Because of the presence of the bromine atom in *cis*-1-(2-bromo-3-phenanthryl)-2-(2-naphthyl)ethylene (**XI**), the upfield shift of H_5 ($H_{\alpha 3}$) is much larger than in the corresponding unsubstituted *cis*-1,2-diarylethylene.

We acknowledge the fact that other co-workers have made similar observations in the course of the last few years. The financial support of the *'Fonds de la Recherche Fondamentale Collective'* is gratefully acknowledged. One of us (*J.J.R.*) expresses his gratitude to the *'Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture'* for the award of a fellowship.

BIBLIOGRAPHY

[1] *N. Defay, D. Zimmerman & R. H. Martin*, Tetrahedron Letters *1971*, 1871.
[2] *Varian* Ass.: NMR. spectra catalog (1962).
[3] *R. H. Martin, N. Defay, H. P. Figeys, M. Flammang-Barbieux, J. P. Cosyn, M. Gelbcke & J. J. Schurter*, Tetrahedron *25*, 4985 (1969).

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220. Reaction of 2-Methylenenorbornane with N-Bromosuccinimide

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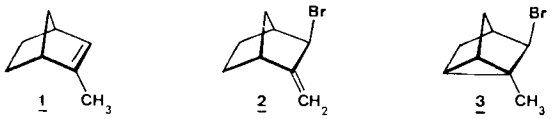
(8. II. 72)

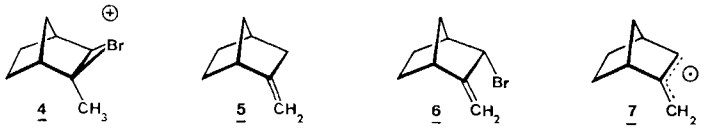
Summary. The reaction of 2-methylenenorbornane with N-bromosuccinimide produced a mixture of six monobromides in an overall yield of about 60%. By irradiation in the presence of benzoyl peroxide *exo*- and *endo*-3-bromo-2-methylenenorbornanes, 2-bromomethylnorborn-2-ene, *Z*- and *E*-2-bromomethylenenorbornanes and 1-bromomethylnortricyclene were found in a percentage ratio of 43.0, 7.5, 6.5, 19.0, 19.0 and 5.0. Without benzoyl peroxide, in the dark, the same products were obtained, but in a percentage ratio of 23.0, 3.0, 17.0, 26.0, 26.0 and 7.0. These results are rationalized in terms of an ionic mechanism in concurrence with some radical mechanism contribution.

Introduction. – The use of N-bromosuccinimide (NBS.) as a reagent for the allylic bromination of olefins is a standard preparative procedure [1]. In general it is thought that the mechanism involves intermediate formation of the free allylic radical which subsequently captures bromine [2]; however, alternative mechanisms have been proposed. A variant of the radical mechanism is that a chain process occurs on the surface of the NBS. [3]. An older suggestion is that the reagent responsible is molecular bromine formed in low concentrations by decomposition of NBS. [4]. However, if the concentration of bromine is allowed to increase, addition to the double bond occurs and thus the course of the reaction can deviate [5]. This diversion becomes the major route for those molecules where a resonance-stabilized allylic radical is forbidden for structural reasons, as exemplified by norbornene and bicyclo[2.2.2]oct-2-ene. In both cases the products obtained can be satisfactorily rationalized in terms of the initial formation of a bromonium ion [6]. Even with 2-methylnorborn-2-ene (**1**) which has an allylic position available, it appears that an ionic mechanism best accounts for the major products [7]. The reaction of **1** with NBS. in boiling carbon tetrachloride with benzoyl peroxide in the light gave *exo*-3-bromo-2-methylenenorbornane (**2**) and

3-bromo-2-methylnortricyclene (**3**) in a ratio of 3:1. Although these are conditions which are expected to generate radicals, we pointed out that the origin of the tricyclic

