Acknowledgment. This study was supported by NSF Grant CHE-8518801 and in part by the UC Riverside Intramural Research Fund. H.E. also acknowledges receipt of a Chancellor's Patent Fund grant from the UC Riverside Graduate Division. Badische-Anilin und Soda Fabrik (Ludwigshafen) generously provided several chemicals utilized in this investigation. Dr. R. Lee, Dr. A. de Lera, and Ms. P. Theobald provided valuable advice during the course of this study.

Registry No. (±)-**9a**, 114582-48-8; (±)-**9b**, 114582-50-2; (±)-**9c**, 114582-52-4; (±)-**9d**, 114582-54-6; **11a**, 114582-55-7; **11b**, 114582-56-8; **12c**, 114582-57-9; (±)-**13c**, 114582-58-0; (±)-**13d**, 114582-59-1; (±)-**14c**, 114613-31-9; (±)-**14d**, 114582-60-4; **18**, 79-77-6; (±)-**20a**, 114582-47-7; (±)-**20b**, 114582-49-9; (±)-**20c**, 114582-51-3; (±)-**20d**, 114582-53-5; (±)-**23a**, 114582-61-5; (±)-**23b**, 114582-62-6; (±)-**24a**, 94369-97-8; (±)-**24b**, 114582-63-7; (±)-**24c**, 114594-79-5; **25a**, 114582-64-8; **25b**, 114582-67-1; (±)-**26a**, 114582-65-9; (±)-**26b**, 114582-66-0; **27a**, 114582-68-2; **27b**, 114582-70-6; **28a**, 114582-69-3; **28b**, 114582-71-7; HC≡CMe, 74-99-7; HC≡CEt, 107-00-6; HC≡CPr-*i*, 598-23-2; HC≡CBu-*t*, 917-92-0.

Supplementary Material Available: Spectral and analytical data (31 pages). Ordering information is given on any current masthead page.

Rearrangements of 6-Tricyclo[3.3.0.0^{2,7}]octyl Cations. Factors Influencing the Relative Stabilities of Bridged Carbocations

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The objective of this work was to explore the effect of ring strain on σ delocalization of carbocations. The 6-tricyclo[3.3.0.0^{2,7}]octyl cation (**3**) incorporates 2-norbornyl and 2-bicyclo[2.1.1]hexyl structures in a highly strained molecular framework. Solvolyses of the epimeric brosylates **22** and **23**, as well as nitrous acid deaminations of the analogous amines, **24** and **21**, served to generate **3**. The exo:endo rate ratios of the brosylates and the exo:endo product ratios of the tricyclo[3.3.0.0^{2,7}]octan-6-ols (**19**, **20**) are close to unity. Product distributions and kinetic data suggest a weak k_s contribution at least for the endo brosylate **23**. Several nondegenerate rearrangements of **3** were elucidated: Migration of C-2 from C-7 to C-6 (**3** → **28**) is followed, in part, by fragmentation (**28** → **31**). A minor fraction of **3** undergoes 4,6-hydride shifts (**3** → **37** ⇄ **38**). The degeneracy of **3** was probed with the aid of a 6-^{2}H label. Migration of C-8 from C-7 to C-6 was found to be rapid, as compared to nucleophilic capture, whereas the norbornyl-type Wagner–Meerwein rearrangement (migration of C-4) was not observed. Product and label distributions indicate that the bridged structure (involving C-6, -7, and -8) **3c** is nearly isoenergetic (±0.5 kcal/mol) with the unsymmetrical ion **3a** while products from the norbornyl-type delocalized ion (**3b**) are not observed, so **3b** must be less stable by at least 3 kcal/mol. The exceptional order of relative stabilities is explained in terms of "olefinic strain", i.e., the additional strain resulting from contraction of the basal bond in bridged carbocations.

Many carbocations are known in which the charge is delocalized in two-electron three-center bonds.[1] By Olah's terminology these are carbonium ions as opposed to the charge-localized carbenium ions.[2] These terms actually refer to limiting cases; there can be a continuum of electron delocalization in carbocations.[3] Electronic effects on σ delocalization have been thoroughly studied. For instance, the classical (C_1) structure of the 2-norbornyl cation (**1a**) was found to be favored by charge-stabilizing substituents at C-1 and C-2,[1,4] as well as by electron-withdrawing groups at C-6.[3a,5] The influence of ring strain has received much less attention. Recent solvolytic[6] and computational studies[7] of the 2-bicyclo[2.1.1]hexyl cation (**2**) indicate that the delocalized structure **2b** should be about 3 kcal/mol more stable than **2a** (the exchange of the methylene groups of **2b** must proceed via **2a**). Estimates of the stabilization energy of the 2-norbornyl cation due to bridging (**1b** vs **1a**) are higher: 6–8 kcal/mol from exo:endo rate ratios[1,4] and from heats of ionization;[8] 10–11 kcal/mol from gas phase hydride affinities.[9] However, such estimates depend on the choice of appropriate models.[10] Any conclusion from

(1) For recent reviews, see: (a) Vogel, P. *Carbocation Chemistry*; Elsevier: Amsterdam, 1985. (b) Olah, G.; Prakash, G. K. S.; Sommer, J. In *Superacids*; Wiley: New York, 1985; Chapter 3.5. (c) Shubin, V. G. *Top. Curr. Chem.* **1984**, *116*, 267. (d) Saunders, M.; Chandrasekhar, J.; Schleyer, P. v. R. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; Vol. 1, p 1. (e) Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 125. (f) Brown, H. C. *The Nonclassical Ion Problem* (with comments by Schleyer, P. v. R.); Plenum: New York, 1977.

(2) (a) Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808. (b) Olah, G. A. *Angew. Chem.* **1973**, *85*, 183; *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173. (c) Olah, G. A. *Top. Curr. Chem.* **1979**, *80*, 211. (d) Olah, G. A. *Chem. Scr.* **1981**, *18*, 97.

(3) (a) Rates: Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426. (b) Isotopic perturbation: Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1980**, *102*, 6867; **1983**, *105*, 3571. (c) X-ray: Laube, T. *Angew. Chem.* **1987**, *99*, 580; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 561. Montgomery, L. K.; Grendze, M. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4749.

(4) Sargent, G. D. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. III, p 1099.

(5) Kirmse, W.; Mrotzeck, U.; Siegfried, R. *Angew. Chem.* **1985**, *97*, 51; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 55.

(6) Kirmse, W.; Zellmer, V.; Goer, B. *J. Am. Chem. Soc.* **1986**, *108*, 4912.

(7) Schleyer, P. v. R.; Laidig, K.; Wiberg, K. B.; Saunders, M.; Schindler, M. *J. Am. Chem. Soc.* **1988**, *110*, 300.

(8) (a) Arnett, E. M.; Petro, C. *J. Am. Chem. Soc.* **1978**, *100*, 2563, 5408. (b) Arnett, E. M.; Pienta, N.; Petro, C. *J. Am. Chem. Soc.* **1980**, *102*, 398.

(9) (a) Lossing, F. P.; Holmes, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 6917. (b) Blanchette, M. C.; Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1987**, *109*, 1392.

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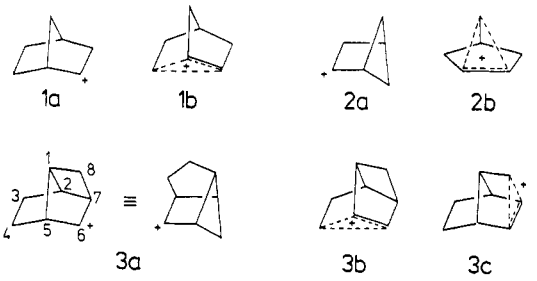
these data, concerning the effect of ring strain on σ delocalization, would be premature.



