Studies of Benzonorbornene and Derivatives. III.
The Solvolysis of *syn*- and *anti*-7-Bromobenzonorbornadiene and Related Bromides[1,2]

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The rates and activation parameters of the solvolysis of the *ac*-bromobenzonorbornenes and -dienes in 80% ethanol have been reported. The bromides show a spread in reactivity of 10^{10} between the slowest bromide amenable to study, *syn*-7-bromobenzonorbornene (4), and the fastest, *syn*-7-bromobenzonorbornadiene (7). All the solvolyses were cleanly first order and nearly theoretical infinity titers were observed. Normal *exo/endo* and *syn/anti* epimeric rate ratios were found. The bromides show a close similarity in these rate ratios to the corresponding brosylates (where known), although entropic factors seem more important for the rates of the bromides. In all but one case, from the solvolyses in aqueous dioxane containing 2,6-lutidine, one member of an epimeric pair gave structurally and stereochemically retained alcohol while the other did not. The exception was the case of the 7-bromobenzonorbornadienes (6 and 7). Each gave retained alcohol product, even though the *syn* epimer 7 is 44,000 times faster in rate than the *anti* epimer 6. The matter is briefly discussed. The bridgehead bromides were essentially inert. 1-Bromobenzonorbornadiene (9) does undergo reaction with hot alcoholic silver nitrate, but the forcing conditions suggest a pathway unrelated to normal solvolysis.

Since Bartlett and Giddings first reported[4] the acetolysis of benzonorbornenyl and -dienyl brosylates in 1960, these systems have ranked among the favorites for studies in solvolytic participation. The results have shown that the aromatic ring participates either as a phenonium ion (A)[5,6] or as a symmetrical ion

A   B

C   D
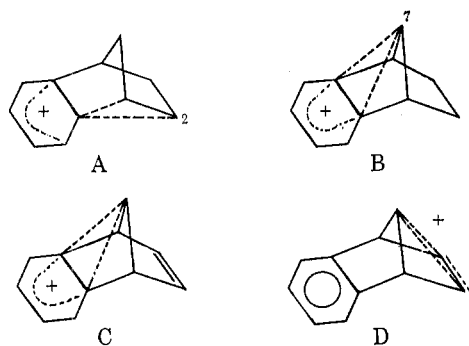
(B),[7] depending upon the site of solvolysis, C-2 or C-7. The rate data imply that assistance *via* A is more effective than *via* B,[4,8] though steric factors aside from participation may play a sizable role in the rate differences observed.[9] The incorporation of a double bond, however, increases participation as in C and an estimate of 10^4 in driving force was given for this increase.[4]

It therefore became of interest to see if the stereoelectronic "holding power" of C could match that of the related *syn*-7-benzonorbornadienyl-derived cation D (shown so as to emphasize its relationship to the firmly holding *anti*-7-norbornenyl cation[10]).[11] Having developed syntheses for the bromide precursors to C and D,[1a] we were able to investigate this point. Our results indicate that C and D are indeed nonequilibrating in 80% ethanol because the bromides solvolyze with retention in each case.

Results and Discussion

Rates.—Table I gives the kinetic and activation parameter data for the bromides while Table II shows some comparisons of the rates within these systems. The solvolyses were smoothly first order in all cases where actual rates are given. It may be seen that the expected *exo/endo* and *anti/syn* epimeric rate ratios are observed in these bromides *vis-à-vis* the corresponding brosylates. Indeed, when compared with *exo*-2-norbornyl, the bromides and brosylates show a close similarity (Table III). Extensive discussion of these rate differences in brosylates has appeared[4,5,7–9] and the matter for the bromides will not be dwelled upon here, but certain aspects are worth mentioning in passing.

First entropic differences appear more significant in the determination of the rates of the bromides than the tosylates. For example, $\Delta(\Delta H^*)$ for 3 and 4 is 0.7 kcal mol^{-1} while $\Delta(\Delta S^*)$ is 10.7 eu. The corresponding values for the brosylates are 3.9 kcal mol^{-1} and 2.7 eu.[13]

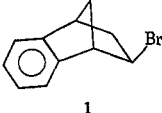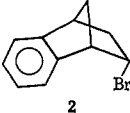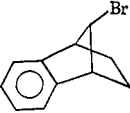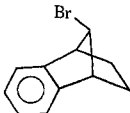Second, the effect of an aromatic ring compared with a double bond in participatory ability can be seen in

(1) (a) For paper II, see J. W. Wilt and P. J. Chenier, *J. Org. Chem.*, **35**, 1562 (1970). (b) Some of this work has appeared in preliminary form: J. W. Wilt and P. J. Chenier, *J. Amer. Chem. Soc.*, **90**, 7366 (1968); the Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wis., June 1968, Abstracts of Papers, p 36.

(2) Taken from the Dissertation of P. J. C., Loyola University of Chicago, 1969.

(3) National Science Foundation Trainee, 1965–1968; University Fellow, 1968–1969.

(4) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

(5) (a) W. P. Giddings and J. Dirlam, *ibid.*, **85**, 3900 (1963). (b) D. V. Braddon, G. A. Wiley, J. Dirlam, and S. Winstein, *ibid.*, **90**, 1901 (1968).

(6) This intermediate has also been demonstrated in certain additions to benzonorbornadiene by S. J. Cristol and R. Caple, *J. Org. Chem.*, **31**, 2741 (1966).