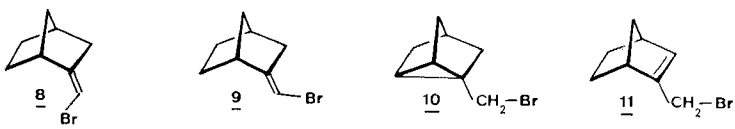


product **3** must be the *exo*-bromonium ion **4**, and furthermore that **4** could also conveniently afford the other product (**2**), although a radical pathway could account for it too. In contrast to these results *Davies et al.* [8] reported that both 2-methylnorborn-2-ene (**1**) and 2-methylenenorbornane (**5**), under apparently the same conditions as ours, gave no 2-methylnortricyclenyl bromide **3**, but only **2** and its *endo*-isomer **6**. On this evidence, they proposed, quite rightly, that both **1** and **5** gave rise to the common allylic radical **7**, thereby leading to the same product mixture. In view of these results we decided to repeat our original work with 2-methylnorborn-2-ene (**1**) and moreover to investigate the reaction of 2-methylenenorbornane (**5**) with NBS. If our earlier contention were correct, namely that the first step is the addition of bromine to the double bond, clearly the two olefins (**1**) and (**5**) should give entirely different products.



Results. – *A.* The reaction of 2-methylnorborn-2-ene (**1**) with NBS. in carbon tetrachloride was carried out under four different sets of conditions; in both the dark and the light, with and without benzoyl peroxide. The results are sensibly identical with those previously reported. Originally we remarked on the presence of 2-methylenenorbornane (**5**) in the product [7]; we now find that the isomerization of **1** to **5** occurs on fractional distillation of the reaction mixture and that no isomerization occurred during reaction. Moreover, from scrutiny of the NMR. spectrum, we deduce the presence of a small amount (3–4%) of *endo*-3-bromo-2-methylenenorbornane (**6**) in the mixture of monobromides.

B. 2-Methylenenorbornane (**5**) and NBS. were allowed to react in boiling carbon tetrachloride with or without benzoyl peroxide, in the dark or in the light. The products were the same in all cases, but the differences in percentage ratios were appreciable (see Table 1). Six products were obtained, of which five were unambiguously identified as *exo*-3-bromo-2-methylenenorbornane (**2**), 2-bromomethylenenorbornanes (**8** and **9**), 1-bromomethylnortricyclene (**10**) and 2-bromomethylnorborn-2-ene (**11**). The sixth product was deduced to be *endo*-3-bromo-2-methylenenorbornane (**6**).



The three major components were separated by vapour phase chromatography into pure **2** and an inseparable mixture of the *Z* and *E* isomers **8** and **9** [9]. Comparison of **2** with an authentic sample [7] gave an immediate confirmation of structure. The identity of **8** and of **9** was obtained from the following evidence; the bromides were inactive towards silver acetate in aqueous acetone and their hydrogenolysis gave the same proportion of *exo*- and *endo*-2-methylnorbornanes as did 2-methylenenorbornane on hydrogenation [10]. The existence of the binary mixture was evident from the

Table 1. *Product Composition*[a]) *in the Reaction of 2-Methylenenorbornane with N-Bromosuccinimide*

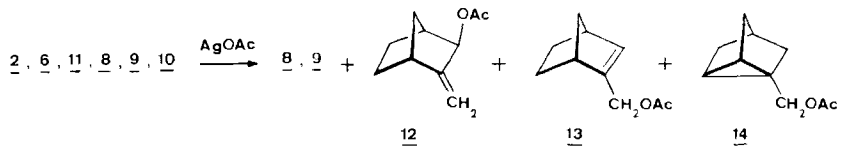
Compound	No.	With benzoyl peroxide[b])		Without benzoyl peroxide	
		in daylight	irradiated[c])	in daylight	in dark
Reaction time	–	4 h	2 h	4 h	4 h
Yield[a])	–	65%[d])	60%[d])	57%[d])	57%[d])
exo-2-methylene-3-bromonorbornane	**2**	40.5%	43%	22.5%	23%
endo-2-methylene-3-bromonorbornane	**6**	7.5%	7.5%	3.5%	3%
2-bromomethyl-norborn-2-ene	**11**	7%	6.5%	18%	17%
Z-2-bromomethylenenorbornane	**8**	20%	19%	25%	26%
E-2-bromomethylenenorbornane	**9**	20%	19%	25%	26%
1-bromomethyl-nortricyclene	**10**	5%	5%	6%	7%

[a]) Obtained by integration of the appropriate signals of the NMR. spectra of the crude mixture, at the end of the reaction.
[b]) 40 mg.
[c]) Without external heating except by the irradiation source (300 W *Osram-Concentra* lamp).
[d]) Total yield of monobromides.

proton NMR. spectrum: two separate solvent-dependent vinyl shifts being a sufficient indication. Further substantiation of the structures of **8** and **9** was forthcoming from their decoupled NMR. spectra (see experimental part).