For further insight, we have studied the 6-tricyclo[3.3.0.0^{2,7}]octyl cation (**3**). This ion incorporates the structural elements of both **1** and **2**. Neither the degeneracy of the Wagner–Meerwein rearrangements nor the symmetry of delocalized intermediates (**3b,c**) is disturbed by the additional bridge. On the other hand, the strain energy of tricyclo[3.3.0.0^{2,7}]octane (48 kcal/mol) is significantly higher than that of norbornane (17 kcal/mol) and bicyclo[2.1.1]hexane (41 kcal/mol).[11]

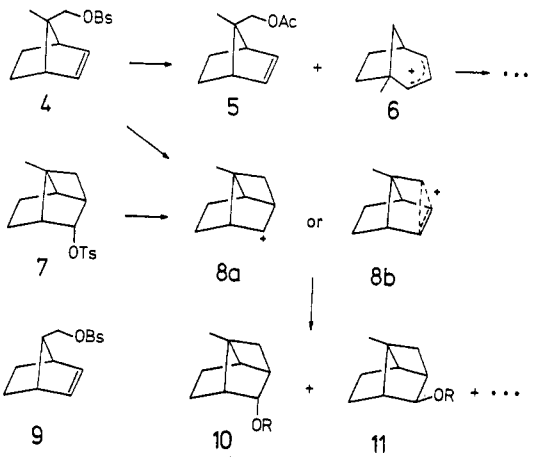
The only previous report on 6-tricyclo[3.3.0.0^{2,7}]octyl cations refers to the 1-methyl derivative **8**.[12] Acetolysis of *anti*-7-methyl-2-norbornene-*syn*-7-carbinyl brosylate (**4**) gave a product mixture which contained, in addition to unrearranged (**5**) and ring-expanded acetates (derived from **6**), a set of five tricyclic products (ca. 45%). Independent syntheses identified two of the tricyclic acetates as **10**-OAc and **11**-OAc. The same products, albeit in different ratios, were obtained by acetolysis of the tosylate **7**, derived from **10**-OH (Scheme I). The efficient cyclization of **4** is to be contrasted with the behavior of the 7-unsubstituted analogue **9**, which gave no detectable cyclization products.[13] The available data did not shed light on the potential degeneracy and stereoselectivity of **8**. Extended studies (now reported), particularly of the parent system **3**, promised a significant advance.

Results

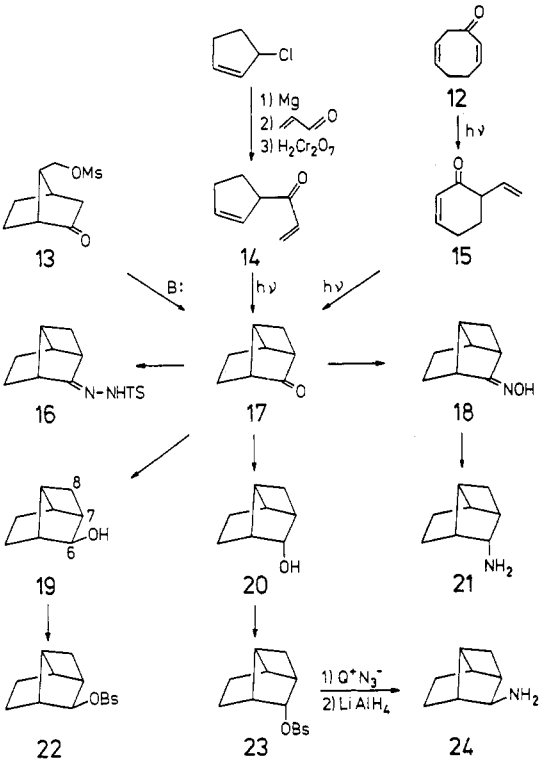
Preparation of Substrates. Tricyclo[3.3.0.0^{2,7}]octan-6-one (**17**), a key intermediate, has been prepared previously by base-induced cyclization of **13**.[14] The route leading to **13**, however, is a rather elaborate, multistep sequence. We obtained **17** (16% yield) by intramolecular photocycloaddition of **14**, which is readily accessible in two steps from 3-chlorocyclopentene and acrolein. A related approach starts from 2,6-cyclooctadien-1-one (**12**) and generates **17** in two sequential photoreactions,[15] but this alternative proved inferior to ours with regard to yield and accessibility of the precursor (Scheme II).

The stereoselectivity of **17** toward lithium aluminum hydride was similar to that of 2-norbornanone: the alcohols **19** and **20**, separable by HPLC, were obtained in a 1:9 ratio. The ^{1}H NMR spectra of all tricyclo[3.3.0.0^{2,7}]octane derivatives contain a sharp doublet of endo 8-H ($J_{8n,8x}$ ca. 8 Hz). In the spectrum of **20** ($CDCl_3$), the doublet is located at δ 1.12, but because of the proximity of the OH

Scheme I



Scheme II



group, it is shifted downfield to δ 1.79 in the spectrum of **19**, thus confirming the configurational assignment. Moreover, 6-H of **19** absorbs at higher field (δ 3.82) as compared with 6-H of **20** (δ 4.11), in agreement with *exo*- (δ 3.75) and *endo*-2-norbornanol (δ 4.20).

The alcohols were converted to the analogous brosylates, **22** and **23**. Inverting displacement of the endo OBs group with hexadecyltributylphosphonium azide,[16] followed by $LiAlH_4$ reduction, afforded the exo amine **24**. The endo isomer **21** was obtained by Pt-catalyzed hydrogenation of the oxime **18**. The tosylhydrazone **16** was prepared as another convenient source of diazonium ions (Scheme II).

Product Studies. Solvolyses of the brosylates **22** and **23** were performed in 70% aqueous dioxane in the presence of 2,6-lutidine. The diazonium ions **25** and **26** were generated by nitrous acid diazotization of the amines **24** and **21**, respectively, and by photolysis of tosylhydrazone **16**

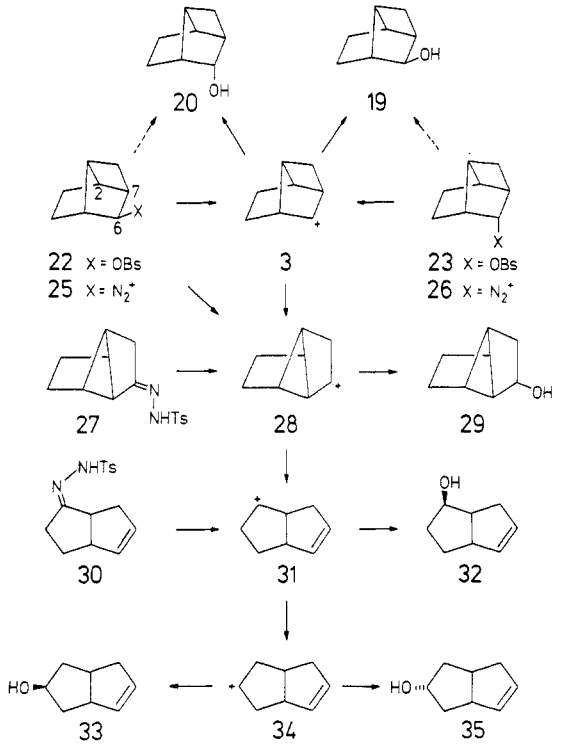
(10) For a criticism of nonclassical stabilization, see: Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432.
(11) Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.
(12) Berson, J. A.; Donald, D. S.; Libbey, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 5580.
(13) (a) Bly, R. K.; Bly, R. S. *J. Org. Chem.* **1966**, *31*, 1577. (b) Berson, J. A.; Gajewski, J. J.; Donald, D. S. *J. Am. Chem. Soc.* **1969**, *91*, 5550.
(14) Nakazaki, M.; Naemura, K.; Kadowaki, H. *J. Org. Chem.* **1976**, *41*, 3725.
(15) (a) Cantrell, T. S.; Solomon, J. S. *J. Am. Chem. Soc.* **1970**, *92*, 4656. (b) Noyori, B.; Inoue, H.; Kato, M. *J. Chem. Soc. D* **1970**, 1695.
(16) (a) Banert, K.; Kirmse, W. *J. Am. Chem. Soc.* **1982**, *104*, 3766. (b) Banert, K. *Chem. Ber.* **1985**, *118*, 1564. (c) Kirmse, W.; Streu, J. *J. Org. Chem.* **1985**, *50*, 4187.