(7) The evidence for this symmetrical ion has been summarized by H. Tanida, *Accounts Chem. Res.*, **1**, 239 (1968).

(8) (a) H. Tanida, T. Tsuji, and S. Teratake, *J. Org. Chem.*, **32**, 4121 (1967). See, however, (b) H. Tanida, H. Ishibobi, and T. Irie, *J. Amer. Chem. Soc.*, **90**, 2688 (1968). For a recent study of A, *cf.* H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *ibid.*, **91**, 4512 (1969).

(9) H. C. Brown and G. L. Tritle, *ibid.*, **88**, 1320 (1966); **90**, 2689 (1968).

(10) (a) S. Winstein, M. Shatavsky, C. J. Norton, and R. B. Woodward, *ibid.*, **77**, 4183 (1955); (b) S. Winstein, M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) W. G. Woods, R. A. Carboni and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

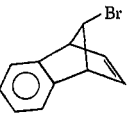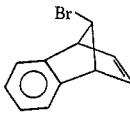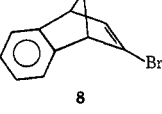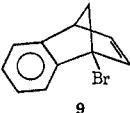(11) During the course of this work, the acetolysis of the epimeric 7-chlorobenzonorbornadienes and 5,12-diphenyl-6,11-dihydro-6,11-(chloromethano)naphthacenes was reported.[12] As do the corresponding bromides,[1b] these chlorides also give retained product. The *syn*-7 chloride analogous to bromide 7 showed peculiar kinetics in acetolysis, unlike the clean behavior of 7 in the present work. We thank Professor Cristol for preprints of this related work.

(12) S. J. Cristol and G. W. Nachtigall, *ibid.*, **90**, 7132, 7133 (1968).

(13) (a) Data for *anti*-7 brosylate from H. Tanida, T. Tsuji, and H. Ishitobi, *ibid.*, **86**, 4904 (1964). (b) Data for the *syn*-7 brosylate from H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *ibid.*, **89**, 2928 (1967).

TABLE I

RATE DATA FOR BROMIDES IN 80% (v/v) ETHANOL CONTAINING 1.2 EQUIV OF SODIUM ACETATE[a]

| Bromobenzonorbornene or -diene	Temp, °C[b]	$10^5 k_1$, sec^{-1} [c]	ΔH^*, kcal mol^{-1}	ΔS^*, eu
1	79.5	5.19 ± 0.49		
	89.2	13.5 ± 1.1		
	100.1	35.6 ± 7.9		
	(25.0)	$(1 \times 10^{-7})^d$	23.3 ± 0.7	−12.5 ± 1.8
2	121.0	0.151 ± 0.012		
	131.7	0.392 ± 0.024		
	139.3	0.676 ± 0.121		
	(25.0)	$(4 \times 10^{-11})^d$	25.0 ± 2.2	−22.3 ± 5.4
3	120.2	0.605 ± 0.161		
	130.4	1.54 ± 0.16		
	137.5	2.90 ± 0.34		
	(25.0)	$(4 \times 10^{-11})^{d,e}$	28.7 ± 0.2	−10.3 ± 0.5
4	179.3	0.173 ± 0.026		
	187.0	0.317 ± 0.042		
	195.7	0.573 ± 0.049		
	(25.0)	$(5 \times 10^{-14})^d$	29.4 ± 1.7	−21.0 ± 3.7
5	196	*ca.* 0[f]		
6	79.2	1.18 ± 0.07		
	89.8	3.27 ± 0.38		
	98.6	7.92 ± 2.12		
	(25.0)	$(2.4 \pm 10^{-8})^d$	23.6 ± 1.3	−14.6 ± 3.5
7	19.4	50.1 ± 7.9[g]		
	25.4	109 ± 16		
	32.9	238 ± 39		
	(25.0)	$(1.05 \pm 10^{-3})^d$	20.6 ± 1.4	−3.3 ± 4.6
8	25	0[h]		
9	100	0[i]		

[a] Except as noted (also, see Experimental Section). [b] Control was within 0.5° except for 4 (±1°) and 7 (±0.2°). [c] Normal increases in rate (1–6%) were observed for bromides 1–3 and 6 when the sodium acetate concentration was doubled. [d] Calculated from data at other temperatures. [e] The temperature coefficients of 2 and 3 cross between 25 and 120°; so the two bromides show comparable reactivity upon extrapolation to 25°, whereas 3 is somewhat faster at the higher temperatures. [f] *Ca.* 7% reaction observed after 24 hr with no further change after 97 hr (see Experimental Section). [g] Rate by conductometry in 80% (v/v) ethanol without sodium acetate present. The Volhard method was used for the others. [h] Immediate reaction with silver nitrate in 95% alcohol. [i] Reaction after 88 hr with alcoholic silver nitrate.