The presence of 2-bromomethylnorborn-2-ene (**11**) and the *endo*-bromide **6** were suspected from an examination of the NMR. spectrum of the initial mixture. The identity of **11** was confirmed by synthesis. The reaction of 2-hydroxymethylnorborn-2-ene with carbon tetrabromide and tri-*n*-octylphosphine gave **11** as a single product which showed itself to be remarkably stable. Prolonged heating of **11** converted it to the thermodynamically more stable *exo* allylic isomer **2**. The presence of the *endo*-bromide **6** was inferred from the broad NMR. signals at 4.78 ppm [8].

The structure of 1-bromomethylnortricyclene (**10**) was elucidated by submitting the entire reaction mixture to acetolysis with silver acetate in aqueous acetone (Scheme 1). The bromides **8** and **9** were untouched, but the others were converted to

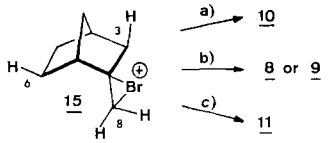


Scheme 1. Acetolysis of the Reaction mixture

the corresponding acetoxy derivatives. *Exo*-3-bromo-2-methylenenorbornane (**2**) and its *endo*-isomer **6**, as well as 2-bromomethylnorborn-2-ene (**11**) gave *exo*-3-acetoxy-2-methylenenorbornane (**12**) and 2-acetoxymethylnorborn-2-ene (**13**) in the usual ratio of 1.7 to 1 [7].

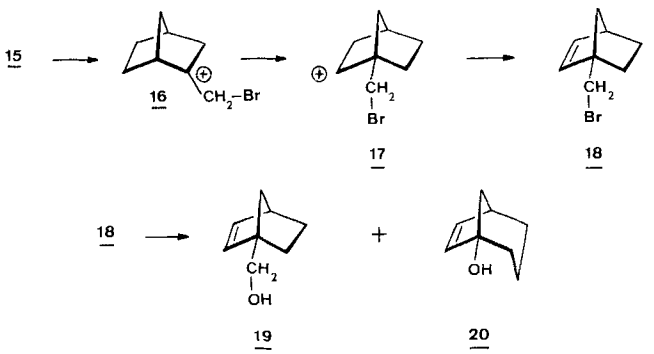
1-Bromomethylnortricyclene (**10**) gave the acetoxy compound **14** in keeping with the behaviour expected of a cyclopropylcarbinyl cation [11]. Column chromatography of the mixture afforded **14** in a pure state, and its identity was confirmed by comparison with a synthetic sample [12]. As the acetolysis was partial, affording the alcohols as well, the foregoing procedure was slightly changed. To facilitate separation, the mixture of alcohols and acetates was reduced with lithium aluminium hydride to the alcohols. At this stage the bromides **8** and **9** were separated from the alcohols by column chromatography. The alcohols were then converted to their acetyl derivatives **12**, **13** and **14** which were separated by column chromatography.

Discussion. – These results demonstrate that the allylic radical **7** cannot be the unique common intermediate in the NBS. bromination of 2-methylnorborn-2-ene (**1**) and 2-methylenenorbornane (**5**). Furthermore, they strengthen our contention that despite the availability of an allylic position in **1** and **5**, the formation of a bromonium ion is highly favoured. In the case of **5**, the appropriate and most likely bromonium ion is the *exo* species **15**. Subsequent loss of a proton can occur in any of four ways (Scheme 2). Elimination from C(6) gives the 1-bromomethylnortricyclene (**10**,



Scheme 2. Loss of a proton from C-(6) (a), C-(8) (b) or C-(3) (c) converts the bromonium ion **15** *to bromides* **10**, **8** *or* **9** *and* **11** *respectively*

Scheme 2, a). Elimination of either of the C(8) protons affords the isomeric vinyl bromides **8** and **9** (Scheme 2, b). Elimination from C(3) gives the 2-bromomethylnorborn-2-ene (**11**) (Scheme 2, c). Conversion of **11** could then subsequently occur to the more stable *exo*-3-bromo-2-methylene-norbornane (**2**) either by ionization or possibly by a suprafacial [1,3]-sigmatropic process [13].