Table I. Product Distributions Obtained from Tricyclo[3.3.0.0^{2,7}]oct-6-yl and Related Substrates[a]

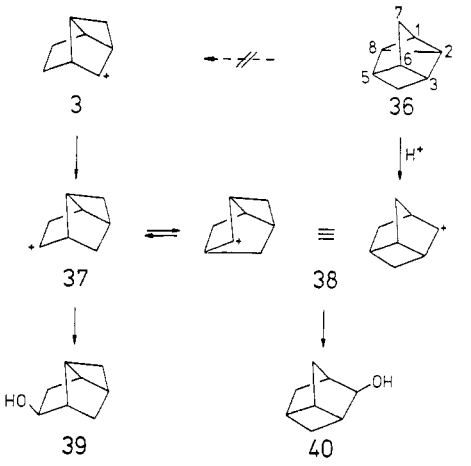
precursor	conditions	products (%)							
		19	**20**	**29**	**32**	**33**	**35**	**39**	**40**
22	70% aqueous dioxane, 80 °C, 20 h	8.7	15.6	43.1	22.6	3.0	3.0	0.8	3.2
23	70% aqueous dioxane, 80 °C, 20 h	35.6	24.2	14.3	9.9	2.0	1.3	2.5	10.2
24	$H_2O/HClO_4$, pH 3.5, $NaNO_2$	12.4	23.1	15.2	35.7	4.2	3.4	1.0	5.0
21	$H_2O/HClO_4$, pH 3.5, $NaNO_2$	32.6	44.2	7.1	9.3	1.0	0.8	0.5	4.5
16	0.2 N NaOH, *hν* (Pyrex)	23.2	33.2	11.0	22.4	2.9	2.2	0.9	4.3
27	0.2 N NaOH, *hν* (Pyrex)[b]	–	–	47.3	41.6	5.3	4.4	–	–
30	0.2 N NaOH, *hν* (Pyrex)[c]	–	–	–	67.8	8.7	12.1	–	–
36	1 N H_2SO_4, 70% aqueous dioxane, 60 °C, 3 days	–	–	–	–	–	–	17	83

[a] Alcohols normalized to 100%. The fraction of bicyclo[3.3.0]octadienes was <5% from tricyclo[3.3.0.0^{2,7}]oct-6-yl precursors, 23% from **27**, and 59% from **30**. [b] 1.4% of bicyclo[3.3.0]oct-6-en-*endo*-2-ol. [c] 11.4% of bicyclo[3.3.0]oct-6-en-*endo*-2-ol.

Scheme III



Scheme IV



in 0.2 N NaOH. Light-induced elimination of sulfinate from sulfonylhydrazone anions produces diazo compounds,[17] which are protonated by hydroxylic solvents to give diazonium ions.[18] Comparison of the product distributions obtained from **16**, **21**, and **24** (Table I) indicates that a 1:1 mixture of exo and endo diazonium ions (**25**, **26**) is generated from **16**. All tricyclo[3.3.0.0^{2,7}]oct-6-yl substrates gave mixtures of eight alcohols, which were analyzed by GC and identified by comparison with authentic samples (Table I).

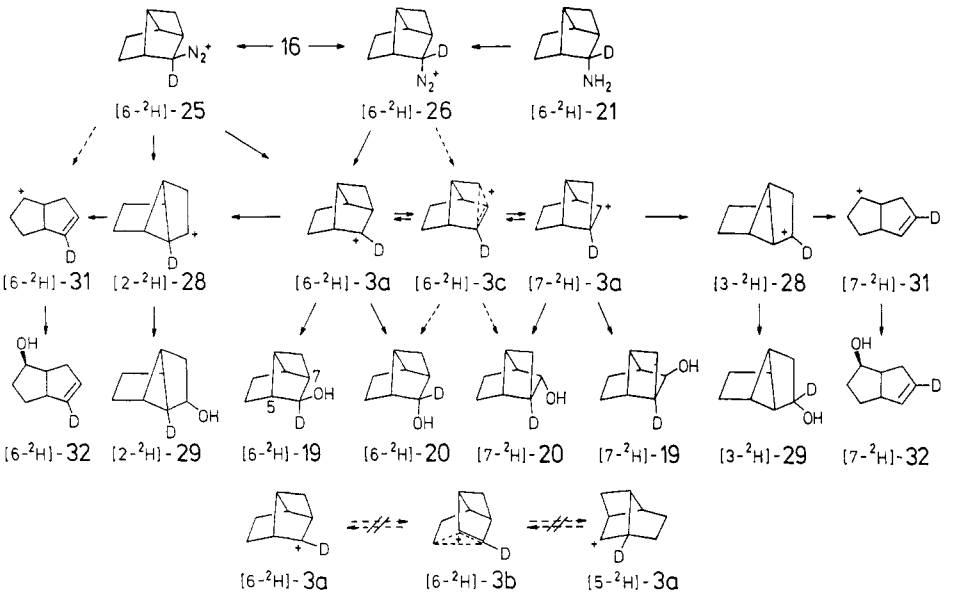
Pathways leading to the products have been formulated in terms of open (classical) carbocations, for the sake of simplicity (Schemes III and IV). The epimeric brosylates (**22** and **23**) give widely different ratios of the analogous alcohols (**19** and **20**); in both cases the inverted product predominates. In contrast, the **19**:**20** ratios obtained with the epimeric diazonium ions (**25** and **26**) are similar, though not identical (0.54 vs 0.74). As endo attack is preferred, these results suggest a significant k_s component giving rise to **19** from **23**. The excellent leaving group and the enhanced polarity of the medium minimize inverting displacement in the dediazoniation process.

A major reaction path is migration of C-2 from C-7 to C-6, with formation of the 3-tricyclo[3.3.0.0^{2,6}]octyl cation (**28**). The corresponding alcohol **29** and the analogous ketone are readily accessible by oxidation of tricyclo[3.3.0.0^{2,6}]octane.[19] The behavior of **28** under our reaction conditions was explored by its generation from the tosylhydrazone **27**. In addition to nucleophilic capture (→**29**, 47%), fragmentation occurred to give the 2-bicyclo[3.3.0]oct-6-enyl cation (**31**) and was followed, in part, by a 1,2-hydride shift (**31** → **34**). The nucleophilic substitution of cation **31** was highly exo selective (→**32**), while **34** yielded the epimeric alcohols **33** and **35** in comparable amounts (Table I). The fragmentation of **28** was also observed in a previous solvolytic study of **29**-OTs,[19] in which no reference to the hydride shift was made. Generation of **31** from the tosylhydrazone **30**, as well as solvolyses of **32**-OTs,[20] confirms the formation of **32** and products derived from a 1,2-hydride shift, **33** and **35**.

The rearrangement leading to **28** (and subsequently to **29**, **32**, **33**, and **35**) is favored by the exo configuration of the leaving group (**22**, 72%; **25**, 59%) which allows participation of the (nearly) antiperiplanar C-2–C-7 bond. However, this stereoelectronic effect is not mandatory as substantial amounts of **28**-derived products arise from the corresponding endo precursors (**33**, 28%; **26**, 18%). Not only the yield but also the relative amounts of these four products depend on the precursor. For brosylates **22** and **23**, the **29**:(**32** + **33** + **35**) ratio is higher (**22**, 1.50; **23**, 1.08) than for diazonium ions (**25**, 0.35; **26**, 0.64). Differences between solvolyses of brosylates and dediazoniation may be due to internal return, i.e., to the intervention of **29**-OBs, which, in part, gives **29** in a k_s process. In accordance

(17) Dauben, W. G.; Willey, F. G. *J. Am. Chem. Soc.* **1962**, *84*, 1497.
(18) For a review, see: Ando, W. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley-Interscience: Chichester, 1978; Part I, p 362.
(19) Meinwald, J.; Kaplan, B. E. *J. Am. Chem. Soc.* **1967**, *89*, 2611.
(20) Nee, M.; Roberts, J. D. *J. Org. Chem.* **1981**, *46*, 67.

Scheme V



with these ideas, kinetic studies showed deviations from first-order kinetics, consistent with formation of a slower reacting compound from **22**. The ratio of substitution: fragmentation observed with **27** is 0.92, intermediate between the figures recorded above. These data indicate that concerted fragmentation (**22**, **25** → **31**) is at best a minor route to bicyclo[3.3.0]octenyl products. The redistribution of a deuterium label also argues against concerted fragmentation (see below).

The remaining components of the product mixture, **39** and **40** are readily attributed to a 1,3-hydride shift, converting **3** into **37**. This process is analogous to the familiar 6,2-shift in 2-norbornyl cations.[1,4] While **39** derives directly from **37**, Wagner–Meerwein rearrangement to **38**, followed by nucleophilic capture, gives the less strained alcohol **40** (strain energy of tricyclo[3.2.1.$0^{3,6}$]octane: 41 kcal/mol[11]) (Scheme IV). Acetolysis of **40**-OTs has been reported to yield **40**-OAc as the only product.[21] However, on acidolysis of tetracyclo[3.2.1.$0^{2,8}$.$0^{3,6}$]octane (**36**)[22] in 70% aqueous dioxane, we obtained **39** and **40** in a 1:5 ratio. Although the **39**:**40** ratios from tricyclo[3.3.0.$0^{2,7}$]octyl precursors are less precise, due to the small amount of **39**, they agree within experimental error. In view of its rapid equilibration and exo-selective capture, the Wagner–Meerwein pair **37**,**38** might be replaced by a single, delocalized ion.[23] Remarkably, protonation of **36** at C-1 does not compete with protonation at C-2,8; no products derived from **3** were detected.