Table IV. Unfortunately, several desirable norbornenyl bromides have not apparently been studied and the data in places involves some extrapolation from the analogous chlorides, as indicated. In any event, the values confirm the belief[4] that aromatic π participation is less favorable than olefinic π participation in all instances. However, at C-2 the difference between the two is much less, indicating that less participation is involved and that steric factors are important in the *exo/endo* ratio at this position.[8,9]

Products.—In Table V are collected the products of solvolysis for most of the bromides. The procedure involved and the characterization of the products is reserved for the Experimental Section. Bromide 1 solvolyzed with *retention* (albeit undoubtedly *via* the phenonium ion A which would allow racemization in an

TABLE II

RELATIVE SOLVOLYTIC REACTIVITIES OF BENZONORBORNENYL
AND -DIENYL SUBSTRATES

Bromides[a]
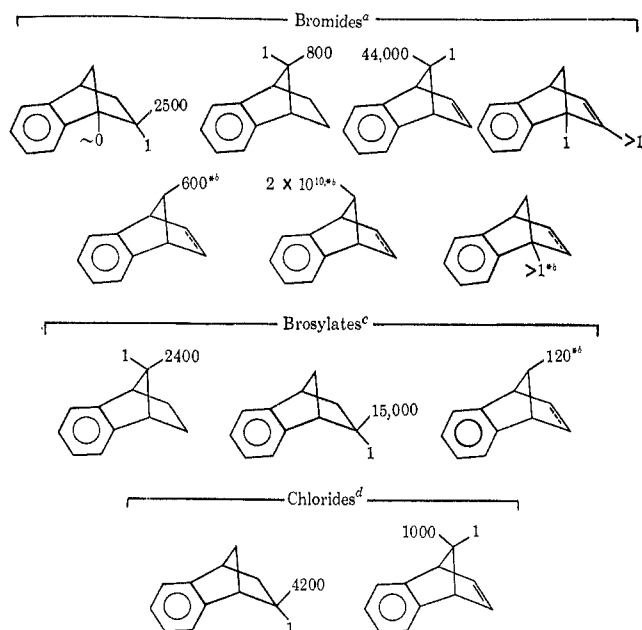
[a] In 80% ethanol, 25°. From Table I. [b] Value marked with an asterisk is the benzonorbornadienyl/benzonorbornenyl rate ratio. [c] In acetic acid, 25°; for the *anti/syn* ratio at 50°, see ref 13b; for the *exo/endo* ratio, see ref 4 and 8a; for the asterisk value, see ref 4. [d] For the *exo/endo* ratio at 77.6° in 70% acetone, see ref 8b; for the *syn/anti* ratio at 81.9° in acetic acid, see ref 12.

TABLE III

BROMIDES[a] *vs.* BROSYLATES[b] RELATIVE TO *exo*-2-NORBORNYL[c]
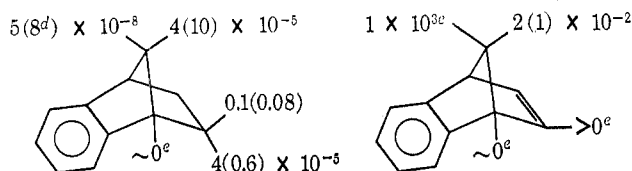
[a] Present work in 80% ethanol at 25°. [b] Brosylate rates in HOAc at 25° were taken from ref 4, 8a, and 13b. The brosylate ratios are in parentheses. [c] The values used for *exo*-2-norbornyl: bromide, 1.1×10^{-6} sec^{-1} [J. W. Wilt and W. J. Wagner, *J. Amer. Chem. Soc.*, **90**, 6135 (1968)]; brosylate, 8.82×10^{-5} sec^{-1} [S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *ibid.*, **74**, 1127 (1952)]. The ratios are rounded off to one significant figure. [d] Extrapolated from data in ref 13b. [e] As yet unknown.

active substrate[5a]), whereas its epimer **2** solvolyzed with *inversion*. Presumably, the process took the following course, analogous to that followed by *endo*-2-norbornyl bromide[14] and by *endo*-2-benzonorbornenyl
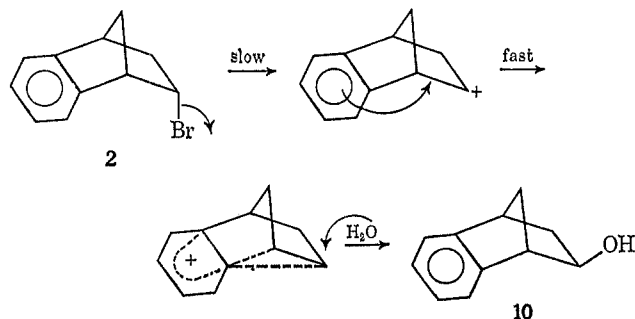
(14) (a) J. D. Roberts, W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72**, 3329 (1950). (b) J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

TABLE IV

PARTICIPATION OF AROMATIC (Ar π) *vs.* OLEFINIC (π)
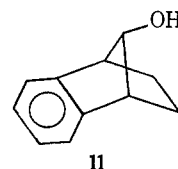π-ELECTRON SYSTEMS
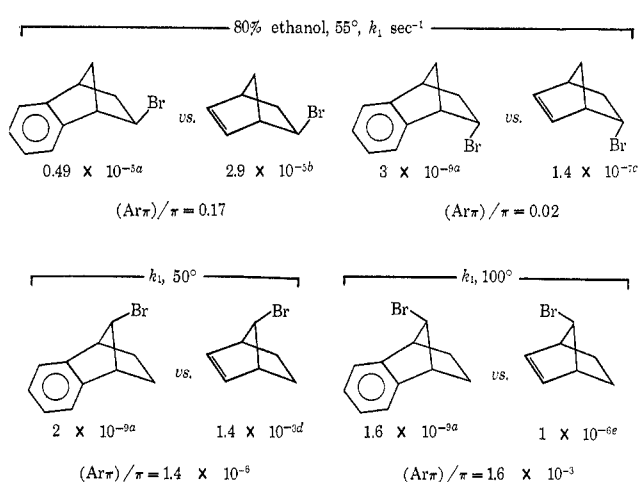
[a] Calculated from data in Table I. [b] Extrapolated from data in ref 10b. [c] The value 0.017 hr^{-1} is given in ref 14a. As this is in error,[14b] but has not been corrected, we have assumed that the bromide is as fast at 55° as is the chloride at 85°. The latter has the value 1.4×10^{-7} sec^{-1} at 85°. [d] Calculated from data for the chloride[10c] increased by 16-fold. This factor was employed because it is the ratio of rates of *exo*-2-norbornyl and *exo*-2-benzonorbornenyl bromides *vs.* chlorides (for the former, *cf.* ref 10b and c; for the latter, *cf.* this work and ref 6). [e] Calculated from data for the chloride[10c] again using the factor 16.[d] As the chloride was studied in 50% ethanol, an additional factor of $1/36$ was used to correct its rate to 80% ethanol. This factor was found by comparing the rates of other chlorides studied in both solvents.[10c]

