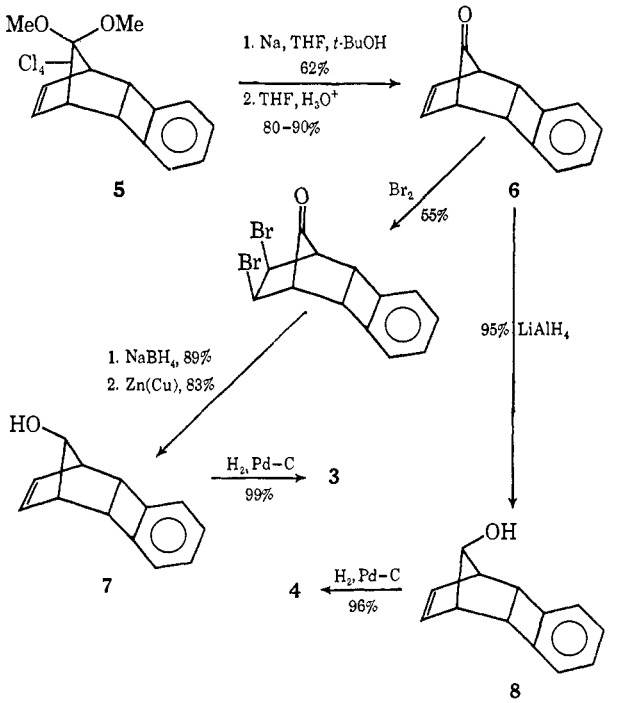


1 **2** **3**, X = OH; Y = H; **4**, X = H; Y = OH

examples of cyclobutyl participation, similar, though less extensive, "edge" participation can be envisaged for the four-membered ring on the basis of theoretical estimates[3] of the deviation from rectilinear bonding in the smaller cycloalkanes. Again, incorporation of the cyclobutane ring into a rigid 7-norbornyl skeleton should provide the most favorable geometry for participation. In this communication we describe the synthesis and solvolytic reactivity of two such bridged derivatives, *endo-anti*-benztricyclo[4.2.1.$0^{2,5}$]non-3-en-9-yl brosylate (**3**-OBs) and its *endo-syn* isomer **4**-OBs, which provide direct insight into the question of cyclobutyl participation.

The epimeric alcohols essential to this study were prepared according to the scheme outlined in Chart I.

Chart I



(1) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); J. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(2) M. A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl, and S. Winstein, *ibid.*, **92**, 2144 (1970).

(3) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); 3161 (1963).

Table I. Acetolysis Rate Constants and Activation Parameters

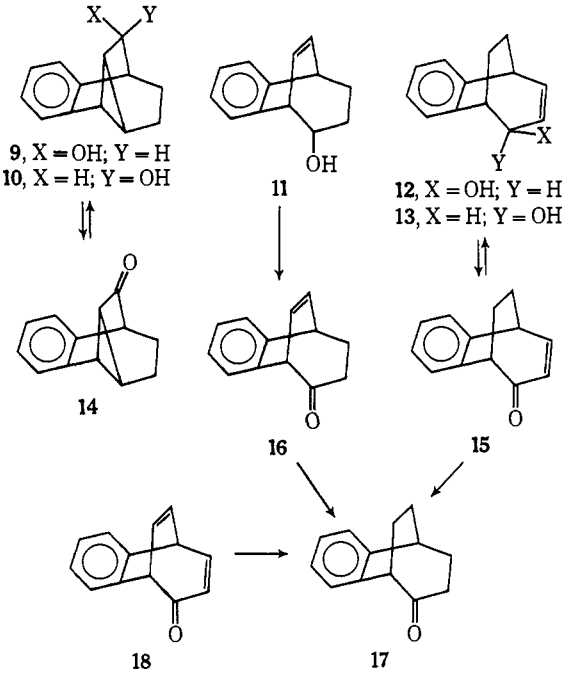
ROBs[a]	Temp, °C	$10^5 k_1$, sec^{-1}	Rel k_1 (25°)	$\Delta H^{\ddagger}$,[b] kcal/mol	$\Delta S^{\ddagger}$,[b] eu
3-OBs	100	2.69 ± 0.07	72,200	28.6 ± 0.7	−3.1 ± 2.0
	125	32.8 ± 1.1			
4-OBs	175	2.05 ± 0.06	1.1	35.8 ± 0.8	+0.1 ± 2.0
	200	18.4 ± 0.3			
7-Norbornyl	205	25.2[c]	1.0	35.7 ± 0.6	−3.5 ± 1.7