Redistribution of a Deuterium Label. Product studies cannot reveal degenerate rearrangements that might precede the transformations of **3**. For further insight, we introduced a deuterium label at C-6 of tricyclo[3.3.0.$0^{2,7}$]oct-6-yl precursors. Diazonium ions were preferred to brosylates, in order to minimize k_s contributions. The simplest approach is photolysis of tosylhydrazone **16** in NaOD, which generates a 1:1 mixture of labeled exo and endo diazonium ions, [6-²H]-**25** and [6-²H]-**26**. For comparison, the deuteriated endo amine, [6-²H]-**21**, prepared by $LiAlD_4$ reduction of oxime **18**, was diazotized to give [6-²H]-**26**. The major products, **19**, **20**, **29**, and **32** were isolated by HPLC and analyzed by NMR. A crucial point is the assignment of the bridgehead protons 5-H and 7-H of **19** and **20**, respectively. A discriminating feature, coupling of 7-H with exo 8-H, is obscured by overlap of the exo 8-H signals with those of other protons. For an unequivocal assignment, we prepared [7-²H]-**19** and [7-²H]-**20** by an adaption of Scheme II, using [2-²H]propenal.[24] ²H NMR quantitated the deuterium distribution of **19**, **20**, and **29**, but was not applicable to **32**, due to overlapping signals of the olefinic protons. In this case, we made use of the isotope effect exerted by deuterium on the ^{13}C chemical shift of C-5 in [6-²H]-**32** and of C-8 in [7-²H]-**32**. For example, the mixture of isotopomers of **32**, obtained from **16**, displayed original and shifted signals of 5-^{13}C in a 20:80 ratio (±5%) while the analogous ratio for 8-^{13}C was 80:20.

Table II. Deuterium Distributions in Products (19, 20, 29, and 32) Obtained from [6-²H]Tricyclo[3.3.0.$0^{2,7}$]oct-6-yl Substrates (16 and 21)

	precursor	
products	**16**, NaOD, *hν*	[6-²H]-**21**, HNO_2
[6-²H]:[7-²H]-**19**	52:48	53:47
[6-²H]:[7-²H]-**20**	52:48	51:49
[2-²H]:[3-²H]-**29**	75:25	50:50
[6-²H]:[7-²H]-**32**	80:20	50:50

We observed that deuterium was distributed about equally between positions 6 and 7 of **19** and **20** (Table II). This remarkable result requires rapid equilibration of the classical ions [6-²H]-**3a** and [7-²H]-**3a**. We cannot exclude the endo-selective bridged ion [6-²H]-**3c** as a third component of the equilibrium, but we can establish a lower limit of its relative energy. If the endo alcohol **20** were to arise exclusively from **3c**, the bridged ion **3c** would be 0.2–0.3 kcal/mol more stable than **3a** (**20**:**19** = 1.4). Alternatively, if **3c** were the transition state of the degenerate rearrangement of **3a**, **3c** should be less stable than **3a** by 0.5 kcal/mol; otherwise nucleophilic capture of [6-²H]-**3a** (diffusion controlled, apparent $\Delta G^{\ddagger}$ ca. 1.7 kcal/mol) would produce a significant excess of [6-²H]-**19** over [7-²H]-**19**. We conclude from these two alternative estimates that **3c** must be nearly isoenergetic with **3a** to account for the

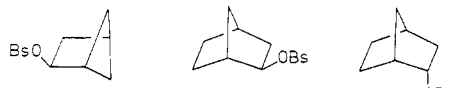
(21) Sauers, R. R.; Parent, R. A. *J. Org. Chem.* **1963**, *28*, 605. Sauers, R. R.; Parent, R. A.; Damle, S. B. *J. Am. Chem. Soc.* **1966**, *88*, 2257.
(22) Freeman, P. K.; Ziebarth, T. D.; Mallikarjuna Rao, V. N. *J. Org. Chem.* **1973**, *38*, 3823.
(23) For examples of protonated cyclopropanes = alkyl bridged carbocations, formed from tricycloalkanes, see: Kirmse, W.; Streu, J. *J. Org. Chem.* **1987**, *52*, 515.
(24) Renaud, R. N.; Stephens, J. C. *J. Labelled Compd.* **1972**, *8*, 509.

Table III. Rate Constants (k) for Solvolyses of *p*-Bromobenzenesulfonates in 80% (v/v) Ethanol/Water[a]

substrate[b]	T, °C	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$ eu
22 (exo)	50.0	$(4.65 \pm 0.02) \times 10^{-4}$		
	25.0	$(2.02 \pm 0.02) \times 10^{-5}$	23.4	−1.5
23 (endo)	50.0	$(5.7 \pm 0.1) \times 10^{-4}$		
	25.0	$(2.59 \pm 0.03) \times 10^{-5}$	23.1	−2.2
41	75.0	$(6.11 \pm 0.04) \times 10^{-4}$		
	50.0	$(4.12 \pm 0.14) \times 10^{-5}$	23.5	−6.2
	25.0[c]	1.8×10^{-6}		
42 (exo)	25.0[d]	$(1.41 \pm 0.02) \times 10^{-3}$	(20.0)[e]	(−7.9)[e]
43 (endo)	25.0[c,f]	1.6×10^{-6}		

[a] Determined conductimetrically in duplicate except where noted otherwise; errors shown are average deviations. [b] Structural formulas shown in Schemes III and VI. [c] Calculated from data at other temperatures. [d] Average of 28 spectrophotometric determinations; personal communication from Prof. B. L. Murr. See also ref 25. [e] For the tosylate (ref 26). [f] Extrapolated from data in 70% ethanol/water (ref 26) using the mY_{OTs} equation with $m = 0.69$ (ref 27).

Scheme VI



41 42 43

distribution of products and labels. In contrast, the norbornyl-type bridged ion **3b** appears to be inaccessible from **3a** since no deuterium is found at C-5 of **19** (Scheme V).

With **16** as the starting material, deuterium is distributed in a 3:1 ratio between positions 2 and 3 of **29** (Table II). This result is most reasonably interpreted in terms of concerted dediazoniation and rearrangement of the exo diazonium ion **25** to give the 3-tricyclo[3.3.0.$0^{2,6}$]octyl cation (**28**). The concerted route is not available to the endo diazonium ion **26**. Consequently, nitrous acid deamination of the endo amine [6-^{2}H]-**21** leads to a 1:1 ratio of [2-^{2}H]-**29** and [3-^{2}H]-**29**. The deuterium distribution in **32** is similar to that in **29**, suggesting that concerted fragmentation of **25** (→**31**) plays a minor role.

Kinetic Studies. Rate constants for solvolyses in 80% (v/v) ethanol/water are shown in Table III for the exo and endo brosylates (**22**, **23**) and, for comparison, the 2-bicyclo[2.1.1]hexyl (**41**) and 2-norbornyl brosylates (**42**, **43**) (Scheme VI). The exo:endo (**22**:**23**) rate ratio is 0.78 at 25 °C, much lower than the corresponding ratio of 880 for 2-norbornyl (**42**:**43**). Similar relative rates (1.05 and 1000 respectively) are shown in Table IV for solvolyses in 97% (w/w) trifluoroethanol/water (97T), a solvent of higher ionizing power and lower nucleophilicity than 80% ethanol/water.[31] The endo brosylate (**23**) solvolyzes in 97T, 64 times faster than **41** and 37 times faster than **43**, at least partly because of the inductive/hyperconjugative effects of the extra carbon atom(s).[32] Solvent effects (Table IV), shown as rate ratios in 97T/80% ethanol, for **22** and **23** are very similar to those for solvolyses of 2-adamantyl and

Table IV. Solvolysis Rate Constants in 97% (w/w) Trifluoroethanol/Water (97T) at 25 °C and Solvent Effects on the Reactivity of Secondary Alkyl *p*-Bromobenzenesulfonates

substrate	k_{97T}, s^{-1}	k_{97T}/k_{80E}[a]	m[b]	Q'[b]
22 (exo)	$(5.39 \pm 0.04) \times 10^{-4}$	27		
23 (endo)	$(5.13 \pm 0.16) \times 10^{-4}$	20		
41	$(8.0 \pm 0.2) \times 10^{-6}$	4.4		
42 (exo)	1.4×10^{-2}	10[c]	0.82	0.74
43 (endo)	1.4×10^{-5}	9[d]	0.69	0.60
pinacolyl		13[e]	0.82	0.76
1-adamantylmethylcarbinyl		58[f]	1.05	1.07
2-adamantyl		41[c,g,h]	1.0[i]	1.0[i]
2-propyl		0.14[e]	0.33	0.0[i]

[a] Rate ratio in 97% (w/w) trifluoroethanol/water:80% (v/v) ethanol/water; kinetic data for 80% ethanol from Table III. [b] For tosylates (see Table VII of ref 27). [c] Rate constant for 97T obtained by assuming a brosylate:tosylate rate ratio of 3 in 97% trifluoroethanol (ref 26). [d] Rate constant for 97T extrapolated from data in 85% trifluoroethanol (ref 26) using the mY_{OTs} equation with $m = 0.69$ (ref 27); the effect of added water is small (see also ref 28 and 29). [e] Data from ref 28. [f] Data from ref 29. [g] Assuming a brosylate:tosylate rate ratio of 5 in 80% ethanol/water (based on data from various sources, e.g., ref 30). [h] Data from ref 31. [i] By definition.