TABLE V

PRODUCTS OF THE SOLVOLYSIS OF THE BROMIDES IN
70% DIOXANE CONTAINING 2,6-LUTIDINE[a,b]

Bromide	Product	% yield[c]
1	10	~100
2	10	98
3	11	92
4[d]	12	*anti*,[e] 90.5
		syn, 9.5
5	[f]	
6	13	74[g]
7	14	85[g]
8	[h]	
9	[i]	

[a] Except as noted. [b] This system was chosen to simplify product analysis. Use of sodium acetate in aqueous dioxane gave some acetate ester products. [c] Isolated yields. The crude reaction materials showed no contamination by other alcohols. [d] Products obtained from kinetic study (Table I). [e] By nmr analysis; see Experimental Section. [f] No product study made as **5** is inert. [g] These alcohols are somewhat sensitive substances and the lower yields reflect this. No other products were observed in the crude product, however. [h] Benzonorbornen-2-one is the probable, but not proved, product. [i] Not determined.

brosylate.[4] Similarly, bromides **3** and **4** behaved as expected. Bromide **3** *via* ion B[7] afforded *retained* product (*anti*-7 alcohol **11**) just as does the corresponding brosylate[4] and *anti*-7-norbornenyl brosylate.[10] The *rearrangement* to **12** attending **4** in sol-

volysis, shown below, is the same as that found by Tanida and coworkers for the brosylate,[13b,15] and by Winstein's group for *syn*-7-norbornenyl brosylate.[16]
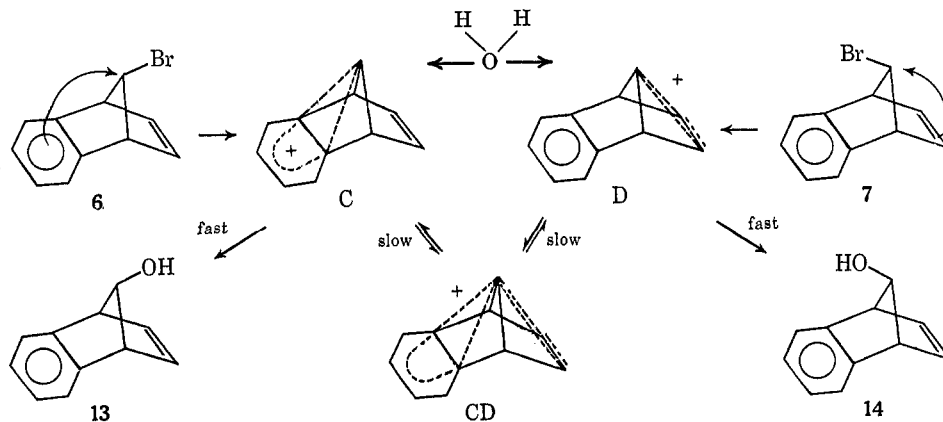

4

12
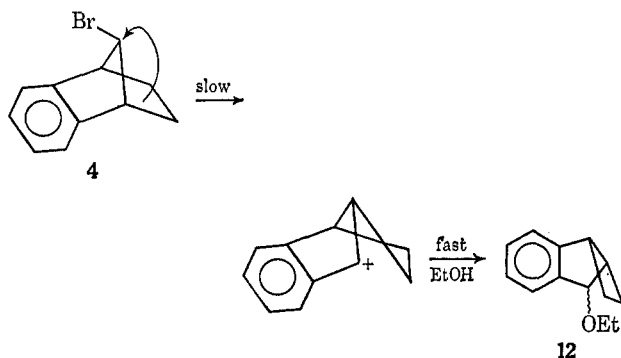
The most noteworthy aspect of the study is, of course, the behavior of bromides **6** and **7** which is unprecedented. Even though much different in rate (k_7/k_6 = 44,000), and even though the driving force due to the *anti* π system in each bromide is much different (600-fold in **6**, 2 × 10^{10} fold in **7**), each epimer gave *retained alcohol*. The *anti*-7 alcohol **13** (mp 104°, CHOH, δ 3.89) is readily differentiable from the *syn*-7 alcohol **14** (mp 94°, CHOH, δ 4.25).