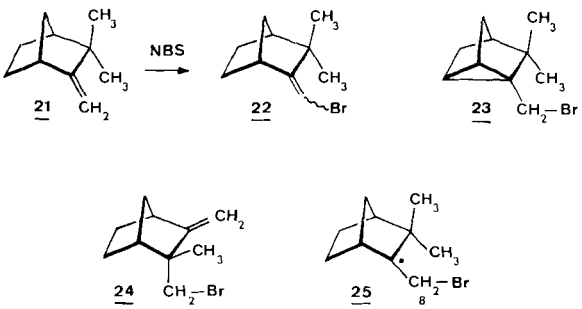
Another course of reaction available in principle to the bromonium ion **15** is ring opening to give the 2-norbornyl species **16** which on *Wagner-Meerwein* rearrangement to the cation **17** would furnish 1-bromomethyl-norborn-2-ene (**18**). No sign of **18** or of its putative solvolysis products 1-hydroxymethyl-norborn-2-ene (**19**) and 1-hydroxy-bicyclo[3.2.1]oct-6-ene (**20**) were detected in the reaction mixture [14]. The absence of such products can be attributed to the stability of the bromonium ion **15** under the non-polar solvent conditions.

Once again we emphasize that all products, except the *endo* bromide **6**, can be conveniently rationalized in terms of the common ionic precursor **15**. This does not mean to say that the overall reaction does not have some radical component. Nevertheless, several of the products, certainly **10**, and most probably **8** and **9**, *require* the intermediacy of **15**. However, products **2** and **11** could conceivably arise from the allylic radical **7**. If this is so, it is remarkable that 2-bromomethylnorborn-2-ene (**11**) is *not* observed in the NBS. bromination of 2-methylnorborn-2-ene which in principle should give the same precursive radical **7**. As for *endo*-3-bromo-2-methylene-norbornane (**6**), it can only be derived convincingly from the allylic radical **7**.

Indeed inspection of Table 1 gives a clear indication that a mixed ionic-radical process is operating; varying the conditions of bromination causes quantitative differences in product composition. For example the formation of *endo*-product **6** and of its *exo*-isomer **2** is favoured under conditions most conducive to the creation of radicals. On the other hand, considerably smaller amounts of the *Z*- and *E*-bromides (**8** and **9**) and 2-bromomethylnorborn-2-ene (**11**) are found under the conditions favouring radical formation.

In their paper on the NBS. bromination of camphene (**21**) *Roberts* & *Trumbull* [**15**] state that a physically inseparable mixture of three monobromides was formed. They classified the bromides as very reactive, less reactive and unreactive. The unreactive bromide they managed to identify as 8-bromocamphene (**22**), but the others remained unidentified. On the basis of our findings, it would appear that both *Z*- and *E*-isomers of **22** should have been formed and that the other two bromides are most likely tricyclenyl bromide **23** and possibly the rearranged product **24**[1]).

As a resonance-stabilized allylic radical cannot be obtained from camphene, *Roberts* formulated the mechanism as involving attack by a bromine atom on the



[1]) The action of chlorine on camphene in carbon tetrachloride gives mainly the chloro analogue of **23** (*H. G. Richey, Jr., J. E. Grant, T. J. Garbacik & D. L. Dull*, J. org. Chemistry, *30*, 3909 (1965)).

double bond to give the 2-norbornyl-type radical (**25**) which subsequently donates a hydrogen atom from C(8) to a suitable acceptor. For 2-methylenenorbornane the formation of the analogous norbornyl radical would scarcely be competitive with that of the more stable allylic radical, and thus it is unlikely that products **8** and **9** would have a radical origin.

