and was isolated by filtration. The material obtained in this way was washed with water, dried, and recrystallized from ethanol–hexane; yield 2.1 g, mp 181.5–182.5°, ν_{max}^{Nujol} 3135, 2218, 1644, 1606, and 1582 cm^{-1}; λ_{max}^{EtOH} 220 (16,640) and 291 mμ (ϵ 8120).

Anal. Calcd for $C_{12}H_{11}O_2N$: C, 71.63; H, 5.51; N, 6.96. Found: C, 71.62; H, 5.64; N, 6.91.

Preparation of *p*-Toluenesulfonate (19b). The product of the preceding experiment (**19a**), 2.15 g, was dissolved in benzene, and 6.8 ml of pyridine and 2.84 g of *p*-toluenesulfonyl chloride were added. After standing at room temperature for 3 hr, the reaction mixture was poured into ice and concentrated hydrochloric acid. The product was taken into methylene chloride, and after the usual washing and drying operations, the solvent was evaporated. Crystallization of the crude product from methylene chloride–heptane afforded 3.3 g of material melting at 146.5–147.5°; ν_{max}^{Nujol} 2220, 1640, 1595, and 1575 cm^{-1}; λ_{max}^{EtOH} 215 (20,800), 285 (10,000), and 290 mμ (ϵ 10,400).

Anal. Calcd for $C_{19}H_{17}O_4NS$: C, 64.21; H, 4.82; N, 3.94; S, 9.02. Found: C, 64.33; H, 4.92; N, 3.55; S, 8.79.

Preparation of Cyano Malonate (20). A mineral oil dispersion of sodium hydride, 445 mg, containing 50% of the hydride, was washed with benzene and suspended in 45 ml of dry dioxane. Dimethyl malonate, 7.1 ml, was added with stirring. A dioxane solution of 3.17 g of tosylate **19b** was then introduced by dropwise addition, and the reaction mixture was stirred at room temperature for 2 days and at 80° for 2 hr. The product was isolated in the usual way by water dilution and ether extraction; yield 2.5 g, mp 103–106° (from hexane); ν_{max}^{film} 2210, 1733, 1620, and 1580 cm^{-1}; λ_{max}^{EtOH} 213 (15,300) and 285 mμ (ϵ 10,400).

Anal. Calcd for $C_{17}H_{17}O_5N$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.98; H, 5.50; N, 4.20.

Alkylation of Compound 20 with Trimethylene Dibromide. Cyano malonate (**20**), 1.16 g, was dissolved in 8.5 ml of dimethylformamide containing 1.05 equiv of potassium *t*-butoxide. The reaction vessel was flushed with nitrogen, and a threefold excess of trimethylene dibromide was added. The mixture was allowed to stand at room temperature for 4 days, at the end of which time another molar equivalent of trimethylene dibromide was added. The reaction was completed by heating to 60° for 8 hr and was then diluted with water and extracted with ether. After washing and drying, the solvent was removed, and the residual oil was chromatographed on silica gel. In addition to starting material there was obtained an amorphous product, ν_{max}^{film} 2210, 1740, 1618, and 1580 cm^{-1}.

Anal. Calcd for $C_{20}H_{22}ONBr$: Br, 18.3. Found: Br, 18.0.

The crude mixture obtained from 1.24 g of **20** was taken without chromatography and heated for several hours under vacuum to remove trimethylene dibromide. The material was then dissolved in 20 ml of benzene and 20 ml of dimethyl sulfoxide. To this solution there was added a twofold excess of benzene-washed sodium hydride–mineral oil dispersion, and the reaction mixture was stirred until hydrogen evolution ceased (24–48 hr). Standard work-up, followed by chromatography on silica gel afforded 770 mg of product (**22**), which melted at 130.5–131° after recrystallization from ether–petroleum ether; ν_{max}^{film} 2200, 1732, and 1600 cm^{-1}; λ_{max}^{EtOH} 273.5 (2340) and 281 mμ (ϵ 2450).

Anal. Calcd for $C_{20}H_{21}O_5N$: C, 67.59; H, 5.96; N, 3.94. Found: C, 67.49; H, 6.02; N, 3.97.

Catalytic Hydrogenation of Compound 22. A 300-mg sample of nitrile diester **22** in 50 ml of methanol was shaken with 30 mg of 10% palladized charcoal at 50–60° in a hydrogen atmosphere. When the uptake of hydrogen ceased, the solution was filtered, and the filtrate was evaporated to dryness. Chromatography of the residue on alumina afforded starting material **22**, a second substance which appeared to be dihydro **22**, and lactam ester **23**, mp 241.5–243.5°; $\lambda_{max}^{CH_2Cl_2}$ 2.95, 5.78, and 6.0 μ.

Anal. Calcd for $C_{19}H_{23}O_4N$: C, 69.28; H, 7.04; N, 4.25. Found: C, 69.35; H, 6.76; N, 3.99.

The Solvolysis of Bridgehead-Substituted *exo*-2-Norbornyl Bromides[1]

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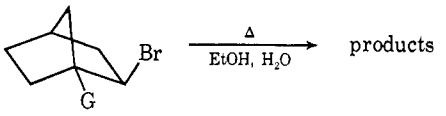
Abstract: The solvolysis of six bridgehead-substituted *exo*-2-norbornyl bromides in 80% aqueous ethanol is described: namely, the 1-carbomethoxy (**2**), 1-acetoxy (**3**), 1-benzamido (**4**), 1-amino (**5**), and 1-carboxylate (**6**), together with the parent bromide (**1**) itself. The solvolytic reactivity at 25° of the bromides **2**–**6** relative to that of **1** varies by 10^5-fold, the values being for **2**, 4.9×10^{-4}; for **3**, 2.4×10^{-3}; for **4**, 1.1; for **5**, 46; and for **6**, 4.0. Arguments are presented that these bromides represent a spectrum of solvolysis behavior. The rates illustrate a competition between inductive retardation and anchimeric acceleration by the bridgehead function, the latter effect growing in importance from **2** through **5**, with **6** being a somewhat special case apart. In no case does 1,6 σ-electron delocalization seem far advanced in the slow step of the solvolysis, thus affording a rationale for the greater deactivation by $-$I groups (**2** and **3**) than activation by +R groups (**4** and **5**). Even though unbridged ions intervene in some of these solvolyses, the solvolysis products are always *exo* substituted. Thus from **2** resulted the *exo*-ethoxy and *exo*-hydroxy analogs **9** and **10**, respectively. Some of the bromides underwent total rearrangement to norcamphor (**13**) *via* stabilized ions engendered by a Wagner–Meerwein rearrangement. The timing of this rearrangement varied from *after* the slow step (in **3**) to *simultaneously* with it (in **4** and **5**) The bromo acid anion **6** led to extensively rearranged products, again *exo* in nature, in this case the 2-ethoxy and 2-hydroxy esters **14** and **15**, respectively.