The integrity of 7-norbornadienyl cations is well established by low temperature nmr studies.[17] There is an energy barrier to bridge flipping, dependent
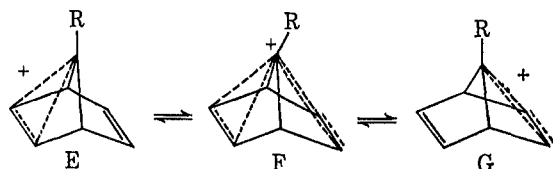
upon the nature of R, ranging from under 7.6 to over 19 kcal mol^{-1}. The behavior of bromides **6** and **7** illustrates this barrier to bridge flipping in another way, *viz.*, the formation of retained alcohol product faster

is clouded in controversy, some of which has been touched upon in the present systems by Cristol and Nachtigall.[18]

The Bridgehead and Vinyl Bromides.—Lastly, the lack of reactivity (Table I) in the bridgehead bromide **5** is not unexpected because such halides are characteristically inert. The possibility for benzylic stabilization of the cation from **5** is absent, undoubtedly for stereoelectronic reasons. Interestingly, both 2- and

5

14
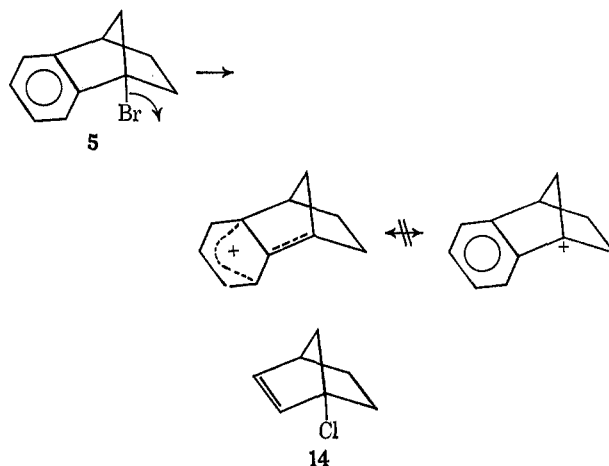
1-bromobenzonorbornadiene (**8** and **9**) appeared to undergo to slight solvolysis (Table I). Similar slight reactivity has been reported for 1-chloronorbornene (**14**)[19] and its origin is intriguing,[20] but, because our studies on these halides are continuing, discussion of this point will be deferred.

Experimental Section

Melting points and boiling points are uncorrected for stem exposure. The former were taken on a Fisher-Johns block. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. Nuclear magnetic resonance (nmr) spectra are given in δ values and were determined on a Varian A-60A spec-

from C and D than their equilibration under the conditions employed, as shown.

It should also be mentioned as a disclaimer that the representations C, CD, and D are used for simplicity. The "real" nature of 7-norbornenyl and -dienyl cations

trometer, using 15% solutions in the solvent listed with 1% TMS (δ 0.0) added. The usual abbreviations for splittings are used. Proton integrations were within 10% of the proper value. Infrared (ir) spectra were taken on a Beckman IR-5A instrument

(15) H. Tanida, Y. Hata, and H. Ishitobi, *Tetrahedron Lett.*, 361 (1967).

(16) S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, **79**, 505 (1957); S. Winstein, F. Gadient, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(17) R. K. Lustgarten, M. Brookhart and S. Winstein, *ibid.*, **89**, 6350, 6352, 6354 (1967). E, F, and G may be even more complex than shown.

(18) See ref 12 for citations on the controversy and brief discussion.

(19) J. W. Wilt, C. F. Parsons, C. A. Scheider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

(20) The addition of hydrogen chloride (CCl₄, −78°) proceeds much faster to 2-chloronorbornene than to **14** [A. J. Fry and W. B. Farnham, *Tetrahedron Lett.*, 3345 (1968)]. This may be relevant to the reactivities of **8** and **9** found in the present work if in some way a proton addition is indeed involved in their solvolyses.

and are given in microns (μ). Only significant absorptions are recorded. Gas-liquid partition chromatography (glpc) was performed on a Wilkens (Varian) Aerograph Model A-90P with helium gas carrier. Reoplex 400 is polypropylene glycol adipate.

Materials.—The bromides were available as described:[1a] **1**, thrice distilled, bp 88–89° (1 mm) n^{16}D 1.5950, d^{27}_4 1.405, no *endo* by nmr, glpc inapplicable as **1** decomposes; **2**, twice distilled, bp 105–106° (2 mm), 96% pure by glpc, contained some **8** and some *endo*-2-*t*-butoxybenzonorbornene; **3**, twice distilled, bp 91–103° (0.9–1.1 mm), low-melting solid, 99% pure by glpc (contained 1% benzonorbornene); **4**, thrice recrystallized, mp 122–123°, pure by glpc; **5**,[21] once distilled, bp 68–70° (0.1 mm), 96% pure by glpc, contaminant(s) unknown; **6**, twice distilled, bp 100–107° (1.2 mm), mp 52°, pure by glpc; **7**, once recrystallized, mp 60°, glpc inapplicable as **7** decomposes; **8**, once distilled, bp 80.5–81° (0.9 mm), 98% pure by glpc, contained some 2-*t*-butoxybenzonorbornadiene; **9**, collected twice by glpc, negative to alcoholic silver nitrate at room temperature.