Conclusion. – Our experiments demonstrate that 2-methylnorborn-2-ene and 2-methylenenorbornane on treatment with NBS. give an entirely different mixture of products, although both mixtures contain *exo*- and *endo*-3-bromo-2-methylene-norbornane (**2** and **6**). This behaviour parallels that of the reaction of **1** and **5** with lead tetraacetate in which each olefin yields different cations leading to structurally different acetates [16]. Similarly for our NBS. reaction we are forced to conclude on the basis of the product composition that each olefin generates different cations, *viz.* bromonium ions, which account for those bromides which are not common to both reactions. Additionally we conclude that the 2-methylenenorborn-2-yl radical is concomitantly formed and could be the source of the bromides common to both reactions.

We are indebted to the *Swiss National Science Foundation* for the support of this research (2236.69) and for the purchase of spectrometers (5202.2).

Experimental

Boiling points are uncorrected. – IR. spectra were recorded using a *Perkin-Elmer* 257 spectrometer and films on NaCl plates. – NMR. spectra were determined on a *Perkin-Elmer* Model R12 instrument equipped with a double resonance accessory. Carbon tetrachloride was used as solvent, unless otherwise noted. Chemical shifts are expressed as ppm on the scale (internal tetramethylsilane = 0.0 ppm). – Mass spectra were obtained on an *Atlas* CH-4 mass spectrometer, operating with an ionization energy of 70 eV. – Gas-liquid partition chromatography (GLC.) was performed for analytical purposes on a *Perkin-Elmer* F11 instrument, and preparative chromatography was effected on a *Perkin-Elmer* F21 apparatus. – Microanalyses were performed by Dr. *Kurt Eder*, Laboratoire Microchimique, Ecole de Chimie, Genève.

2-Methylenenorbornane (**5**). The *Wittig* addition to 2-norbornanone yielded high purity (99%; GLC.) 2-methylene-norbornane (b.p. 121–122°) [17].

Reaction of 2-Methylenenorbornane (**5**) *with N-Bromosuccinimide*[2]). 2-Methylene-norbornane (**5**) (5.4 g; 0.05 mol) was dissolved in carbon tetrachloride (30 ml) and NBS. (7.12 g; 0.04 mol) was added. The resulting suspension was stirred and boiled under reflux. On cooling, succinimide was removed by filtration and the filtrate was subjected to GLC. and NMR. analysis; no isomerization of the starting material was detected. The solvent was distilled and the resulting oil was fractionated through a short *Vigreux* column to afford firstly the unreacted olefin (b.p. 45°/52 Torr), then a mixture of monobromides (b.p. 100–104°/50 Torr).

The NMR. spectrum of the low boiling fraction revealed a mixture of 2-methylene-norbornane (**5**) and 2-methylnorborn-2-ene (**1**) in the ratio (89 ± 2):(11 ± 2). The analytical GLC. (Apiezon L 20% on Chromosorb W 2 m/2 mm at 90°) and the NMR. spectra of the high boiling fractions indicated the presence of six products, namely *exo*-3-bromo-2-methylenenorbornane (**2**), *endo*-3-bromo-2-methylenenorbornane (**6**), 2-bromomethylnorborn-2-ene (**11**), *Z*-2-bromomethylene-norbornane (**8**), *E*-2-bromomethylenenorbornane (**9**) and 2-hydroxymethyl-nortricyclene.

Z- and E-2-bromomethylene-norbornanes (**8** and **9**). Compounds **8** and **9** were separated from the mixture of bromides by preparative GLC. An Apiezon L column (20% on Chromosorb W; 2.7 m/8.0 mm) was used at 145° with nitrogen as carrier gas (200 ml/min); their separation by distillation or preparative GLC. proved impossible in our hands. IR. spectrum: max. at 3070, 1655 and

[2]) General scheme. Details are listed in Table 1.

1650 cm^{-1} due to the exocyclic methylene groups. Mass spectrum: M^+ 188 (22) and 186 (22); *m/e:* 160 (22), 158 (22), 107 (47), 91 (29), 80 (32), 79 (100), 78 (25), 77 (30).