The solvolytic reactivites of many types of substituted norbornanes have been extensively investigated.[2] Bridgehead-substituted *exo*-2-norbornyl derivatives, however, are one of the less pursued classes. Only two groups, that of Schleyer[3] and that of Brown,[4]

(1) Taken from portions of the dissertation of W. J. W., June 1967. Part of this material was presented at the Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wis., June 1968, Abstracts of Papers, p 37.

(2) The solvolysis of no other system has been so extensively discussed and the references are myriad. However, for some reviews largely devoted to the norbornyl derivatives, *cf.*, J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3; B. Capon, *Quart. Rev.* (London), **18**, 45 (1964); P. D. Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965; G. D. Sargent, *Quart Rev.* (London), **20**, 301 (1966); G. E. Gream, *Rev. Pure Appl. Chem.*, **16**, 25 (1966); H. C. Brown, *Chem. Brit.*, 199 (1966); and H. C. Brown, *Chem. Eng. News*, **45**, No. 7, 87 (Feb 13, 1967).

Table I. Kinetic Data for Compounds 1–6[a]



Compound (G)	Temp, °C	$10^5 k_1$,[b] sec^{-1}	ΔH^*, kcal mol^{-1}	ΔS^*, eu	$k_{rel}^{25°}$
1 (–H)[c]	58.9	5.42 ± 0.14			
	66.0	10.8 ± 0.05			
	80.2	43.1 ± 2.2			
	(25.0)[d]	(1.1×10^{-6})	22.1 ± 0.5	−11.6 ± 1.2	1.0
2 ($-COOCH_3$)	102.3	0.316 ± 0.018			
	112.6	0.846 ± 0.089			
	119.8	1.28 ± 0.18			
	(25.0)[d]	(5.4×10^{-10})	24.4 ± 0.5	−19.5 ± 1.1	4.9×10^{-4}
3 ($-OCOCH_3$)	101.5	1.15 ± 0.06			
	112.0	3.44 ± 0.07			
	124.5	7.62 ± 0.14			
	(25.0)[d]	(2.6×10^{-9})	24.2 ± 1.0	−17.0 ± 2.4	2.4×10^{-3}
4 (–NHCOPh)	56.6	5.44 ± 0.16			
	66.5	15.6 ± 0.20			
	78.9	53.5 ± 0.20			
	(25.0)[d]	(1.2×10^{-6})	23.3 ± 0.4	−7.9 ± 1.2	1.1
5 ($-NH_2$)	20.3	2.99 ± 0.14			
	30.0	7.58 ± 0.72			
	37.7	15.2 ± 2.0			
	(25.0)[d]	(5.1×10^{-5})	16.4 ± 2.0	−23.5 ± 6.5	46
6 ($-COO^-$)[c]	40.6	5.06 ± 0.18			
	46.2	11.2 ± 0.10			
	51.1	22.9 ± 0.70			
	(25.0)[d]	(4.4×10^{-6})	29.2 ± 1.5	13.6 ± 3.3	4.0

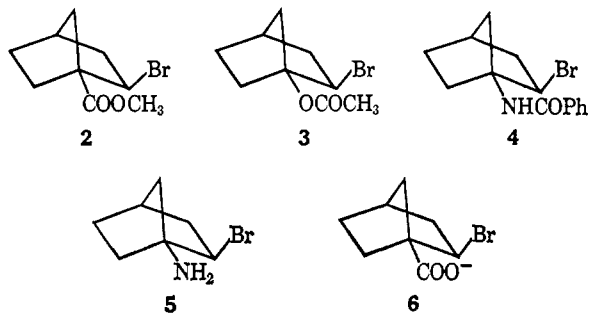
[a] The solvent was 80% ethanol–20% water (v/v). The initial bromide concentrations ranged from 0.01 to 0.04 *M*. An equivalent of sodium acetate trihydrate was employed to neutralize liberated acid for bromides **1–4**, while 2.3 equiv of sodium hydroxide was similarly used for bromide **5** (weighed as the hydrochloride salt) and bromide **6** (weighed as the free acid). The rates were followed titrimetrically by bromide ion release, using the Fajans method for bromides **1–4** and the Volhard method for bromides **5** and **6**. See the Experimental Section for details. [b] The reactions were cleanly first order to over 90% completion. [c] For data obtained by others, see text. [d] Rate constant calculated from data at other temperatures.

seem to have reported work in this area. They demonstrated that 1-positioned alkyl or aryl groups of various kinds did not dramatically affect (less than 100-fold) the acetolytic reactivity of the corresponding *exo*-2-norbornyl arenesulfonate.[5]

In the course of our work on the chemistry of 1-substituted norbornenes[6] we developed convenient syntheses of several 1-substituted *exo*-2-norbornyl bromides. With a view toward giving a wider range of substituents at the bridgehead position for mechanistic evaluation, we have determined the rates and products of the solvolysis of 1-carbomethoxy- (**2**), 1-acetoxy- (**3**), 1-benzamido- (**4**), 1-amino- (**5**), and 1-carboxy- (as the salt **6**) *exo*-2-norbornyl bromides. Decided rate effects, rearrangement differences, and persistent *exo* substitution attended these solvolyses, making their study particularly intriguing in view of the intense interest these days in the area of 2-norbornyl cationic species.

Results

The syntheses of the reactants **2–6** have been described earlier.[6] Their solvolysis in 80% ethanol was studied at various temperatures in the presence of either sodium acetate or sodium hydroxide. The kinetic data obtained for them, as well as for *exo*-2-norbornyl bromide (**1**) itself, are collected in Table I.



Preparative solvolyses were also performed. The products obtained are collected in Table II. The complex acidic product mixture from bromide **6** was analyzed after conversion to the methyl esters.