Kinetic Procedure. Volhard.[22]—Solutions of the bromide and sodium acetate trihydrate, 0.03 M and 0.036 M, respectively, were made in 80% absolute ethanol–20% water (v/v). Aliquots were sealed in ampoules and thermostated at the given temperature (see Table I). For determinations, the contents of the ampoules were vigorously shaken with petroleum ether (bp 30–60°) followed by water. The aqueous phase was then titrated for bromide ion by the Volhard method. The first point (0 time) was taken after 10 min at the temperature used. The rates are believed accurate to within 5%. Identical runs were made using 0.072 M sodium acetate trihydrate to check salt effects and SN2 components. The increased rates were 1–6% higher (normal salt effects).

Kinetic Procedure. Conductance.[22]—Bromide **7** was much too fast for the Volhard procedure above (its half-time is 11 min at 25° whereas that of **4** is 4 million years). A typical conductance run is described. Bromide **7** (46.4 mg) was quickly dissolved in absolute ethanol (4 ml) in a Freas cell at the appropriate temperature, followed by 80% ethanol (2 ml) and distilled water (1 ml), giving 0.03 M bromide. The conductance was measured immediately using an Industrial Instruments, Model RC-16B2, 1000-cps, ac, bridge. The infinity conductance was taken after 10 half-lives. The technique was checked with pure *t*-butyl bromide, k_1 = 4.2 × 10^{-4} sec^{-1} at 25.9°, lit.[23] k_1 = 3.85 × 10^{-4} at 25°. Bromide **7** is nearly three times faster.

Calculations.[22]—For the Volhard method, a plot of $-\ln$ [milliliters of KSCN$_t$ − milliliters of KSCN$_\infty$] *vs.* time gave the first-order rate constant, while, for the conductance method, a plot of $-\ln$ ($C_\infty - C_t$) *vs.* time was used. First-order kinetics were very good throughout the runs. The infinity titers follow (average of four determinations): **1**, 96%; **2**, 93%; **3**, 93%; **4**, 98%; **6**, 92%; **7**, 92% (one value by Volhard method after 21 hr at 25°). The activation parameters were calculated in the usual way from the Eyring equation. The errors listed in Table I for these parameters are average deviations for ΔH^* and ΔS^* computed graphically *via* the best (visual) straight-line fit of the data.

Product Studies.—Bromide **1** (0.5 g) in 70% purified dioxane–20% water (v/v, 25 ml) containing redistilled 2,6-lutidine (0.29 g, 1.2 equiv) was refluxed for 22 hr. Water (200 ml) was added and the solution then was thoroughly extracted with ether. The ether extracts were made neutral, rinsed, dried, and evaporated to afford crude *exo*-2-benzonorbornenol (**10**, 0.38 g, quantitative yield, homogeneous on Reoplex 400 at 193°) which was recrystallized from petroleum ether (bp 30–60°)–ether: mp 71–74°, lit.[4] mp 74.1–75.4°; δ^{CCl_4} 7.26–6.9 (m, ArH, AA'BB'), 4.05–3.83 (m, CHOH), 3.63 (s, OH, variable), 3.4–3.15 (m, bridgehead H's), 2.25–1.6 (m, other ring H's). The ir,[4] nmr, and glpc comparisons of **10** with authentic material confirmed its structure. No *endo* alcohol [ir;[4] δ^{CCl_4} 7.3–6.8 (m, ArH, AA'BB'), 4.5–4.1 (m, CHOH), 3.3–3.0 (m, bridgehead H's), 2.4–1.9 (seven-line m, *exo*-3 H, 1.9–1.4 (m, bridge H's), 1.0 (s, OH, variable), 0.8–0.5 (dt, *endo*-3 H)[24]] was observed in the ir or nmr spectra of the crude solvolysis product. Use of sodium acetate (1.2 equiv) instead of lutidine produced 12% *exo*-2-benzonorbornenyl acetate (δ^{CCl_4} 2.04 (s, –OCOCH₃, confirmed with that known) along with **10**.

Bromide **2** (1.22 g) similarly treated in 70% dioxane (100 ml) and lutidine at 150° for 310 hr gave crude **10** (0.86 g, 98%, purified mp 71.5–74.0°), again confirmed *via* ir, nmr, and glpc analysis. No other product was found.
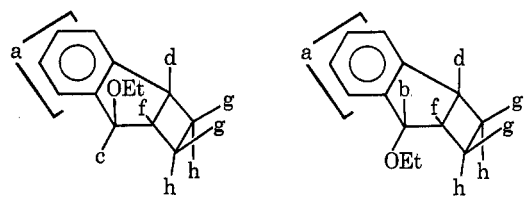
Bromide **3** (2.01 g) so treated at 150° for 144 hr gave *anti*-7-**benzonorbornenol** (**11**, 1.33 g, 92%, mp 92–100°, recrystallized as above to mp 100–104°, lit.[4] mp 104.1–105.7, 105.6–107.1, and 103–104.6°). Identification was made *via* ir,[4] nmr,[25] and glpc comparison with authentic material. No other product was seen.

Since sealed vessels containing bromide **4** in 70% dioxane at 200° exploded, the petroleum ether washes of the kinetic study ampoules were combined, washed, dried, and evaporated. The oily solid residue was studied by glpc on Reoplex 400 at 185°. The first fraction was a mixture of ethyl ethers **12** (see following text) while bromide **4** was the second. Alcohol products were not observed, presumably being retained on this column. The bulk residue was therefore taken up in acetone and chilled to precipitate unchanged **4**. The mother liquor was then chromatographed on Reoplex 400 at 185° to afford *anti*- and *syn*-2-**ethoxybenzo[3,4]bicyclo[3.2.0]hept-3-ene** (**12**) as an oil: ir λ^{neat} 3.4–3.6, 7.54, 9.15–9.30, and 13.32 μ.