1-adamantylmethylcarbinyl sulfonates, and these data alone do not permit a distinction to be made between weak k_s and weak k_Δ mechanisms.[27]

Considering also the product data, it is suggested that solvolyses of **23** may proceed via equilibrating classical and weakly bridged cations (**3a** and **3c**) and by a weak k_s process with inversion of configuration. The results well illustrate the close approach to limiting (k_c) behavior as nucleophilic solvent assistance (k_s solvolysis) and anchimeric assistance (k_Δ solvolysis) are reduced. A direct route from exo substrates (**22**, **25**) to **28** (→**29**), and hence the possibility of a weak k_Δ pathway for solvolysis of **22**, is indicated by the incomplete equilibration of the deuterium label in **29**, produced from the photolysis of **16** (Table II). The results for **41** (Table IV) show a lower response to changes in solvent ionizing power, consistent with the more strongly assisted k_s and k_Δ processes discussed previously.[6]

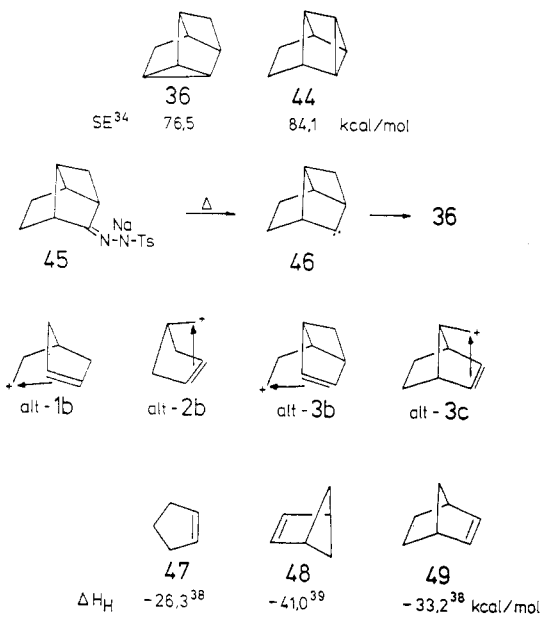
Discussion

Degenerate and nondegenerate rearrangements of 6-tricyclo[3.3.0.$0^{2,7}$]octyl cations both involve the cyclobutane ring. The exo products derive from the rapidly equilibrating unsymmetrical ion **3a**. The σ-delocalized structure **3c**, a likely contributor to the formation of endo products, was shown to be nearly isoenergetic (±0.5 kcal/mol) with **3a**. Hence, formation of **3c** can make at most only a small contribution to the greater reactivity of **23** compared with **43**. Both rate and product data are consistent with the absence of norbornyl-type Wagner–Meerwein rearrangement; i.e., the bridged ion **3b** must be ≥3 kcal/mol higher in energy than **3a**. At the MINDO/3 level of calculation, the energy of **3b** lies about 11 kcal/mol above **3c**.[33] The reduced extent of σ-bond delocalization, as compared to the parent systems (**1a** → **1b**,[1] **2a** → **2b**[6]), will be considered in terms of ring strain.

The tetracycloalkanes **36** and **44** were chosen initially as models for the cations **3b** and **3c**, respectively, although by incorporating a cyclopropane ring these models greatly exaggerate the strength of the partial bonding in the cations. According to MM2 force field calculations,[34] the

(25) Murr, B. L.; Conkling, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 3462.
(26) Harris, J. M.; Mount, D. L.; Raber, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 3139.
(27) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5466.
(28) Shiner, V. J., Jr.; Fisher, R. D.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 7748.
(29) Shiner, V. J., Jr.; Neumann, T. E.; Fisher, R. D. *J. Am. Chem. Soc.* **1982**, *104*, 354.
(30) Kevill, D. M.; Kolwyck, K. C.; Shold, D. M.; Kim, C.-B. *J. Am. Chem. Soc.* **1973**, *95*, 6022.
(31) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.
(32) Bentley, T. W.; Liggero, S. H.; Imhoff, M. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 1970.
(33) Bremer, M.; Schleyer, P. v. R., personal communication.
(34) MM2 force field, modified to account for the interaction of three- and four-membered rings: Roth, W. R., unpublished results.

Scheme VII



strain energy (SE) of **44** exceeds that of **36** by about 8 kcal/mol, i.e., the opposite order of stability from that deduced for the corresponding cations. In search for experimental support, we pyrolyzed the sodium salt **45** of tosylhydrazone **16**. C–H insertion of the carbene **46** afforded **36**[22] while **44**[35] was not detected (Scheme VII). These results support the MM2 predictions for **36** and **44**; hence "cyclopropane strain" does not model adequately the relative stabilities of **3b** and **3c**. In retrospect this is not surprising since computed structures of **1b**[36] and **2b**[7] display short basal (C-1–C-2) bonds (about 1.38 Å) and long distal (C-6–C-1,2) bonds (about 1.88 Å). Therefore, we should focus on the increase in strain associated with contraction of the basal (C-1–C-2) bond ("olefinic strain"), as shown in the π-complex alternative representation of bridged ions, emphasized by Dewar;[37] both alt-**1b** and alt-**2b** (Scheme VII) contain a cyclopentene ring while the C=C bonds of alt-**3b** and alt-**3c** are part of bicyclo[2.1.1]hexene (**48**) and norbornene (**49**), respectively. The heats of hydrogenation[38,39] indicate an extra strain energy of ca. 7 kcal/mol for norbornene (**49**) and of ca. 15 kcal/mol for bicyclo[2.1.1]hexene (**48**). Thus "olefinic strain" provides a rationale for the behavior of 6-tricyclo[3.3.0.$0^{2,7}$]octyl cations and appears to be a major factor in determining the relative stabilities of bridged ions.[40]

Experimental Section

General Methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Bruker WP-80 and AM-400 instruments in $CDCl_3$ solution, with tetramethylsilane as an internal reference. ^{2}H NMR spectra were determined in CCl_4 solution on the Bruker AM-400 spectrometer (61.42 MHz). Analytical GC separations were carried out on a Siemens Sichromat equipped with glass capillary columns. Varian Aerograph 920 instruments, equipped with packed glass columns, were used for preparative gas chromatography (PGC). High-pressure liquid chromatography (HPLC) was performed on a LDC instrument with 25 × 1.5 cm silica gel columns (Si 60, 5 μm, Macherey and Nagel).

Tricyclo[3.3.0.$0^{2,7}$]octan-6-one (17). A mixture of magnesium turnings (36 g, 1.6 mol) and THF (250 mL) was "activated" by dropwise addition of methyl iodide (0.5 mL). A solution of 3-chlorocyclopentene[41] (82 g, 0.8 mol) in THF (300 mL) was added over 6 h with stirring at −10 °C. The mixture was stirred at −10 °C for 1 h, and then a solution of acrolein (33.6 g, 0.6 mol) in THF (40 mL) was added slowly at −5 °C. The resulting solution was allowed to warm to room temperature. After being stirred for 1 h, the mixture was poured into ice (100 g) and decanted from excess magnesium. The precipitate was dissolved with 2 N H_2SO_4, and the organic layer was separated. The aqueous layer was extracted with ether (4 × 100 mL), and the combined organic extracts were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated. The residue was distilled to give 54.5 g (73%) of 1-cyclopent-2-en-1-ylprop-2-en-1-ol: bp 75–76 °C (15 mmHg); ^{1}H NMR δ 1.55–2.5 (m, 5 H), 2.85 (m, 1 H), 4.0 (m, 1 H), 5.0–5.4 (m, 2 H), 5.5–6.1 (m, 3 H). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.34; H, 9.56. GC indicated a 57:43 mixture of diastereomers.