Some of the solvolysis products are known compounds and literature routes were employed to synthesize authentic samples for comparison. Compounds **9**, **10**, **14**, and **15** were apparently new, however. They were prepared from the corresponding acids **17** and **18** (both known, see later) by acid-catalyzed methylation followed by ethylation with ethyl iodide and silver oxide (Purdie method) as shown. The structures of these esters followed from their composition, manner of synthesis, and spectra. The spectra are listed in the Experimental Section, but those of the esters **9** and **14** were of enough interest to warrant brief mention here. The ethoxy group *exo* at C-2 in

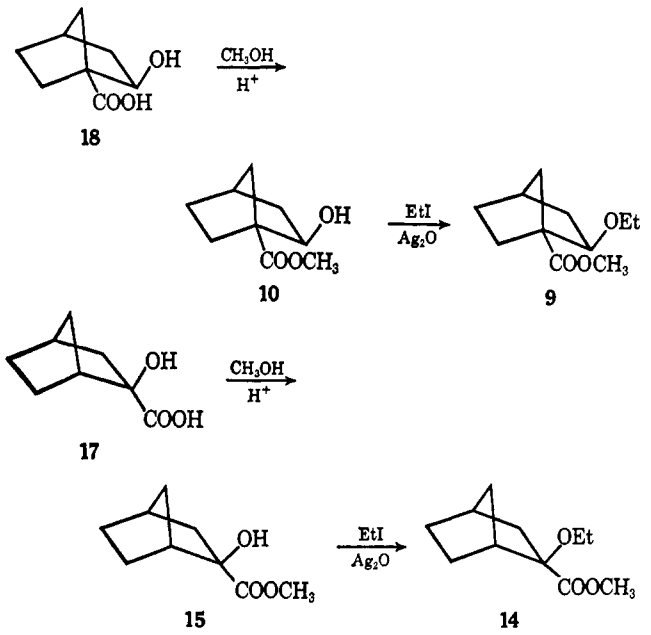
(3) D. C. Kleinfelter and P. von R. Schleyer, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept 1960, Abstracts, Paper 43P. For the syntheses and characterization of these compounds, *cf.*, D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961), and D. C. Kleinfelter, *ibid.*, **32**, 3526 (1967).

(4) H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1246 (1964). For related studies, see H. C. Brown and H. M. Bell, *ibid.*, **86**, 5003, 5006, 5007 (1964), and H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5005 (1964).

(5) H. C. Brown[2] has viewed this as incompatible with a delocalized 2-norbornyl cationic intermediate, while S. Winstein disagrees, *ibid.*, **87**, 381 (1965).

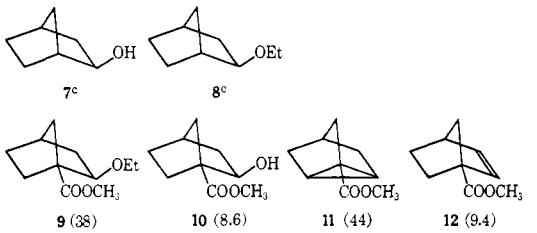
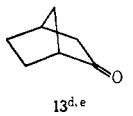
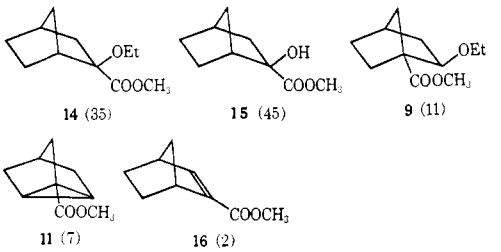
(6) J. W. Wilt, C. F. Parsons, C. A. Schneider, D. G. Schultenover, and W. J. Wagner, *J. Org. Chem.*, **33**, 694 (1968).

each ester presented an interesting case of magnetic nonequivalence of methylene protons.[7] Such non-



equivalence is customarily seen when a system $-CH_2-CXYZ$ is present, but even more distant asymmetry can cause the same effect. Undoubtedly the asymmetric carbon C-2 in each ester is responsible[8] for this nonequivalence in **9** and **14**. The $-OCH_2CH_3$ pattern from each ester was complex, but the AB nature of the methylene protons was clear. Depending on the rotational isomerization of the various conformations possible, contributions from A_2X_3 and ABX_3 spin patterns would be present. We were unable, however, to ascribe coupling constants with certainty other than $J_{AX} = 7$ cps. The spectra otherwise were those expected for norbornane derivatives, many of which have by now been discussed.[9]

Table II. Product Data[a] for Compounds 1–6

Compound	Product composn (%)[b]
2	
3,4, and 5	
6[f]	

[a] The preparative solvolyses employed *ca.* 0.04 *M* bromide under the same conditions used for the kinetic study (Table I). Bromides **1**, **4**, **5**, and **6** were refluxed for a short time, while bromides **2** and **3** were heated in sealed ampoules at 118° for 3 days and 20 hr, respectively. See the Experimental Section for details. [b] Isolated product yields were not determined in all cases but no other bicyclic products were seen in glpc analysis. The identity of the products was established by spectral and glpc comparison with authentic samples. [c] These products are assumed on the basis of prior findings in the literature. They were not determined in this work. [d] Norcamphor (**13**) was isolated on occasion as such, but normally its yield was based on its 2,4-dinitrophenylhydrazone derivative. No other bicyclic product was detected, although acetic acid and an ammonium salt undoubtedly accompanied **13** from **3** and **5**, respectively. [e] Benzamide was identified as a product from **4**. [f] Most of the *exo*-2-hydroxynorbornane-*endo*-2-carboxylic acid (**17**) was isolable as such. The rest of it and all of the other acidic products were determined as their methyl esters by treatment with diazomethane.

Discussion

***exo*-2-Norbornyl Bromide (1).** Several studies of the solvolysis of this bromide in 80% ethanol exist.[10,11] Perhaps the most recent data have been supplied by Vaughn, *et al.*:[12] $k_1 = 5.72 \times 10^{-5}$ sec^{-1} at 60° and 9.14×10^{-5} sec^{-1} at 65° in the presence of sodium carbonate; $E_{act.} = 21.9$ kcal mol^{-1} and $\Delta S^* = -17$ eu. Our conditions resembled those of Vaughn's group and the correspondence of our results (see Table I) with theirs is considered satisfactory.