Anal. Calcd for C₁₃H₁₆O: C, 82.93; H, 8.57. Found: C, 82.89; H, 8.45.

The nmr spectrum was quite complex and is given in Table VI. From the integrations of protons b and c there appeared to

TABLE VI

anti-12   *syn*-12

Proton	δ^{CCl_4}	J, cps
a	7.0–7.6 (m)	
b	4.98 (d)	bf, 7
c	4.55 (broad s)	cf, 0
d	3.5–4.0 (m)	
–OCH₂CH₃ (e)	3.42 (q)	ei, 7
f	2.9–3.2 (m)	
g	1.9–2.6 (m)	
h	1.4–1.9 (m)	
–OCH₂CH₃ (i)	1.1 (t)	

be 87–94% *anti*-12 and 6–13% *syn*-12. Tanida and coworkers reported the corresponding alcohols: proton b, δ^{CCl_4} 5.26 (d, J = 7.1 cps); proton c, δ^{CCl_4} 4.66 (s). The ratio of alcohols (*anti/syn* = 98.6:1.4) found by the Tanida group was sensitive to conditions (*syn* epimerized to *anti*).

No product was isolated from bromide **5** because of its inertness (Table I). The slight reaction (*ca.* 7%) is believed to be due to contamination of **5** by a 1,2-dibromide by-product of the Hunsdiecker reaction used to prepare **5**.

Treatment of bromide **6** (1.33 g) in aqueous dioxane–lutidine as above (reflux, 71 hr) afforded crude *anti*-7-**benzonorbornadienol** (**13**, 0.7 g, 74%, mp 90–104°, lit.[4] mp 106.3–108.2°). The nmr[26] and ir[4] spectra of the crude product were identical with those of authentic material. Alcohol **13** decomposed on Reoplex 400 at 200°. The two major fractions were apparently aldehydes (yellow oil): ir λ^{neat} 3.58, 3.70, and 5.96 μ; nmr δ^{CDCl_3} 9.77 (s) and 20.5 (s), naphthalene pattern in aromatic region. Similar behavior has been noted for **13** by others.[4] The crude **13** was acetylated in pyridine to only *anti*-7-**benzonorbornadienyl acetate** (oil, 183° from Reoplex 400): ir λ^{neat} 3.3, 5.76, 8.15, 9.6, and 14.3; δ^{CCl_4} 7.07 (m, ArH, A₂B₂), 6.55 (m, HC=CH), 4.65 (m,

(21) We thank Dr. Henry F. Dabek, Jr., for this bromide, prepared as given in his dissertation, Loyola University of Chicago, 1969.

(22) For complete details, the dissertation of P. J. C.[2] should be consulted.

(23) O. T. Benfey, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2494 (1952).

(24) G. Gutman, M.S. Thesis, Loyola University of Chicago, 1966.

(25) K. Tori, K. Aono, Y. Hata, R. Muneyuki, T. Tsuji, and H. Tanida, *Tetrahedron Lett.*, 9 (1966).

(26) S. J. Cristol and G. W. Nachtigall, *J. Org. Chem.*, **32**, 3738 (1967).

-CHOAc), 3.97 (q, bridgehead H's), 1.92 (s, -OCOCH₃); lit.[27] mp 56-57°.

Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.79; H, 6.18.

The *crude* solvolysis product (0.13 g) was also hydrogenated in absolute ethanol (2.5 hr, 5% Pd–C) to afford *only anti-7-benzonorbornenol* (11, 0.12 g), the spectra and glpc behavior of which matched that of authentic 11. No nmr resonance at δ 3.97 due to the saturated *syn* epimer[25] could be detected, even at high amplitude.

The small quantity of bromide 7 available necessitated a smaller scale product study. Bromide 7 (0.1 g) was allowed to stand in 70% dioxane (5 ml) containing lutidine (0.058 g, 1.2 equiv) at room temperature for 22 hr. Processing as before gave *syn-7-benzonorbornadienol* (14, 0.061 g, 85%): mp 94-94.8° after three recrystallizations from petroleum ether (bp 30-60°); ir λ^{KBr} 3.01, 3.34, 9.22, 9.41, 13.71, and 14.40; δ^{CDCl_3} 7.0-7.6 (m, ArH, A₂B₂), 6.7 (t, HC=CH), 4.1-4.4 (broad m, CHOH), 3.73 (q, bridgehead H's, $J_{\text{bridgehead vinyl}}$ = 2.5, $J_{\text{bridgehead CHOH}}$ = 1.5 cps), 2.1-2.6 (broad s, OH).

Anal. Calcd for $C_{11}H_{10}O$: C, 83.51; H, 6.37. Found: C, 83.43; H, 6.37.

The crude solvolysate showed no trace of the *anti* epimer 13, whose –CHOH resonance at δ 3.89 (m)[26] is readily discernible from that of 14 [δ 4.1-4.4 (m)]. Also, the two epimers have several differences in the ir that make contamination obvious, and the crude solvolysate showed only 14. Alcohol 14, like 13,

decomposed over Reoplex at 200°, apparently again yielding aldehydes of as yet unknown structure.