To a solution of 1-cyclopent-2-en-1-ylprop-2-en-1-ol (42 g, 0.34 mol) in acetone (1 L) was added dropwise at 0–5 °C Jones reagent[42] (125 mL) until a red coloration persisted. After $NaHSO_3$ (3 g) and excess $NaHCO_3$ were added, the precipitate was separated and extracted with pentane. On addition of the pentane extracts to the aqueous acetone solution, two layers formed. The aqueous layer was extracted with pentane (3 × 100 mL), and the combined organic extracts were washed with brine and dried ($MgSO_4$). GC indicated 87.5% of 1-cyclopent-2-en-1-ylprop-2-en-1-one (**14**) and two more volatile, unidentified byproducts. A small sample of **14** was isolated by PGC (1.5 m, Carbowax, 90 °C): ^{1}H NMR δ 1.9–2.5 (m, 4 H), 3.87 (m, 1 H), 5.56–6.7 (m, 5 H).

The crude pentane solution of **14** (also containing some acetone) was irradiated for 24 h with a medium-pressure mercury arc (150 W). The conversion of **14** was monitored by GC. The mixture was concentrated to 150 mL under reduced pressure (300 mmHg). The remaining solvent was removed by fractional distillation (18-cm Vigreux column), and the residue was purified by bulb-to-bulb distillation in vacuo (0.1 mmHg). The crude product (10.3 g, containing 63% of **17**; yield 16%) was used in the preparation of alcohols, amines, etc. Pure samples were obtained by PGC (1.5 m, Carbowax, 100 °C): ^{1}H NMR δ 1.42 (dt, endo 3-H, $J_{3n,3x}$ = 13.5 Hz, $J_{3n,4n} \simeq J_{3n,4x}$ = 8.0 Hz), 1.60 (m, exo 3-H), 1.68 (d, endo 8-H, $J_{8n,8x}$ = 8.0 Hz), 2.0 (m, 4-H), 2.20 (dt, exo 8-H, $J_{8n,8x}$ = 8.0 Hz, $J_{1,8x} \simeq J_{7,8x}$ = 3.0 Hz), 2.53 (br s, 5-H), 2.71 (m, 1-H), 2.80 (dt, $J_{1,7}$ = 7.0 Hz, $J_{7,8x} \simeq J_{2,7}$ = 3.0 Hz), 2.87 (m, 2-H). The assignments were confirmed by H/H COSY.

Tricyclo[3.3.0.$0^{2,7}$]octan-6-one Tosylhydrazone (16). Ketone **17** (520 mg, 4.26 mmol) was added to a hot, saturated solution of tosylhydrazine (880 mg, 4.73 mmol) in methanol. Three drops of a saturated solutions of hydrogen chloride in methanol were added, and the mixture was heated at reflux for 2 h. After cooling slowly to room temperature, the mixture was left overnight in the refrigerator. The crystals of **16** were filtered with suction and recrystallized from ethanol to give 877 mg (71%) of **16**: mp 123–124 °C; ^{1}H NMR δ 1.3–2.15 (m, 7 H), 2.44 (s, 3 H), 2.45–2.75 (m, 2 H), 2.8–3.0 (m, 2 H), 7.30 (d, J = 8 Hz, 2 H), 7.85 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25; N, 9.65. Found: C, 61.80; H, 6.75; N, 10.26.

Tricyclo[3.3.0.$0^{2,7}$]octan-6-ols 19 and 20. To a suspension of $LiAlH_4$ (650 mg, 17 mmol) in ether (50 mL) was added ketone **17** (2.0 g, 16.5 mmol) in ether (30 mL). The mixture was stirred at reflux for 1 h. After cooling of the mixture to room temperature, water was added dropwise until a flaky hydroxide precipitate had formed. The solution was filtered, and the precipitate was washed several times with ether. The combined ethereal solutions were

(35) Stapersma, J.; Rood, I. D. C.; Klumpp, G. W. *Tetrahedron* **1982**, *38*, 191.

(36) (a) Yoshimine, M.; McLean, A. D.; Liu, B.; De Frees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185. (b) Goddard, J. D.; Osamura, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1982**, *104*, 3258. (c) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1983**, *105*, 5915.

(37) Dewar, M. J. S.; Reynolds, C. H. *J. Am. Chem. Soc.* **1984**, *106*, 1744 and references cited.

(38) Jensen, J. L. *Prog. Phys. Org. Chem.* **1976**, *12*, 189.

(39) Roth, W. R., unpublished results.

(40) The π-complex representation of the 4-tricyclo[3.3.0.$0^{2,7}$]octyl cation (**37**) includes a cyclopentene ring, so it will have less olefinic strain and the Wagner–Meerwein shift (→**38**) is then observed (Scheme IV).

(41) Moffett, R. B. *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 238.

(42) Curtis, R. G.; Heilbron, I.; Jones, E. R. H.; Woods, G. F. *J. Chem. Soc.* **1953**, *457*.

washed with brine, dried ($MgSO_4$), and concentrated to 2–3 mL by distillation through a Vigreux column. GC of the residue indicated a 10:90 ratio of **19** and **20**. The isomers were separated by HPLC (pentane/ether, 70:30) and purified by sublimation (60 °C, 15 mmHg).

Tricyclo[3.3.0.$0^{2,7}$]octan-*exo*-6-ol (**19**): 0.15 g (7.3%); mp 102 °C; ^{1}H NMR δ 1.25 (dt, endo 3-H, $J_{3n,3x}$ = 13 Hz, $J_{3n,4n} = J_{3n,4x}$ = 8 Hz), 1.32 (dddd, exo 3-H, $J_{3n,3x}$ = 13 Hz, $J_{3x,4x}$ = 10 Hz, $J_{3x,4n}$ = 8 Hz, $J_{2,3x}$ = 2.5 Hz), 1.52 (br s, OH), 1.62 (dddd, exo 4-H, $J_{4n,4x}$ = 12.5 Hz, $J_{3x,4x}$ = 10 Hz, $J_{3n,4x}$ = 8 Hz, $J_{4x,5}$ = 3 Hz), 1.77 (m, exo 8-H), 1.79 (d, endo 8-H, $J_{8n,8x}$ = 7.5 Hz), 1.83 (ddm, endo 4-H, $J_{4n,4x}$ = 12.5 Hz, $J_{3x,4n}$ = 8 Hz), 1.99 (br s, 5-H), 2.28 (m, 1-H), 2.35 (m, 2-H), 2.48 (m, 7-H), 3.82 (d, 6-H, $J_{6,7}$ = 2.8 Hz). The assignments were confirmed by H/H COSY and by the ^{1}H NMR spectrum of [7-^{2}H]-**19**, which showed strongly reduced signal intensity at δ 2.48 and a singlet at δ 3.82 (6-H). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.03; H, 9.65.

Tricyclo[3.3.0.$0^{2,7}$]octan-*endo*-6-ol (**20**): 1.1 g (53.6%); mp 107 °C; ^{1}H NMR δ 1.12 (d, endo 8-H, $J_{8n,8x}$ = 7.5 Hz), 1.35–1.6 (m, 5 H), 2.03 (m, endo 4-H), 2.30 (dt, 7-H, $J_{1,7}$ = 7 Hz, $J_{2,7} = J_{7,8x}$ = 3 Hz), 2.34 (m, 2-H), 2.38–2.43 (m, 1-H, 5-H), 4.11 (d, $J_{5,6}$ = 6.2 Hz). The partial assignment was confirmed by H/H COSY and by the ^{1}H NMR spectrum of [7-^{2}H]-**20**, which showed strongly reduced signal intensity (25%) at δ 2.30 and two doublets ($\Delta\delta$ = 2 Hz, ratio 25:75) at δ 1.12. Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.29; H, 9.82.

Tricyclo[3.3.0.$0^{2,7}$]oct-6-yl *p*-Bromobenzenesulfonates 22 and 23. To a solution of **19** (0.12 g, 1.0 mmol) in anhydrous pyridine (2.5 mL) was added at 0 °C *p*-bromobenzenesulfonyl chloride (0.31 g, 1.2 mmol). The mixture was stirred at 0 °C for 2 h, kept in the refrigerator for 2 days, poured into ice/water (10 mL), and extracted with ether (4 × 10 mL). The extracts were washed with dilute sulfuric acid, aqueous $NaHCO_3$, and water. Drying ($MgSO_4$) and evaporating the ether solution afforded **22** (203 mg, 58%) as a solid, which was recrystallized from ether/pentane: mp 82–83 °C; ^{1}H NMR δ 1.2–1.9 (m, 6 H), 2.2–2.7 (m, 4 H), 4.53 (d, J = 2.4 Hz, 1 H), 7.75 (m, 4 H).