[a] *Ca.* 0.02 *M*. [b] Errors were computed according to the method of R. C. Peterson, J. H. Markgraf, and S. D. Ross, *J. Amer. Chem. Soc.*, **83**, 3819 (1961). [c] Estimated on the basis of three times the rate for 7-norbornyl tosylate in ref 8.

The configurations of the starting tetrachloroketal **5**, a readily available adduct of benzcyclobutadiene with 5,5-dimethoxytetrachlorocyclopentadiene, and the corresponding dechlorinated ketal have been previously established.[4] The structure of tricyclic ketone **6**,[5] mp 43–44°, $\nu_{C=O}^{KBr}$ 1770 cm^{-1}, was supported by its spectral properties and facile decarbonylation to benzcyclooctatetraene at temperatures (90–100°) considerably lower than for the corresponding *exo* isomer recently described.[6] Alcohol **4**, mp 127–128°, was obtained from **6** in a straightforward manner whereas **3**, mp 109–110°, required a more subtle approach involving addition of a sterically large but readily removable blocking reagent to the double bond prior to carbonyl reduction. The *anti* configuration of alcohol **7**, and hence of **3** also, was substantiated by the presence of long-range coupling of the vinyl protons with the bridge (C-9) proton.[7] The brosylate esters **3**-OBs, mp 109–110°, and **4**-OBs, mp 104–105°, were obtained from the corresponding alcohols without rearrangement.

The measured rates of acetolysis and appropriate activation parameters for **3**-OBs and **4**-OBs are summarized in Table I along with similar data for 7-norbornyl brosylate.[8] A comparison of relative reactivities in this series reveals that *endo-syn*-**4**-OBs is equally as unreactive as 7-norbornyl brosylate whereas the *endo-anti* ester **3**-OBs displays considerable rate enhancement over that for 7-norbornyl. The latter rate factor is $10^{4.9}$ at 25° which in order of magnitude is roughly one-third of the anchimeric effect produced by the cyclopropyl group in **1**. It is perhaps fortuitous, but nevertheless intriguing, that the calculated degree of "bent-bonding" for cyclobutane is also about one-third of that calculated for cyclopropane.[3]

The products from acetolysis of *anti*-**3**-OBs under conditions identical with those in the kinetic runs (125°, ten half-lives) revealed extensive rearrangement, with no structure of unrearranged skeleton detected. Nmr examination of the crude acetate product mixture (98% yield) indicated five major acetate components. Glpc analysis of this product mixture after lithium aluminum hydride reduction confirmed the presence of five major alcohols in a combined yield of 90%. Isolation of each of these components by preparative glpc followed by recrystallization and/or vacuum sublimation gave homogeneous samples of the following