Some early attempts to study the rate of solvolysis of 7 in 80% ethanol containing 1.2 equiv of sodium acetate as described for the ether bromides afforded petroleum ether washes of the reaction material. Work-up of these as detailed for 1 led to an oily product that decomposed upon attempted glpc (see 14). Its spectra indicated it to be principally *syn-7-ethoxybenzonorbornadiene* [δ^{CCl_4} 6.8-7.4 (m, Ar, H, A₂B₂), 6.67 (t, HC=CH), 3.97 (t, -CHOEt), 3.77 (q, bridgehead H's, $J_{\text{bridgehead vinyl}}$ = 2, $J_{\text{bridgehead CHOET}}$ = 1.5 cps), 3.39 (q, -OCH₂CH₃, J = 7 cps), 1.00 (t, -OCH₂CH₃)], although some acetate ester (λ^{neat} 5.79 μ) was also present. The triplet nature of the -CHOEt resonance indicated the *syn* stereochemistry of the ether.[28] Unfortunately, analytical material *via* glpc could not be obtained because of the lability of the compound.

Registry No.—1, 23526-72-9; 2, 23526-73-0; 3, 7605-11-0; 4, 23526-75-2; 5, 23537-58-8; 6, 7605-10-9; 7, 22436-26-6; *anti-12*, 23526-77-4; *syn-12*, 23552-88-7; 14, 23526-79-6; *anti-7*-benzonorbornadienyl acetate, 16031-3-9.

(27) Cristol and Nachtigall[12] in their preliminary report give this melting point. Our sample has not yet solidified, but the multiplet shown by the -CHOAc proton in the nmr spectrum and the other work described above support the structure.

(28) The stereochemistry of the proton at the bridge in 7-substituted benzonorbornenes and -dienes is better established by the nmr splittings than by chemical shifts. The matter has been discussed.[1a]

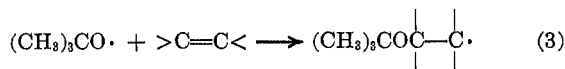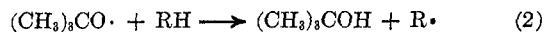# Reactions of Alkenes with Di-*t*-butyl Peroxide and *t*-Butyl Peroxypivalate

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A variety of alkenes structurally related to 4-vinylcyclohexene have been allowed to react with *t*-butoxy radicals from both di-*t*-butyl peroxide (DTBP) and *t*-butyl peroxypivalate (TBPP) to relate variations in reactivity and products to the structure of the alkenes. The major products were *t*-butyl alcohol and dehydro dimers when allylic hydrogen was present and vinyl unsaturation absent, as in the cycloalkenes (C₅–C₇). Addition dimers and polymer were also obtained when nonallylic radicals were formed in the presence of double bonds, as in cyclooctene and vinylcyclohexane. Minor amounts of acetone and *t*-butyl ethers were produced from β scisson and addition of *t*-butoxy radicals, respectively. More addition occurred with cyclooctene, alkenes with no allylic hydrogens, and conjugated alkenes. A decrease in relative reactivity toward hydrogen abstraction by *t*-butoxy radical was observed with increasing ring size from cyclopentene to cyclooctene. Other products from TBPP decomposition include carbon dioxide and products derived from *t*-butyl radical by addition, hydrogen transfer, and coupling reactions. Interactions of *t*-butyl and *t*-butoxy radicals, in or near the perester solvent cage, account for the formation of di-*t*-butyl ether and a portion of the *t*-butyl alcohol and isobutylene.

Three modes of reaction are available to *t*-butoxy radicals generated in the presence of alkenes.

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + CH_3\cdot \quad (1)$$

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot \quad (2)$$

$$(CH_3)_3CO\cdot + >C=C< \longrightarrow (CH_3)_3COC-C\cdot \quad (3)$$

Acetone indicates those *t*-butoxy radicals that are wasted by β scission (eq 1), *t*-butyl alcohol measures hydrogen abstraction (eq 2), and *t*-butyl ethers provide a measure of the addition reaction (eq 3).

Previous studies have shown[2-4] that *t*-butoxy radicals preferentially abstract the secondary allylic hydrogens

of 4-vinylcyclohexene to form *t*-butyl alcohol and biallyls rather than add to either double bond. On the other hand, an investigation[5] of the liquid-phase oxidation of cyclic alkenes disclosed that some 70% of the cyclooctene reacted by addition of oxy and peroxy radicals, although other cycloolefins gave mostly products derived from allylic hydrogen abstraction. Moreover, the overall rate of oxidation decreased in progressing from cyclopentene to cyclooctene.

These results led us to examine the reaction of a variety of alkenes structurally related to 4-vinylcyclohexene with *t*-butoxy radicals obtained by photolysis of di-*t*-butyl peroxide (DTBP) and by thermal decomposition of *t*-butyl peroxypivalate (TBPP). The objective of this work was to relate the observed reaction products and the relative reactivities toward *t*-butoxy radical attack to the structure of the alkenes. Ques-

(1) Taken from the Ph.D. Thesis of C. W. Uzelmeier, Case Institute of Technology, 1967.

(2) J. R. Shelton and J. N. Henderson, *J. Org. Chem.*, 26, 2185 (1961); J. R. Shelton and A. E. Champ, *ibid.*, 28, 1393 (1963).

(3) W. J. Farrissey, *ibid.*, 29, 391 (1964).

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(5) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Amer. Chem. Soc.*, 87, 4824 (1965).