$C_8H_{11}Br$ (187.07) Calc. C 51.36 H 5.92 Br 42.72% Found C 51.42 H 5.83 Br 42.90%

Hydrogenolysis of Z- *and* E-*2-Bromomethylenenorbornanes* (**8** and **9**). The 1:1 mixture of **8** and **9** (187 mg; 1 mmol) in ethanolic sodium hydroxide (7 ml containing 70 mg of NaOH) was hydrogenated at room temperature and atmospheric pressure over a catalytic amount of *Raney* nickel. 2 mmol of hydrogen were absorbed with the liberation of hydrogen bromide (1 mmol). The mixture of *exo-* and *endo*-2-methylnorbornanes was identical (GLC., NMR.) with that obtained by hydrogenation, under the same conditions, of 2-methylenenorbornane [10].

Treatment of the mixture of bromides with silver acetate. To a solution of the mixture of the products from the NBS. reaction (935 mg) in 50% aqueous acetone (10 ml), silver acetate (1 g) was added in one portion. Silver bromide precipitated immediately. The mixture was stirred at room temperature for 1 h, the precipitate removed by filtration and the filtrate diluted with water and worked-up in the usual way. After distillation of the bulk of the ether, the solution was treated for 4 h at room temperature with an excess (1 g) of lithium aluminum hydride. The unreacted hydride was decomposed by the dropwise addition of a small amount of water, the resulting mixture filtered, the solution dried over anhydrous sodium sulfate and the solvent removed by distillation. A colourless oil was obtained (609 mg) which consisted of **8** and **9**, and a mixture of alcohols, namely: *exo*-3-hydroxy-2-methylene-norbornane, 2-hydroxymethylnorborn-2-ene and 2-hydroxymethylnortricyclene. The bromides were separated from the alcohols by column chromatography over silica gel (20 g). The bromides (262 mg) were eluted with petroleum ether, the alcohols (308 mg) with ether. The less polar fraction was in all respects identical with the bromides separated by GLC. from the reaction of 2-methylene-norbornane with NBS., thereby demonstrating the inertness of these bromides towards silver ion and lithium aluminum hydride.

1-Acetoxymethylnortricyclene (**14**). – a) *Isolation.* The mixture of alcohols (1 g) from the above reaction was converted into the acetyl derivatives by treatment with acetic anhydride (10 ml) in dry pyridine (10 ml) for 4 h at room temperature. The reaction mixture was poured into ice-water and worked-up in the usual fashion. The yellowish oil obtained (1.25 g; 96%) was chromatographed over silica gel (60 g) impregnated with 10% silver nitrate. Elution with 2.5% of ethyl ether in petroleum ether yielded 1-acetoxymethylnortricyclene (**14**) (165 mg). Further elution with 4–5% and 8–10% ethyl ether in petroleum ether yielded *exo*-3-acetoxy-2-methylenenorbornane (**12**) (645 mg) and 2-acetoxy-methylnorborn-2-ene (**13**) (390 mg) respectively. These three products were identical with authentic samples.

b) *Synthesis of* **14**. 2-Hydroxymethylnortricyclene (200 mg) [12] was dissolved in dry pyridine (2 ml) and acetic anhydride (2 ml) was added. The mixture was allowed to stand at room temperature for 2 h and was then poured into ice-water. Working-up gave a colourless oil (212 mg; 80%). IR. spectrum: max. at 3055, 1740, 1235, 857 and 788 cm^{-1}, characteristic of the cyclopropane ring and the acetoxy group.

$C_{10}H_{14}O_2$ (166.21) Calc. C 72.26 H 8.49% Found C 72.06 H 8.53%

1-Bromomethylnortricyclene (**10**). Tri-*n*-octylphosphine (741 mg; 2 mmol) in 1 ml of dry ether was added slowly (2 min) to a stirred solution of 2-hydroxymethyl-nortricyclene (124 mg; 1 mmol) and carbon tetrabromide (663 mg; 2 mmol) in dry ether (2 ml) [18]. An exothermic reaction ensued and the solution became yellow. The mixture was stirred for an additional 15 min and then analysed by GLC. when the presence of a small amount of the starting alcohol and a new product having the same retention time as one of the minor products of the original reaction mixture was detected. The bromide proved to be very unstable. All attempts at separation resulted in hydrolysis. 1 drop of diluted HCl added to a small sample of the mixture of bromide and the corresponding alcohol in an NMR. tube caused the immediate disappearance of the signal due to the bromide.