alcohols: **9** (41%), mp 140–142°, **10** (10%), mp 118–120°, **11** (7%), mp 115–117°, **12** (16%), mp 95–97°, **13** (16%), mp 83–84°. The structure of the major alcohol product **9** was supported by spectral data [nmr ($CDCl_3$) τ 2.80 (m, 4 H), 5.74 (bt, 1 H, J = 3.0 Hz), 7.05 (m, 1 H), 7.8–9.0 (m, 8 H); ir (CCl_4) 3590, 3025, 2940, 2860, 1050 cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 186 (45), 168 (21), 145 (39), 142 (42), 141 (24), 129 (100), 128 (60), 115 (40)] and conversion to the tricyclic ketone **14**: $\nu_{C=O}^{CCl_4}$ 1709 cm^{-1}; nmr (CCl_4) τ 2.90 (m, 4 H), 6.90 (m, 1 H), 7.2–8.3 (m, 7 H); mass spectrum (70 eV) *m/e* (relative intensity) 184 (42), 166 (17), 129 (35), 128 (100), 115 (30). Lithium aluminum hydride reduction of **14** afforded a 40:60 mixture of alcohols **9** and **10**, thus establishing the epimeric relationship of these two alcohols. The *syn* configuration was assigned to **9** on the basis of strong intramolecular O–H $\cdots$ π absorption in its infrared spectrum.[9] The epimeric relationship of the unsaturated alcohols **12** and **13** was established by a similar interconversion sequence *via* ketone **15**, $\nu_{C=O}^{CCl_4}$ 1665 cm^{-1}. Oxidation of the remaining alcohol **11** gave ketone **16**, $\nu_{C=O}^{CCl_4}$ 1710 cm^{-1}, which on hydrogenation yielded the known[10] saturated bicyclic ketone **17** obtained independently by hydrogenation of the benzyne–tropone adduct **18**.[10] Ketone **15** similarly afforded **17** on hydrogenation, thus confirming the structural relationships of the unsaturated

(4) A. J. Boulton and J. F. W. McOmie, *J. Chem. Soc.*, 2549 (1965).
(5) All new compounds reported gave correct elemental analyses and/or glpc–mass spectral assurances of sample purity and molecular weight. Other spectral data were in accord with assigned structures.
(6) M. A. Battiste and J. W. Nebzydoski, *J. Amer. Chem. Soc.*, **91**, 6887 (1969).
(7) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); M. E. Brennan and M. A. Battiste, *J. Org. Chem.*, **33**, 324 (1968).
(8) S. Winstein, M. Shatavaky, C. Norton, and R. B. Woodward, *J. Amer. Chem. Soc.*, 77, 4183 (1955).
(9) M. Tichy, *Advan. Org. Chem.*, **5**, 115 (1965).
(10) J. Ciabattoni, J. E. Crowley, and A. S. Kende, *J. Amer. Chem. Soc.*, **89**, 2778 (1967).

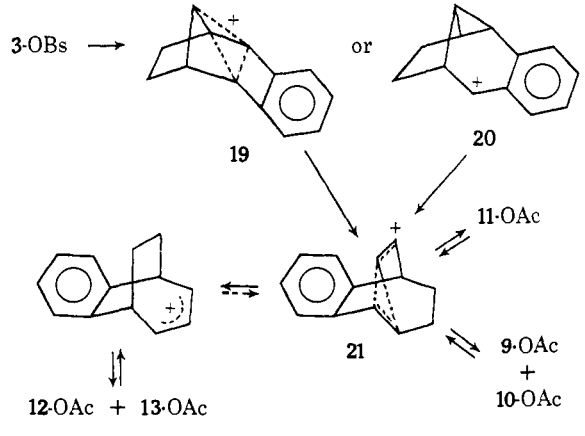
products. The configurations of alcohols **11–13** were established by hydrogenation and examination of the infrared spectra of the saturated alcohols for intramolecular O–H $\cdots$ π absorption.

Since alcohols **12** and **13** appeared to be the products of multiple rearrangements and hence likely of thermodynamic rather than kinetic origin, the stability of the five acetates **9**-OAc–**13**-OAc was examined under the solvolysis conditions (HOAc–NaOAc, 125°, ten half-lives). With the exception of some epimerization at C-2 acetates **12**-OAc and **13**-OAc are largely (85–90%) unscrambled as is acetate **11**-OAc (77 ± 2% recovery). On the other hand **9**-OAc and **10**-OAc are converted to essentially identical mixtures of the five acetates and in almost the same relative proportions as obtained in the original solvolysis of **3**-OBs.