Methyl *exo*-2-bromonorbornane-1-carboxylate (2) has been known for some time,[13] but no solvolytic data on it seem available. The bridgehead carbomethoxy group retarded the loss of bromide ion from **2** to a greater extent than did any other substituent studied (Table I, $k_{rel} = 4.9 \times 10^{-4}$). The Taft inductive parameter (σ^*) for a carbomethoxy group positioned β to a leaving group may be calculated[14] to be *ca.* +0.7, a sizeable −I inductive effect. Moreover, the relative rate of **2** is close to that observed by Gassman and Marshall[15] in the acetolysis of 7-keto-*exo*-2-norbornyl tosylate (**19**) compared to *exo*-2-norbornyl tosylate itself (6.2×10^{-4} at 25°). Because both **2** and **19** have carbonyl groups β to an *exo*-2 reaction site, each could exert similar inductive retardation.[16] Gassman and Marshall concluded that classical ionic intermediates were involved in the solvolyses of their 7-keto substrates, and we believe the same for **2**, as shown. All the products are those expected of the C-2

(7) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, p 99 ff.

(8) For nmr studies on benzyl alkyl ethers and neopentyl alkyl ethers where methylene proton nonequivalence resulted from asymmetry in the alkyl group, *cf.* G. M. Whitesides, *et al.*, *J. Amer. Chem. Soc.*, **87**, 1058 (1965), and references therein.

(9) For leading references, *cf.* R. V. Moen and H. S. Makowski, *Anal. Chem.*, **39**, 1860 (1967).

(10) J. D. Roberts, W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72**, 3329 (1950).

(11) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956).

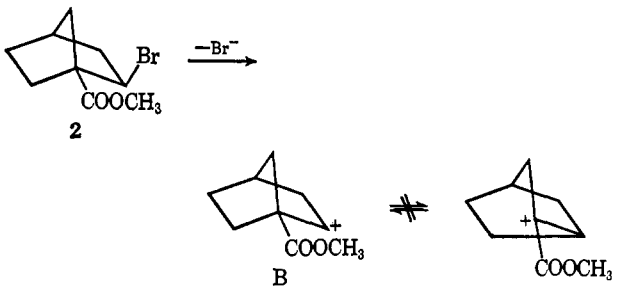
(12) W. R. Vaughn, R. Caple, J. Csapilla, and P. Scheiner, *ibid.*, **87**, 2204 (1965).

(13) W. R. Boehme, *ibid.*, **81**, 2762 (1959).

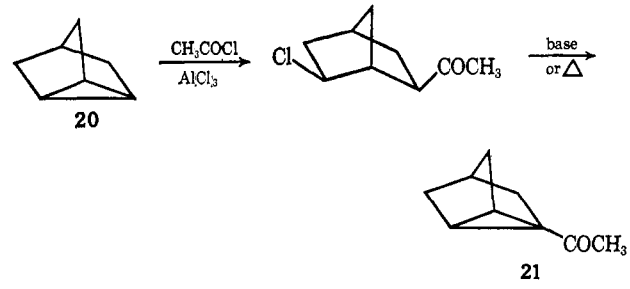
(14) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 125.

(15) P. G. Gassman and J. L. Marshall, *J. Amer. Chem. Soc.*, **88**, 2822 (1966). For a recent example of another study where the inductive effect of a carbonyl system has been determined in a molecule where participation is precluded, *cf.* R. M. Moriarty, C. R. Romain, and T. O. Lovett, *ibid.*, **89**, 3927 (1967).

(16) This perhaps overemphasizes the similarity of the systems and neglects their dissimilarity. The *exo*-tosylate **19** was slower in acetolysis than its *endo* epimer and both gave mixtures of *exo*- and *endo*-acetate products. In the case of **2**, no data are as yet available on the reactivity of its epimer, but the substitution products from **2** are only *exo*.



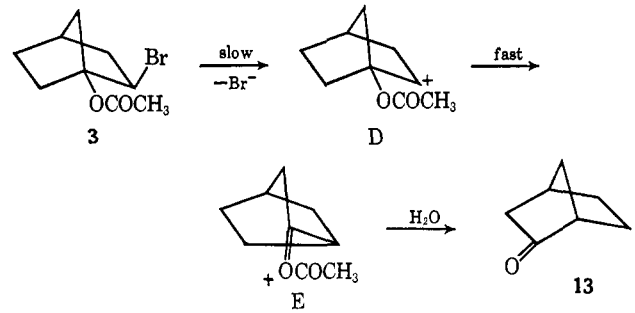
cationic intermediate B formed without 1,6 σ-electron participation, *i.e.*, an unassisted dissociation of **2** directly to B. Solvent capture from the *exo* side, by now a recognized feature of 2-norbornyl cation species that does not result necessarily from their possible delocalization but which is otherwise still somewhat obscure in origin,[17] can give **9** and **10**. Proton loss from C-6 and from C-3, again well-recognized processes,[18] can afford **11** and **12**. No product with a C-2 carbomethoxy function was observed. The high yield of ester **11** is of interest. In previous studies of *exo*-2-norbornyl derivatives, this type of product has been minimal (0–8%).[15,18–20] The present instance of 44% is thought to be a consequence of the conjugation possible in the activated complex between the incipient cyclopropane ring and the carbonyl group of the ester. Ester **11** has its carbonyl stretch at 1724 cm^{-1} (5.80 μ), indicating that the conjugation is similar to that of α,β-unsaturated or aromatic esters.[21] It is interesting that one other process leading to a high yield of a nortricyclene, *viz.*, the conversion of nortricyclene (**20**) to the ketone **21** by the treatment shown,[22] also results



in a carbonyl group at the bridgehead of the product.

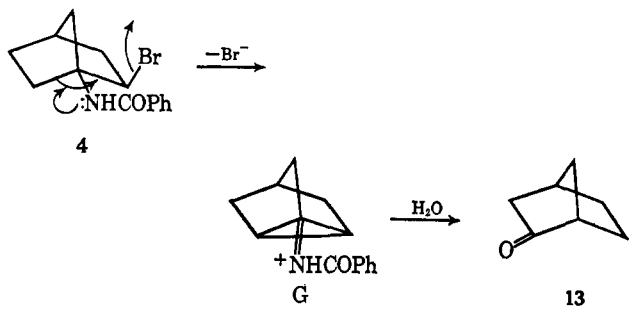
***exo*-2-Bromo-1-norbornyl Acetate (3).** The acetoxy function, unlike the carbomethoxy function, is known to be an active anchimeric group.[23–25] Its inductive effect, however, is nearly the same as that of the carbomethoxy group—σ_I 0.39 and 0.30, respectively.[26] Therefore, if the stereochemistry of **3** is such that participation by the acetoxy function is absent, then **3** and **2** should be comparable in their rates of solvolysis. Indeed, their rates differ by only fivefold. The rate constant of **3** relative to that of **1** at 25° (2.4×10^{-3}) is very close to that observed in *cis*-2-acetoxycyclohexyl derivatives relative to the unsubstituted ones at 25°: *ca.* 5×10^{-4} for the tosylates (acetolysis)[23] and 3.8×10^{-4} for the brosylates (acetolysis).[24] In the bromides the *cis* is much less reactive than the *trans*, but no kinetic data were given.[27] Because the rates of these *cis*-2-acetoxycyclohexyl compounds are generally agreed to reflect the inductive effect of the acetoxy function, the similar rate of **3** probably reflects the same thing.