Analogously, alcohol **20** (0.50 g, 4.03 mmol) and *p*-bromobenzenesulfonyl chloride (1.24 g, 4.86 mmol) in pyridine (6 mL) afforded the endo brosylate **23** (1.21 g, 88%): mp 85–87 °C; ^{1}H NMR δ 1.17 (d, J = 8.0 Hz, 1 H), 1.3–1.9 (m, 4 H), 2.05 (m, 1 H), 2.3–2.7 (m, 4 H), 4.80 (d, J = 6.0 Hz, 1 H), 7.75 (m, 4 H). Anal. Calcd for $C_{14}H_{15}BrO_3S$: C, 48.99; H, 4.40. Found for **22**: C, 49.10; H, 4.54. Found for **23**: C, 49.04; H, 4.54.

Tricyclo[3.3.0.$0^{2,7}$]octan-*endo*-6-amine (21). The ketone **17** (1.3 g, 10.7 mmol), hydroxylamine hydrochloride (1.12 g, 16.1 mmol), ethanol (12 mL), and pyridine (1.11 g, 14.1 mmol) were heated at reflux for 3 h. After evaporation of the solvents in vacuo, the residue was extracted with ether. The extracts were washed with water, dried ($MgSO_4$), and evaporated. The solid was recrystallized from pentane to yield 0.90 g (55%) of oxime **18**: mp 83–85 °C; ^{1}H NMR δ 1.15–2.35 (m, 6 H), 2.4–2.8 (m, 2 H), 3.29 (br s, 0.73 H), 3.65 (br s, 0.27 H) (syn/anti isomers), 7.8 (br s, 1 H).

To a solution of oxime **18** (0.69 g, 4.5 mmol) in anhydrous acetic acid (70 mL) was added Adams' catalyst (PtO_2, 100 mg). The mixture was hydrogenated at atmospheric pressure and room temperature. After filtration, concentrated hydrochloric acid (15 mL) was added. The mixture was evaporated to dryness, and the residue was dissolved in water (80 mL). The aqueous solution was washed with ether, made alkaline (NaOH), and extracted with ether. The extracts were dried (K_2CO_3) and concentrated by distillation (normal pressure, Vigreux column). GC indicated **21** and **24** in a 98:2 ratio. Anhydrous hydrogen chloride was passed into the solution. The precipitate was filtered with suction and recrystallized from ethyl acetate/methanol to give **21**·HCl (552 mg, 77%): mp 195 °C; ^{1}H NMR (D_2O) δ 1.23 (d, J = 7.6 Hz, 1 H), 1.3–1.9 (m, 5 H), 2.35–2.7 (m, 4 H), 3.48 (br d, J = 6 Hz, 1 H). Anal. Calcd for $C_8H_{14}ClN$: C, 60.16; H, 8.84; N, 8.78. Found: C, 60.13; H, 8.82; N, 8.84.

Tricyclo[3.3.0.$0^{2,7}$]octan-*exo*-6-amine (24). Brosylate **23** (0.35 g, 1 mmol), tributylhexadecylphosphonium azide[43] (615 mg, 1.3 mmol), and anhydrous toluene (40 mL) were stirred at 90 °C for 3 days. Progress of the reaction was monitored by IR ($Q^+N_3^-$ 2000 cm^{-1}, RN_3 2100 cm^{-1}). The mixture was concentrated (80 °C, 300 mmHg) and distilled bulb-to-bulb (0.01 mmHg). The toluene solution of the azide thus obtained was hydrogenated (PtO_2, room temperature, atmospheric pressure). After filtration, anhydrous hydrogen chloride was passed into the solution. Evaporation to dryness gave a colorless solid (0.14 g, 87%). A small sample of the crude hydrochloride was converted to the amine ($NaOH/Et_2O$) and analyzed by GC: **21** (4.8%), **24** (95.2%). The major portion was recrystallized from ethyl acetate/methanol to give **24**·HCl: mp 192–194 °C; ^{1}H NMR (D_2O) δ 1.1–2.0 (m, 6 H), 2.15–2.65 (m, 4 H), 3.10 (br s, 1 H). Anal. Calcd for $C_8H_{14}ClN$: C, 60.16; H, 8.84; N, 8.78. Found: C, 60.13; H, 8.77; N, 8.76.

Tricyclo[3.3.0.$0^{2,6}$]octan-3-one tosylhydrazone (27) was obtained from the analogous ketone,[19] as described for **16**: yield, 58%; mp 186–188 °C; ^{1}H NMR δ 1.75–2.7 (m, 8 H), 2.42 (s, 3 H), 7.29 (d, J = 8 Hz, 2 H), 7.85 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25; N, 9.65. Found: C, 61.89; H, 6.30; N, 9.56.

Bicyclo[3.3.0]oct-6-en-2-one tosylhydrazone (30) was prepared analogously from the appropriate ketone:[20] yield, 69%; mp 122–123 °C; ^{1}H NMR δ 1.55–3.8 (m, 8 H), 2.45 (s, 3 H), 5.35–5.75 (m, 2 H), 7.30 (d, J = 8 Hz, 2 H), 7.85 (d, J = 8 Hz, 2 H). Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 62.04; H, 6.25; N, 9.65. Found: C, 62.25; H, 6.30; N, 9.82.

Solvolyses of the Brosylates. Product Studies. The brosylates **22** and **23** (34 mg, 0.1 mmol), 2,6-lutidine (65 mg, 0.6 mmol), and dioxane/water (70:30, 1 mL) were heated at 80 °C for 20 h. The mixture was diluted with brine and extracted with ether. The extracts were washed with dilute hydrochloric acid and with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and concentrated to 1–2 mL by distillation (Vigreux column). The figures in Table I are averages values from GC analyses on three different capillary columns (30 m, heptaglycol isononyl phenyl ether, 100 °C; 39 m, Carbowax 2000, 100 °C; 75 m, neopentyl glycol sebacate, 130 °C). The products were identified by comparison with authentic samples, in the order of elution: **29**,[19] **35**,[20] **39** (see below), **19**, **20**, **40**,[21] **32**,[20] **33**.[20]

Kinetic Studies. Rate constants were obtained by using dilute solutions ($<10^{-3}$ M) as described previously,[27] with extensive use of ultrasonics to dissolve the substrates before kinetic data were obtained (Tables III and IV).

Dediazoniation Reactions. The tosylhydrazones **16**, **27**, and **30** (30 mg, 1 mmol) were photolyzed (medium-pressure mercury arc, 150 W, Pyrex vessel) in 5 mL of 0.2 M NaOH for 30 min. The solution was saturated with sodium chloride, extracted with ether, and analyzed as above (Table I). For the redistribution of a 6-^{2}H label (Table II), the tosylhydrazone **16** (0.36 g, 1.2 mmol) was irradiated for 3 h in 20 mL of 0.2 M $NaOD/D_2O$. The product mixture, isolated as above, was separated by HPLC (pentane/ether, 70:30) to give pure (>98%) **19** and **20**, as well as a mixture of **29**, **32**, and **35**. PGC (2.5 m, Carbowax, 150 °C) served to isolate **29** and **32**. ^{2}H NMR revealed the distribution of deuterium in **19** (δ 2.30, 48%; 3.60, 52%), **20** (δ 2.21, 48%; 4.00, 52%), and **29** (δ 1.84, 75%; 4.38, 25%). Overlap of the signals of 6-H and 7-H precluded analogous analysis of **32**. The ^{13}C NMR spectrum of **32** ($CDCl_3$: δ 28.5, C-4; 32.9, C-3; 37.9, C-8; 49.0, C-5; 49.5, C-1; 80.9, C-2; 128.4, C-7; 134.1, C-6) has been assigned.[44] The following isotopic shifts and intensities were observed with our sample of ^{2}H-**32**: δ 37.863 (20%, [7-^{2}H]-**32**), 37.962 (80%, [6-^{2}H]-**32**); 49.050 (80%, [6-^{2}H]-**32**), 49.156 (20%, [7-^{2}H]-**32**).