2-Bromomethylnorborn-2-ene (**11**). Tri-*n*-octylphosphine (741 mg; 2 mmol) in 1 ml of dry ether was added (2 min) to a stirred solution of 2-hydroxymethylnorborn-2-ene (124 mg; 1 mmol) and carbon tetrabromide (663 mg; 2 mmol) in dry ether (2 ml) [18]. An exothermic reaction ensued and the solution became yellow. The mixture was stirred at room temperature for an additional 15 min. The ether was removed at water pump pressure and the residual oil was extracted three times with 1 ml portions of pentane. The solvent was removed at room temperature and the product was sub-

jected to GLC., IR. and NMR. analyses. GLC. revealed the absence of the starting alcohol and the presence of a new product with a retention time identical with that of *exo*-3-bromo-2-methylene-norbornane (**2**). The NMR. spectrum indicated that the mixture consisted of 20% of **2** and 80% of 2-bromomethylnorborn-2-ene (**11**). The IR. spectrum showed a strong absorption band at 788 cm^{-1} characteristic of a trisubstituted olefin. After 8 h at the temperature of boiling carbon tetrachloride, **11** was entirely converted into **2**. 2-Bromomethylnorborn-2-ene was stable towards acids; addition of 1 drop of conc. HCl to a NMR. sample did not produce any change after 1 h at room temperature.

NMR. Data. The chief spectral features of compounds **6**, **8**, **9**, **10**, **11** and **14** are listed in Table 2. Compounds **10**, **11** and **14** present no difficulty for structure assignment. The structure of compound **6** is based on the broadness of the resonance at 4.78 ppm indicating that the C(3) bromide substituent has the *endo* configuration [8].

As we were unable to separate the isomers **8** and **9**, the mixture was analysed by double irradiation. The attribution of the various signals to **8** and **9** was based on the difference between the chemical shifts of the bridgehead protons at C(1) and C(4). For 2-methylenenorbornane itself this difference is 0.33 ppm. For the *exo*-3-substituted 2-methylenenorbornanes (*i.e.* **2**, **12** (and the corresponding alcohol)), and their *endo*-3-hydroxy- and acetoxy-derivatives [19] this difference lies between 0.16 and 0.40 ppm. In the case of the pair of isomers **8** and **9**, the differences are 0.69 and 0.35.

Clearly, the expected deshielding of the C(1) proton by the contiguous bromine atom enables the correct identification of the *Z*-isomer [20]. Irradiation of the resonance at 3.21 ppm due to the C(1) proton of **8** revealed which resonance belongs to the C(8) proton.

Table 2. *Chemical Shifts*[a]) *and Splitting*[b]) *of Signals due to the C(1), C(3), C(4) and C(8) protons*

Compound	C(1)—H	C(3)—H	C(4)—H	C(8)—H
6		4 78		5.02
11	2.92[c])	6.01	2.92[c])	4.04
8	3.21 (*m*, *w* = 5.3)	~2.06 *m*	~2.52 *m*	5.65 (*m*, *w* = 4.6 *J* = 4.0[e]))
9	2.87 (*m*, *w* = 6.2)	~2.06[d])	~2.52[d])	5.93 (*t*, *J* = 5.3)
10			~2.04 *m*	3.61 *s*
14			~1.98[f]) *m*	4.21 *s*

a) In ppm (δ) taken in CCl_4.
b) *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *w* = width at half-height, all values in Hz.
c) Signal overlapped with that of C(4) proton.
d) Signal overlapped with that of **8**.
e) Value obtained from decoupled spectrum.
f) Signal overlapped with acetyl signal.

BIBLIOGRAPHY

[1] *A. Wohl*, Chem. Ber. *52*, 51 (1919); *K. Ziegler, A. Späth, E. Schaaf, W. Schumann & E. Winkelmann*, Liebigs Ann. Chem. *551*, 80 (1942); *C. Djerassi*, Chem. Rev. *43*, 271 (1948).
[2] *G. F. Bloomfield*, J. chem. Soc. *1944*, 114; *J. M. Tedder*, Qu. Rev. *14*, 336 (1960).
[3] *S. Wolfe & P. G. C. Campbell*, Canad. J. Chem. *43*, 1184 (1965); *S. Wolfe & D. V. C. Awang, ibid. 49*, 1384 (1971).