The solvolysis of **3** can be viewed as shown. The



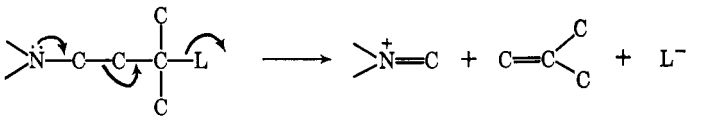
rapid rearrangement of D that follows the loss of bromide ion reflects the increased electron deficiency now at C-2. Routine hydrolysis then affords norcamphor (**13**). Rapid rearrangement subsequent to rate-determining loss of the leaving group but prior to product formation is by now well documented.[6,28] While no rearrangement exactly comparable to that of **3** is known to us in norbornane chemistry, the reaction is essentially a Tiffeneau halohydrin rearrangement,[29] many of which have been studied in other systems.[30]

1-Benzamido-*exo*-2-norbornyl Bromide (4). While the inductive effect of −NHCOPh is electron withdrawing (σ_m 0.22),[31] it has considerable electron-releasing power as well, as reflected in the much decreased value of σ_p (0.08),[31] and in its increased anchimeric ability compared to acetoxy.[32] Most of the 460-fold rate difference between **3** and **4** can therefore be ascribed to this source. Although not the only visualizable

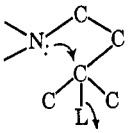


path, the course shown appears best in accord with the data. This path involves a rearrangement *in* the rate-

(17) A recent explanation involves torsional strain considerations: *cf.* P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967).
(18) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965).
(19) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963).
(20) H. C. Brown and H. M. Bell, *ibid.*, **86**, 5006 (1964).
(21) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 92.
(22) H. Hart and R. A. Martin, *J. Org. Chem.*, **24**, 1267 (1959).
(23) B. Capon, *Quart. Rev.* (London), **18**, 68 (1964).
(24) See ref 14, p 115 ff.
(25) E. M. Kosower, "An Introduction to Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1968, p 105.
(26) Reference 25, p 49.
(27) S. Winstein and R. E. Buckles, *J. Amer. Chem. Soc.*, **64**, 2780, 2787 (1942).
(28) J. E. Nordlander, S. P. Jindal, P. von R. Schleyer, R. C. Fort, Jr., J. J. Harper, and R. D. Nicholas, *ibid.*, **88**, 4475 (1966).
(29) M. Tiffeneau *C. R. Acad. Sci., Paris*, **145**, 593 (1907).
(30) *Cf.* D. Y. Curtin and E. K. Meislich, *J. Amer. Chem. Soc.*, **74**, 5905 (1952).
(31) H. H. Jaffé, *Chem Rev.*, **53**, 191 (1953).
(32) S. Winstein and R. Boschan, *J. Amer. Chem. Soc.*, **72**, 4669 (1950).



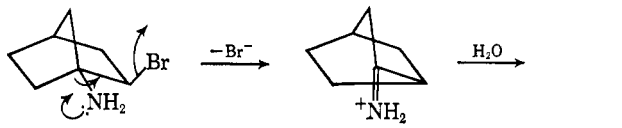
frangomeric process



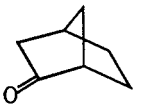
anchimeric process

determining step. If otherwise not counteracted, this phenomenon should accelerate the rate of **4** relative to **1**. But it is possible that the inductive effect of the benzamido function does counteract the acceleration, fortuitously leading to essentially the same rates for **4** and **1**. Total rearrangement would be expected nonetheless because no unrearranged intermediates intervene. Benzamide would also be a likely by-product, as found. The pathway actually may be likened to the "frangomerically" accelerated process[33] shown. Perhaps the normally enountered anchimeric process is reduced in importance because of steric effects in **4**.

1-Amino-*exo*-2-norbornyl Bromide (5). The solvolysis of **5** is clearly related to that of **4**. *n*-Electron participation from the amino function would be expected to be quite favorable as shown. Even though **5**



5 **H**



13

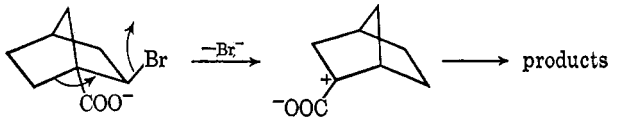
is a β-haloamine, the normally encountered nitrogen participation *via* aziridinium ion formation is ruled out here for steric reasons. So again the frangomeric type of assistance in suggested, leading to the iminium ion H which hydrolyzes to **13**. This path explains the total rearrangement found, but the only modest rate increase (k_{rel} = 46) deserves comment. The *n*-electron-donating ability of the amino group (σ_p −0.66)[26] is customarily of greater importance than its small electron-withdrawing effect (σ_I 0.10).[26] One must note, however, that for the most effective participation, the *n*-electrons of the nitrogen atom in **5** should maximally overlap with a developing p orbital at C-1. But if only a small rehybridization of C-1 attends the solvolysis, as indicated by earlier studies,[3,4,34] then only some fraction of the potential *n*-electron participation is possible. The inductive retardation by the amino function, on the other hand, should be less sensitive to the geometry of the activated complex because its action is through σ bonds. So a balancing of these factors could result in the less-than-expected rate increase found for **5**.

(33) C. A. Grob, *Gazz. Chim. Ital.*, **92**, 902 (1962).
(34) J. P. Schaefer, M. J. Dagani, and D. S. Weinberg, *J. Amer. Chem. Soc.*, **89**, 6938 (1967).