The acetolysis product mixture from *syn*-**4**-OBs (200°, ten half-lives) was exceedingly complex with over 20 components detected by glpc analysis of the crude alcohol product obtained after lithium aluminum hydride reduction. Of the six major alcohol components (69% by peak area) three were separated by preparative glpc and identified as **11** (7%), **12** (8%), and **13** (9%). The remaining three major components, comprising 45% of the total acetolysis product, have not been identified as yet owing to their poor separation by preparative glpc. However, it is clear from their glpc retention times and composite nmr spectra that they are not identical with any other alcohols previously characterized in this study. In any event the forcing conditions (200°) required for the solvolysis of **4**-OBs tend to rule out mechanistic speculation based on product analyses of acetates already shown to be moderately unstable at lower temperatures (125°)

Although critical data regarding the precise nature of the initial ion(s) produced upon ionization of **3**-OBs are not available from this study, homocyclobutylcarbinyl rearrangement to give ion **19** or **20** is clearly implicated. Subsequent rearrangement to the cyclopropylcarbinyl cation **21** followed by solvent attack and/or further rearrangement provides an adequate rationale for the observed products as indicated in Scheme I. Alternatively, the failure to detect products

Scheme I



arising from ion **20** (or **19**) may be attributed to the anticipated reactivity of such benzylic acetates and their facile rearrangement under the imposed conditions. Further clarification of these points is now under investigation.

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(11) Alfred P. Sloan Foundation Fellow, 1967–1969.

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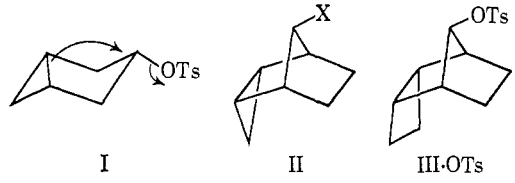
Edge Participation by a β-Cyclobutane Ring in a 7-Norbornyl System[1]

Sir:

Edge participation of a β-cyclopropyl group in solvolysis with formation of a trishomocyclopropenyl cation was first observed with system I.[2] When the cyclopropyl group is placed in a 7-norbornyl system (II), the anchimeric acceleration observed (10^{14}) is most impressive.[3] Similar edge participation by a cyclobutane ring, at least to some degree, can be visualized on theoretical grounds, and this is the subject of the present communication.



Since a 7-norbornyl system would appear to be most suitable for disclosing cyclobutane participation if it should prove to be marginal, we have studied the *endo,anti*-III system as well as the epimeric *endo,syn*-X system. The results are reported and discussed in the present communication.

The synthetic route to the III and X systems started most conveniently in these laboratories with the bicyclo[4.2.1]nonatrienol IV, available from another investigation.[4] Irradiation of a 2% solution of alcohol IV in pentane in a Pyrex flask, followed by column chromotography and recrystallization, gave alcohol[5] V, mp 88.0–89.0°, in 50–60% yields. The structure and configuration of V are clear from its chemical properties and nmr spectrum. Conclusive proof of the *endo* fusion of the cyclobutene ring to the norbornene moiety in V is the photochemical conversion of V to homocubyl alcohol[6] IX. Thus, without any attempt to optimize the conversion, irradiation of V in acetone solvent, followed by preparative vpc and recrystallization, led to a 30% yield of homocubyl alcohol, mp 158.0–158.5° (lit.[6b] mp 157°), with nmr and ir spectra

(1) This research was supported in part by the National Science Foundation.

(2) (a) S. Winstein, J. Sonnenberg, and L. de Vries, *J. Amer. Chem. Soc.*, **81**, 6523 (1959); (b) S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235, 3244 (1961); (c) S. Winstein, E. C. Friedrich, R. Baker, and Y. Lin, *Tetrahedron, Suppl.*, No. 8, Part II, 621 (1966).

(3) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); (b) M. A. Battiste, C. L. Dreyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (c) J. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(4) M. Sakai and J. B. Smith, unpublished work.

(5) All new compounds reported gave elemental analyses and spectral data in accord with their assigned structures.

(6) (a) W. G. Dauben and D. L. Whalen, *J. Amer. Chem. Soc.*, **88**, 4739 (1966); (b) P. v. R. Schleyer, *et al.*, *ibid.*, **89**, 698 (1967).