The amine hydrochlorides **21**·HCl and **24**·HCl (24 mg, 0.15 mmol) were dissolved in 10 mL of water and 10 mL of ether. The aqueous phase was adjusted to pH 3.7 (glass electrode) with dilute perchloric acid. Solutions of sodium nitrite (75 mg, 1.1 mmol in 2 mL of water) and of perchloric acid (0.1 M) were concurrently added to keep the pH at 3.5–3.8. Stirring was continued for 16 h at room temperature. The ether phase was separated, and the aqueous phase was extracted with ether (3 × 10 mL). The combined ether solutions were washed with saturated $NaHCO_3$ solution, dried ($MgSO_4$), and treated with $LiAlH_4$ (0.1 g). The mixture was heated at reflux for 1 h, hydrolyzed with a few drops of water, filtered, concentrated, and analyzed by GC (Table I).

(43) Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796. Landini, D.; Maia, A.; Montanari, F. *Nouv. J. Chim.* **1979**, *3*, 575.

(44) Whitesell, J. K.; Matthews, R. S. *J. Org. Chem.* **1977**, *42*, 3878.

The preparation of **21**, described above, was adapted to give [6-^{2}H]-**21** by using D_2/DOAc in the hydrogenation of **18**. The deamination of [6-^{2}H]-**21**·HCl (0.45 g, 2.8 mmole was achieved with sodium nitrite (1.0 g, 14.7 mmol) and perchloric acid in a biphasic system of water (30 mL) and ether (15 mL). Workup as above, followed by HPLC and GC (cf. photolysis of **16**), afforded the major products. ^{2}H NMR: **19** δ 2.36 (47%), 3.68 (53%); **20** δ 2.26 (49%), 4.03 (51%); **29** δ 1.85 (50%), 4.39 (50%). ^{13}C NMR of **29**: δ 37.797 (50%), 37.894 (50%); 48.948 (50%), 49.048 (50%).

Tetracyclo[3.3.0.0^{2,8}.0^{3,6}]octane (36). The tosylhydrazone **16** (0.80 mg, 2.7 mmol) and sodium hydride (0.11 g, 2.75 mmol, 60% suspension in paraffin) were stirred in anhydrous THF (20 mL) for 3 h. Pentane (30 mL) was added, and stirring was continued for 2 h. The sodium salt of **16** (0.80 g, 95%) was filtered by suction, washed with pentane, and dried in vacuo. The sodium salt was introduced slowly under vacuum (0.005 mmHg) into a flask which was preheated to 230–250 °C. Volatiles were collected in a receiver cooled with liquid nitrogen. According to GC, the product was 99% pure, and the yield was 88%. The spectra were in agreement with literature data for **36**, obtained from a different source.[22]

For acidolysis, samples (20–25 mg) of **36** were stirred in a sealed vessel with dioxane/H_2SO_4 (70:30). The product ratios **39**:**40** were fairly independent of acidity and conversion: 0.5 N H_2SO_4, 25 °C, 3 days, 8% conversion, 20:80; 0.5 N H_2SO_4, 60 °C, 2 days, 93% conversion, 17:83; 1.0 N H_2SO_4, 25 °C, 3 days, 10% conversion, 19:81; 1.0 N H_2SO_4, 60 °C, 2 days, 100% conversion, 17:83. In a preparative run, **36** (0.23 g, 2.6 mmol) was treated with dioxane/1.0 N H_2SO_4 (7:3, 7 mL) at 60 °C for 3 days. The mixture was diluted with ether and washed with water and saturated $NaHCO_3$ solution. The ether solution was dried ($MgSO_4$) and concentrated by distillation (Vigreux column). The products **39** (17%) and **40** (83%) were separated by HPLC (pentane/ether, 70:30). ^{1}H NMR of **39**: δ 0.89 (dt, endo 6-H, $J_{6n,6x}$ = 11.0 Hz, $J_{1,6n} \simeq J_{6n,7}$ = 1.5 Hz), 1.12 (d, endo 8-H, $J_{8n,8x}$ = 7.2 Hz), 1.22 (dm, exo 3-H, $J_{3n,3x}$ = 14.0 Hz), 1.45 (br dd, exo 6-H, $J_{6n,6x}$ = 11.0 Hz, $J_{5,6x}$ = 7.5 Hz), 1.71 (dd, endo 3-H, $J_{3n,3x}$ = 14.0 Hz, $J_{3n,4}$ = 5.8 Hz), 1.73 (m, exo 8-H), 2.23 (m, 3 H), 2.52 (m, 1 H), 4.20 (br d, 4-H, $J_{3n,4}$ = 5.8 Hz). Comparison of this spectrum with those of **19** and **20** strongly suggests that **39** is tricyclo[3.3.0.0^{2,7}]octan-*exo*-4-ol. ^{1}H NMR of **40**: δ 1.16 (d, endo 4-H, $J_{4n,4x}$ = 9.0 Hz), 1.27 (dm, anti 7-H, $J_{7a,7s}$ = 11.0 Hz), 1.36 (dm, endo 8-H, $J_{8n,8x}$ = 12.5 Hz), 1.57 (m, exo 8-H + OH), 1.79 (dm, syn 7-H, $J_{7a,7s}$ = 11.0 Hz), 2.08 (m, 3-H), 2.16 (m, exo 4-H + 5-H), 2.49 (br s, 1-H), 2.78 (m, 6-H), 3.84 (s, 2-H). These data (400 MHz + COSY) are in agreement with the reported 60-MHz spectrum[21] and confirmed the assignment of **40** as tricyclo[3.2.1.0^{3,6}]octan-*exo*-2-ol.

Coupling Reactions of 4-*tert*-Butyl-*o*-benzoquinone with Olefinic Compounds

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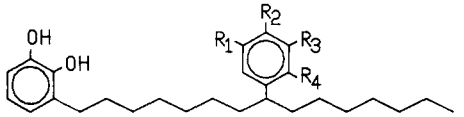
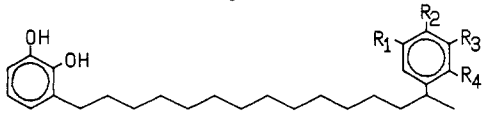
Room-temperature bulk reactions of 4-*tert*-butyl-*o*-benzoquinone (**5**) and four alkenes, 1,4-pentadiene (**6**), methyl sorbate (**7**), methyl linoleate (**8**), and 3-[8′(*Z*),11′(*E*),13′(*Z*)-pentadecatrienyl]veratrole (**9**) have been studied. Reactions with methylene-interrupted olefins **6**, **8**, and **9** afforded C–O and C–C linked 1:1 adducts through dehydrogenation paths, whereas the cycloaddition product **13** was exclusively produced by the reaction with **7**. Comparing the product distribution of these reactions and the orientations predicted by the reactivities of possible reaction species, the hydride ion transfer mechanism has been inferred to dominate in the reaction of **5** and triene **9**. On the other hand, the radical path involving the transfer of a hydrogen atom has been favored for reactions of **6** and **8**.

Quinones and olefins are ubiquitously distributed in biological systems, and reactions between these two classes of substances play significant roles in various stages of biological functions. In the previous paper,[1] we disclosed that physiological oxidation of urushiol in sap of the lac tree, *Rhus vernicifera*, yielded a series of nucleus side chain bound dimers of urushiol, **1** and **2**. It was postulated that

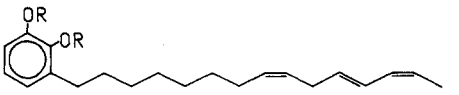


1



2

R_1=R_2=OH, R_3=$C_{15}H_{31}$, R_4=H
R_1=H, R_2=R_3=OH, R_4=$C_{15}H_{31}$
R_1=H, R_2=$C_{15}H_{31}$, R_3=R_4=OH



3 R=H
9 R=CH_3

4 R=$C_{15}H_{31-2n}$ n=1, 2, 3

these dimers were derived through dehydrogenation of the trienyl side chain of the main urushiol congener **3** with urushiol quinone **4** which was produced by laccase-mediated oxidation of urushiol.

Several studies were concerned with dehydrogenation-addition reactions of high-potential quinones with alkenes as hydrogen donors.[2] Diethers were derived from reactions of aryl-substituted olefins with DDQ or *o*-chloranil, and the hydride ion transfer mechanism accounted for features of these reactions.[2b] While some simple olefins undergo dehydrogenation–addition with *o*-chloranil in addition to

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(1) Oshima, R.; Yamauchi, Y.; Watanabe, C.; Kumanotani, J. *J. Org. Chem.* **1985**, *50*, 2613–2621.

0022-3263/88/1953-3073$01.50/0