Lastly, mention should be made of the different activation parameters found for **5** compared to the earlier discussed bromides (Table I). To the degree that the amino group can participate, one would expect a lower ΔH^* because the making of the C=N bond can partially compensate for the breaking of the C–Br bond. One could also expect that the increased alignment of the atoms in the activated complex would decrease the ΔS^*, as found.

***exo*-2-Bromonorbornane-1-carboxylate Ion (6).** The carboxylate group is both inductively electron releasing (σ_m −0.10, comparable to methyl's σ_m −0.07),[26] and capable of anchimeric participation, so one might expect solvolytic rate enhancement here, as found. Actually, during the course of this study, Vaughn and coworkers[12] described the solvolysis of **6** in some detail: $10^5 k_1$ = 4.16 sec^{-1} at 40°, 7.78 at 45°, and 72.5 at 62° in 80% ethanol containing sodium carbonate; $E_{act.}$ = 28.6 kcal mol^{-1} and ΔS^* = 11 eu; k_{rel} (to **1**) = 11 at 60°. Our kinetic results are in fair agreement with theirs, considering the speed of this reaction and the slightly different conditions used, so discussion of this aspect will be omitted. Both the high ΔH^* and ΔS^* values are expected in such a solvolysis involving loss of solvation in the transition state.[35]

The nature of the solvolysis products obtained by Vaughn's group and ourselves differs, primarily in the distribution. This is perhaps because Vaughn studied the product formation in aqueous sodium bicarbonate while we studied it in 80% ethanol. To assist in their determination *via* gas–liquid partition chromatography, the acidic solvolysis products were converted to their methyl esters. The solvolysis may be viewed as shown.



6 **J**

The activated complex leading to J probably has some assistance from the carboxylate group akin to the frangomeric processes described above, but strain considerations preclude an α-lactone structure. Reaction of J with the medium (again exclusively from the *exo* side) would give products eventually isolated as esters **14** and **15**. Elimination of either the 3 or 6 proton would eventuate in **16** or **11**, respectively. Because these esters were 89% of the product, we feel product formation *via* J was predominant. The unrearranged ester **9** probably represents an alternative pathway, perhaps one utilizing attack by the carboxylate group at C-2, *via* a species resembling a β-lactone.

(35) Reference 14, p 119.

Experimental Section

Melting points and boiling points are uncorrected for stem exposure. The former were taken on a calibrated Fisher-Johns block. Only significant infrared absorptions are given (in microns) and the spectra were determined on a Beckman IR-5A instrument. Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer with tetramethylsilane as the internal standard. Samples were normally about 10% solutions in deuteriochloroform or carbon tetrachloride. The resonance values are in parts per million (δ units) and, for the case of most multiplets, are the centers, not the true chemical shifts. Integrations were in agreement with the structures given and the relevant proton is italicized when pertinent. The symbols used for the appearance of the signals are s, singlet; d, doublet; t, triplet; q, quartet or doubled doublet; and m, multiplet. At times higher order splitting was apparent but the symbols used refer to the gross shape of the signal. Gas–liquid partition chromatography (glpc) was performed on Aerograph A-90-P and Anacro 1A (Nester-Faust) instruments using helium as the carrier gas at 60 cc/min. Microanalyses were done by Micro-Tech Laboratories, Inc., Skokie, Ill.

Bridgehead-Substituted *exo*-2-Norbornyl Bromides (1–6). ***exo*-2-Norbornyl bromide (1)** was purchased from the Aldrich Chemical Co., n^{20}D 1.5144, lit.[36] n^{25}D 1.5126, and used as received. Infinity solvolysis titers indicated a purity of over 96%. ***exo*-2-Bromonorbornane-1-carboxylic acid** (the acid of **6**) was prepared as described[13] and recrystallized from cyclohexane, mp 149–149.5° (lit.[13] mp 151°). Its methyl ester **2** and the remaining bromides **3**, **4**, and **5** (as its hydrochloride) were prepared as described.[6]

Kinetic Studies. The solvolysis of bromide **1–4** was followed by Fajans determination of liberated bromide ion. A solution of the appropriate bromide and 1 equiv of sodium acetate trihydrate, each between 0.02 and 0.03 *M*, was prepared in 80% ethanol–20% water (v/v), placed in ampoules, sealed, and thermostated at various temperatures. At certain times an ampoule was withdrawn, chilled, and opened. Exactly 5.00 ml was withdrawn and extracted with purified petroleum ether (bp 30–60°) (20 ml, benzene in the case of **4**). The aqueous alcoholic phase was separated, combined with two distilled water washes of the petroleum ether phase, and titrated with silver nitrate solution (prepared and standardized weekly, *ca.* 0.02 *M*) to the first permanent pink color of the dichlorofluoresceinate–silver bromide absorbate.

The solvolysis of bromides **5** and **6** was followed by Volhard determination of liberated bromide ion. Both **5** and **6** reacted slowly (relative to the titration time) with silver ion at 25° in 1:1 aqueous nitric acid, so no extraction of the solvolysis mixture was necessary. The bromides (**5** as the hydrochloride and **6** as the acid) were made 0.012–0.017 *M* in 80% ethanol containing sodium hydroxide (2.3 equiv) and thermostated as before. At various times an aliquot was removed and the contents were immediately quenched in 1:1 nitric acid. A known volume of excess aqueous standardized silver nitrate was added and the excess silver ion rapidly back-titrated with potassium thiocyanate (ferric ion indicator). Corrections were made for the presence of ionic chloride in the salt of **5** employed. For **5**, removal of the mixed silver halides prior to back-titration gave better precision. This was not needed for **6** provided that the titration mixture was rapidly stirred. The mixing of reagents was taken as initial time for the 20° determination on **5**. In reactions above 20°, a control determination of bromide ion made *when* the reactants were thermostated was taken as the initial titer. The subsequent reaction times were taken when the reaction material was quenched in the nitric acid.

Rate constants were calculated graphically from plots of 2.303 log $a/a - x$ *vs.* time and also, for Fajans determinations, 2.303 log $v_{inf}/v_{inf} - v$ *vs.* time. In this latter method, v_{inf} and v are the titers at ten half-lives and at time t, respectively. For the Volhard titrations the thiocyanate titer could be plotted as ln $(v - v_{inf})$ *vs.* time for the rate constant. The infinity titers were 98 ± 2% of the theoretical values. First-order kinetics were followed by these reactions to over 90% completion, although some first points (under 10% reaction) were disregarded because of erratic volumetric readings at such low values. The activation parameters were calculated from rate constants that were the average of the above two methods employed in their evaluation.