[4] *J. Adam, P. A. Gosselain & P. Goldfinger,* Nature *171,* 704 (1953); Bull. Soc. chim. Belg. *65,* 523 (1956).
[5] *B. P. McGrath & J. M. Tedder,* Proc. chem. Soc. *1961,* 80.
[6] *J. D. Roberts, E. R. Trumbull, W. Bennett & R. Armstrong,* J. Amer. chem. Soc. *72,* 3116 (1950); *N. A. LeBel, J. E. Huber & L. H. Zalkow, ibid. 84,* 2226 (1962); *D. R. Dalton, R. K. Rodebaugh & C. W. Jefford,* J. org. Chemistry 37, 362 (1972); *D. R. Marshall, P. Reynolds-Warnhoff & E. W. Warnhoff,* Canad. J. Chemistry *49,* 885 (1971).
[7] *C. W. Jefford & W. Wojnarowski,* Helv. *53,* 1194 (1970).
[8] *C. K. Alden & D. I. Davies,* J. chem. Soc. (C) *1968,* 709; *D. I. Davies,* Special Publication No. 24, The Chemical Society *1970,* 236.
[9] *J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca & J. E. Rush,* J. Amer. chem. Soc. *90,* 509 (1968).
[10] *N. A. Belikova, A. F. Platé & E. Sterin,* Ž. obšč. Chim. *34,* 126 (1964).
[11] *M. Hanack & H. T. Schneider,* Angew. Chem., Intern. Ed. *6,* 666 (1967); *B. H. Jennings & G. B. Herschbach,* J. org. Chemistry *30,* 3902 (1965).
[12] *H. Hart & R. A. Martin,* J. org. Chemistry *24,* 1267 (1959).
[13] *C. W. Jefford & U. Burger,* Chimia *25,* 297 (1971).
[14] *J. W. Wilt, C. F. Parsons, C. A. Schneider, D. G. Schultenover & W. J. Wagner,* J. org. Chemistry *33,* 694 (1968).
[15] *J. D. Roberts & E. R. Trumbull,* J. Amer. chem. Soc. *71,* 1630 (1949).
[16] *W. F. Erman,* J. org. Chemistry *32,* 765 (1967).
[17] *S. Bank, C. A. Rowe, Jr., A. Schriesheim & C. A. Naslund,* J. Amer. chem. Soc. *89,* 6897 (1967).
[18] *J. Hooz & S. S. H. Gilani,* Canad. J. Chemistry *46,* 86 (1968).
[19] *H. Krieger, K. Maaninen & J. Paasivirta,* Suomen Kemistilehti, *39 B,* 8 (1966); *C. W. Jefford, W. Wojnarowski & M. Laffer,* unpublished work.
[20] *C. W. Jefford & R. T. Medary,* Tetrahedron *23,* 4123 (1967); *R. C. Fort, Jr., G. W. H. Cheeseman & E. C. Taylor,* J. org. Chemistry *29,* 2440 (1964).

221. The Migratory Aptitude of the Ethoxycarbonyl Group in the Pinacol Rearrangement

Preliminary communication

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Summary. The migratory aptitude of the ethoxycarbonyl group in the pinacol rearrangement was deduced from the structure of the products observed after treatment of 2-substituted 2,3-dihydroxy-3-phenylbutyrates with fluorosulfonic acid at 0° for 3 minutes. The migratory aptitude of ethoxycarbonyl is comparable to that of ethyl, greater than that of methyl or hydrogen, but smaller than that of phenyl. Cyclization and fragmentation reactions were also observed.

Our recent observation of a ethoxycarbonyl group migration in the acid-catalyzed rearrangement of glycidic esters [1] encouraged us to reinvestigate the classical pinacol rearrangement from the viewpoint of establishing the migratory aptitude of the ethoxycarbonyl group in this reaction[1]). In order to minimize the possible influence of the nature of the initial carbonium ion on the course of the reaction, we selected a