Product Studies. The products from **1** were not studied because of prior literature data.[10]

Methyl ester **2** was solvolyzed in sealed ampoules in 80% ethanol containing sodium acetate at 118° for 3 days exactly as in the kinetic study except some 10-fold greater in concentration. The material was flushed with more 80% ethanol into excess water and extracted with petroleum ether (bp 30–60°). The extracts were dried and freed of solvent. The residue was fractionated by glpc on a Carbowax 20M column at 155°. The four compounds eluted had relative retention times of 1.0, 1.5, 2.45, and 5.44. By integration of the trace, collection of the samples and spectral comparison with knowns (see later) these were identified as **methyl norbornene-1-carboxylate (12,** 9.4%), **methyl nortricyclene-1-carboxylate (11,** 44%), **methyl *exo*-2-ethoxynorbornane-1-carboxylate (9,** 38%), and **methyl *exo*-2-hydroxynorbornane-1-carboxylate (10,** 8.6%), respectively. The total yield was not determined, but no other products were observed.

The acetoxy bromide **3** was studied similarly at 118° for 20 hr. In this case the petroleum ether phase was dried and allowed to evaporate in air. Waxy **norcamphor (13)** was isolated (17%) and confirmed by infrared comparison with known material. Identification was also made *via* the 2,4-dinitrophenylhydrazone, mp 126–128° (lit.[37] 129.5–130.5°). Only **13** was observed as a product by glpc. The low yield of isolated **13** reflected both its volatility and water solubility. Pure **3** itself did not give a precipitate with 2,4-DNP reagent.

Benzamido bromide **4** was refluxed in 80% ethanol containing 1 equiv of sodium acetate for 2 hr. Treatment of an aliquot with 2,4-DNP reagent afforded the derivative of norcamphor. Pure **4** did not itself give a precipitate with the reagent. Extraction of the reaction material with a petroleum ether–methylene chloride mixture followed. The dried extract was concentrated and diluted with further petroleum ether. Colorless **benzamide** precipitated (30%) and was recrystallized from methylene chloride and carbon tetrachloride, mp 125–127° (lit.[38] mp 128°), mixture melting point undepressed.

The bromoamine **5** (as the hydrochloride, 930 mg, 4.12 mmol) was refluxed with swirling in absolute ethanol (80 ml) containing aqueous sodium hydroxide (0.474 *M*, 20 ml) for 30 min (over ten half-lives). Excess 2,4-DNP reagent was then added and the material was chilled overnight. The precipitated derivative of norcamphor amounted to 1.12 g, 94%, mp 129–130°, mmp 127–129°. Pure **5** (as the hydrochloride) did not react with the reagent.

The solvolysis of bromide **6** (weighed as the acid, 4.5 g, 20.5 mmol) was done in absolute ethanol (400 ml) containing aqueous sodium hydroxide (0.474 *M*, 100 ml) under reflux for 30 min. The mixture was neutralized with dilute hydrochloric acid and stripped of solvent under reduced pressure. The semisolid residue (2.45 g) was taken up in minimal chloroform and diluted with carbon tetrachloride. White ***exo*-2-hydroxynorbornane-*endo*-2-carboxylic acid (17,** *ca.* 520 mg, mp 111–112.5°, mmp with authentic sample 111–112°) precipitated. The solvents were then removed and the residue was treated with excess diazomethane in ether. The resulting methyl esters were purified by codistillation with water and then separated by glpc on a Carbowax 20M column at 155°. Five esters eluted, the relative retention times being 1.0 (a mixture of two esters), 1.4, 1.64, and 3.04. By integration of the trace, collection of the samples and spectral comparison with knowns, these were identified as an unresolved mixture of **methyl norbornene-2-carboxylate (16,** one part) and **methyl nortricyclene-1-carboxylate (11,** four parts, total 15.2%); **methyl *exo*-2-ethoxynorbornane-*endo*-2-carboxylate (14,** 62.4%), **methyl *exo*-2-ethoxynorbornane-1-carboxylate (9,** 18.9%), and **methyl *exo*-2-hydroxynorbornane-*endo*-2-carboxylate (15,** 3.5%). This last compound reflected only a portion of such a product, however, because the free acid **17** was isolated prior to conversion to the methyl ester. The total product represented a yield of 70% with a composition as given in Table II when the yield of **17** was added to those of the esters.

Preparation of Reference Compounds. Methyl norbornene-1- and **2-carboxylates (12** and **16,** respectively) were available from another study.[6]

Methyl nortricyclene-1-carboxylate (11)[39] was prepared from the acid[22] and diazomethane: bp 43–45° (1 mm); n^{20}D 1.4802; d^{30}_4 1.095 (lit.[40] bp 82° (15 mm)); infrared spectrum matched that re-

(36) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, **72,** 3116 (1950).

(37) H. Kwart and L. Kaplan, *ibid.*, **76,** 4072 (1954).

(38) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, John Wiley and Sons, Inc., New York, N. Y., 1964, p 323.

(39) We thank Mr. P. Rabideau for this preparation of the acid and its methyl ester (May 1964).

(40) K. Alder, R. Hartmann, and W. Roth, *Chem. Ber.*, **93,** 2271 (1960).

ported,[40] δ^{CCl_4} 3.62 s (-$COOCH_3$), 2.05 m (C-4 bridgehead H), 1.80 s (cyclopropyl H's), 1.45 d (C-7 H's, $J_{4,7}$ = 2 cps), 1.37 s (other ring H's). The nmr spectrum was very similar to that reported for the acid.[41]

Norcamphor (13) was commercial material (Aldrich) used as received. Its 2,4-DNP derivative was prepared in the usual fashion, mp 129–130° (lit.[37] mp 129.5–130.5°).

***exo*-2-Hydroxynorbornane-*endo*-2-carboxylic acid (17)** was prepared by the permanganate oxidation of norbornane-*endo*-2-carboxylic acid as described[42] in 21.6% yield; mp 111–113° (lit.[42] mp 114°); λ^{KBr} 3.00 (-OH), 3.2–4.4 (-CO*OH*); δ^{CDCl_3} 7.5–6.67 (-OH and -COOH), 2.5–0.84 m (all ring H's). Treatment of the acid with methanol in ethylene chloride under reflux in the presence of a small amount of sulfuric acid led to **methyl *exo*-2-hydroxynorbornane-*endo*-2-carboxylate (15)**, collected by preparative glpc on a Reoplex column at 180°; λ^{neat} 2.90 (-OH), 5.80 (-*CO*OCH_3); δ^{CCl_4} 3.74 s (-$COOCH_3$), 2.60 s (-OH, concentration dependent), 2.30 m (two bridgehead H's), 2.17 and 1.87 m (C-3 methylene H's, J = 8 cps), 1.67–1.05 m (other ring H's).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.69; H, 8.31.

Ester **15** (0.7 g) was heated on a steam bath in a sealed ampoule with excess ethyl iodide (1 g) in the presence of freshly precipitated silver oxide (0.6 g) for 2 hr. The resulting paste was leached with ether and the extract processed by glpc on a Reoplex column at 180° to yield **methyl *exo*-2-ethoxynorborane-*endo*-2-carboxylate (14)** in 35% yield; λ^{neat} 5.77 (-*CO*OCH_3), no -OH absorption; δ^{CCl_4} 3.70 s (-$COOCH_3$), 3.0–2.836, a complex but well-defined multiplet appearing as a pentuplet of doublets with further splitting (-OCH_2CH_3, a nonequivalent pair of methylenes H's), 2.33–2.25, skewed m (two bridgehead H's), 1.97, center of an uneven pair of doublets (*exo* C-3, H, $J_{exo,endo}$ = 12.5 cps, $J_{exo,H-4}$ = 3 cps), 1.80–0.83 m (other ring H's), and 1.07 t (-OCH_2CH_3, J = 7 cps).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.43; H, 9.30.

***exo*-2-Hydroxynorbornane-1-carboxylic acid (18)** was prepared as described by simply boiling an aqueous solution of *exo*-2-bromonorbornane-1-carboxylic acid for 3 days.[12] Methylation of the resulting acid mixture with methanol in ethylene chloride using a trace of sulfuric acid gave a complex mixture of esters separable by preparative glpc on a Reoplex column at 180°. Esters **11**, **12**, and methyl *exo*-2-methoxynorbornane-1-carboxylate (by spectra) accompanied **methyl *exo*-2-hydroxynorbornane-1-carboxylate (10)**, λ^{neat} 2.90 (-OH), 5.80 (-*CO*OCH_3); δ^{CCl_4} 3.87 m (-*CH*OH-), 3.70 s (-$COOCH_3$), 3.28 s (-OH, concentration dependent), 2.25 m (one bridgehead H), 2.02–1.0 m (other ring H's, in which the AB pattern of the C-3 methylene group could be seen, $J_{endo,exo}$ = 8 cps).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.70; H, 8.27.

Ethylation of **10** with ethyl iodide and silver oxide as performed on ester **15** above (10 ml of benzene was used as a solvent in this case and no ether extraction was necessary) led to **methyl *exo*-2-ethoxynorbornane-1-carboxylate (9)** in 50% yield, collected by glpc from a Reoplex column at 180°: λ^{neat} 5.75 (-*CO*OCH_3), 9.00, 9.23 (C-O), no OH absorption present; δ^{CCl_4} 3.60 s (-$COOCH_3$), 3.37, center of a complex well-defined multiplet appearing as a portion of a pentuplet of doublets with further splitting (-OCH_2CH_3, a nonequivalent pair of methylene H's), 2.20 m (one bridgehead H), 1.83, center of an uneven pair of multiplets (*exo* C-3 H, $J_{exo,endo}$ = 10 cps), 1.7–1.25 m (other ring H's), and 1.05 t (-OCH_2CH_3, J = 7 cps).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.48; H, 8.83.

Acknowledgment. This work was supported in part by the Army Research Office (Durham), Contract DA-31-124-ARO(D)-69, to whom we express our appreciation. We thank Dr. Bruno Jaselskis for assistance on analytical methods and Mr. Philip Chenier for the nmr determinations.

(41) R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

(42) H. Kwart and G. Null, *J. Amer. Chem. Soc.*, **82**, 2350 (1960). The method of Alder, *et al.*,[40] reported to give **17**, actually affords the isomeric **18**.[12]

Vapor Phase Thermolysis of 1-Hexen-5-yn-3-ol. An Acetylenic Oxy-Cope Reaction[1]

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Contribution from the Department of Chemistry, Northeastern University, Boston, Massachusetts 02115. *Received February 28, 1968*

Abstract: 1-Hexen-5-yn-3-ol, shown to be free of the internal acetylenic isomer, was subjected to vapor phase thermolysis in a flow system over the range of 350–390° and under various pressures. The extent of β-hydroxyolefin cleavage, which leads to formation of acrolein and allene, was independent of residence time in the thermolysis zone but increased with temperature, indicative of a higher activation energy than the competing rearrangement processes. One of these processes affords 4,5-hexadienal *via* an acetylenic analog of the oxy-Cope reaction. Also produced is 3-cyclopentenecarboxaldehyde in amounts increasing with increasing temperature and/or increasing residence time. The data are consistent with an electrocyclic reaction involving the enol progenitor of the Cope product, which ketonizes only upon condensation in the product trap.

As a part of our investigation of the thermolytic behavior of 3-hydroxy-1,5-hexadienes,[2] the effects due to the presence of an acetylenic bond have been studied. Only a few examples of the participation of triple bonds in Cope-type rearrangements have been reported. Black and Landor[3] found several propargyl vinyl ethers to undergo thermal rearrangements to 3,4-pentadienals in a manner entirely analogous to that reported earlier[4] in the case of allyl vinyl ethers. Also reported[3] was the classical liquid-phase Cope reaction of **1**, although the formation of **2**, which occurred only to the extent of 20%, was accompanied by extensive polymerization. Huntsman has reported the thermal rearrangement of 1-alken-5-ynes to give 1,2,5-

(1) Paper III in series entitled "Vapor Phase Thermolyses of 3-Hydroxy-1,5-hexadienes." For paper II see ref 2.

(2) A. Viola, E. J. Iorio, K. K. Chen, G. M. Glover, U. Nayak, and P. J. Kocienski, *J. Amer. Chem. Soc.*, **89**, 3462 (1967).

(3) D. K. Black and S. R. Landor, *J. Chem. Soc.*, 6784 (1965).

(4) C. D. Hurd and M. A. Pollack, *J. Amer. Chem. Soc.*, **60**, 1905 (1938).