11-Methyl-12-phenyl-6,11-dihydro-6,11-ethanoacridizinium Fluoroborate.—The named salt was prepared essentially as was the previously reported[12] perchlorate salt, yield 90% of colorless microcrystals, mp 227–230°.

Anal. Calcd for $C_{22}H_{20}BF_4N$: C, 68.59; H, 5.23; N, 3.64. Found: C, 68.84; H, 5.26; N, 3.66.

11-Methyl-12-phenyl-1,2,3,4,5,6,11,11a-octahydroacridizinium Fluoroborate (27). A. By Hydrogenation of Adduct 16 from Phenylacetylene and 11-Methylacridizinium Fluoroborate.—To a suspension of 0.5 g of finely powdered **16** in 50 ml of ethanol, 0.1 g of platinum oxide was added and the mixture was hydrogenated at atmospheric pressure until slightly more than the theoretical quantity of hydrogen had been absorbed. After the catalyst had been removed by filtration the solution was concentrated and the residue was crystallized from acetonitrile–ether and then from pure acetonitrile, yield 0.25 g (50%) of colorless prisms, mp 198–199°.

B. By Reduction of 11-Methyl-12-phenyl-6,11-dihydro-6,11-ethanoacridizinium Fluoroborate.—Hydrogenation of 0.25 g of the named compound in 25 ml of ethanol using 0.1 g of platinum oxide catalyst afforded 0.15 g (60%) of colorless crystals, mp 198–199°. The ir spectra of the two preparations are identical.

Anal. Calcd for $C_{22}H_{26}BF_4N$: C, 67.53; H, 6.70; N, 3.58. Found: C, 67.45; H, 6.54; N, 3.24.

(12) C. K. Bradsher and J. A. Stone, *J. Org. Chem.*, **34**, 1700 (1969).

Registry No.—**1**, 32865-43-3; **2**, 32865-44-4; **3** (R_1 = H; R_2 = OH), 32861-29-3, 32861-30-6 (iodide); **3** (R_1 = H; R_2 = *p*-$CH_3C_6H_4SO_2O$), 32861-31-7; **4**, 32861-32-8; **5**, 32861-33-9; **6**, 32861-34-0; **7**, 32861-35-1; **8**, 32958-81-9; **9**, 32861-36-2; **10**, 32846-42-7; **11**, 32846-43-8; **16**, 32846-44-9; **17**, 32981-43-4; **18**, 32865-45-5; **19**, 32865-46-6, **20**, 32865-47-7; **21**, 32865-48-8; **22**, 32839-09-1; **22** free amine, 32861-37-3; **23** free amine, 32861-38-4; **24**, 32861-39-5; **25**, 32839-10-4; **27**, 32839-11-5; 12,13-dichloro-6,-11-dihydro-6,11-ethanoacridizinium tetrafluoroborate, 32846-45-0; 11-methyl-12-phenyl-6,11-dihydro-6,11-ethanoacridizinium fluoroborate, 32846-46-1.

The Cycloaddition of the Acridizinium Ion with Norbornene Derivatives[1]

MARCELLUS E. PARHAM, MARSHALL G. FRAZER, AND CHARLES K. BRADSHER*

Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706

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The adducts obtained by cycloaddition of norbornene derivatives with the acridizinium ion are exo and have one strongly shielded methylene proton that appears in the nmr at higher fields than δ 0. Norbornene derivatives which had an endo ring attached at positions 5 and 6 gave predominantly syn addition with respect to the benzenoid ring, the yields being highest when a heteroatom was in the ring. The acridizinium ion added twice to norbornadiene giving what is believed to be a syn,syn product.

Aromatic quaternary salts are electrophiles and in some instances[2-4] are capable of undergoing cycloaddition with appropriate alkenes. Since the products of the classical Diels–Alder reaction are cyclohexene derivatives, it seemed quite possible that such products might undergo a second cycloaddition reaction with a suitable aromatic quaternary salt. Such successive cycloaddition reactions would permit the easy synthesis of some relatively complex systems.

Although it was found that cyclohexene under sealed tube conditions can be made to add to the acridizinium ion (**1**) (Scheme I), it appeared more promising to carry out the proposed study with the more reactive norbornene and its derivatives (**2**). A great many norbornene derivatives of known stereochemistry are available by the use of the Diels–Alder reaction and many more can be derived from Diels–Alder products.

Addition of the acridizinium ion to norbornene (**2**, R = H_2) yields a mixture which, on the basis of nmr evidence, appears to contain only exo addition products. In the spectra of both components (**3** and **4**) of the mixture, signals arising from one proton (H_A-18)[5] of the methylene bridge appear at a magnetic field so high (above δ 0.0) as to be explicable only if the proton were strongly shielded by diamagnetic ring currents of an aromatic ring.

The addition of cyclopentadiene to norbornene is also reported[6] to occur exo. The H_A-18 signal at the *highest* field was a doublet at δ −0.85[7] which had approximately two-thirds the area of the other H_A-18 doublet at δ −0.42. The assignment of the higher field doublet as anti (with respect to the benzenoid ring) was made by reducing the mixture of syn and anti (**3** and **4**, R = H_2) catalytically. It is known[2,8] that the pyridinium ring is reduced in preference to the benzenoid ring; so it would be expected that the strong shielding effect due to the ring currents of the pyridinium ring would disappear while that due to the benzenoid ring would remain. The crude reduction product from the mixture had lost the resonance at δ −0.85 (**4** H_A-18) as well as another at δ 0.87 (**4**, H_B-18) while those at δ −0.42 (**3**, H_A-18) and 0.60 (**3**, H_B-18) remained. This made it possible to assign the isomer giving the signal at the highest field as the anti (**3**, R = H_2). Recrystallization of the mixture of isomers resulted in the isolation of the pure syn isomer (**3**, R = H_2). The residue from the mother liquors, when subjected to column chromatography using the gradient elution technique,[9] afforded a small quantity of the pure anti isomer (**4**, R = H_2). Nmr with pure samples afforded further evidence for the

(1) This research was supported in part by Public Health Service Research Grant No. HE-2170 of the National Heart Institute.

(2) C. K. Bradsher and T. W. G. Solomons, *J. Amer. Chem. Soc.*, **80**, 933 (1958).

(3) D. L. Fields, T. H. Regan, and J. C. Dignan, *J. Org. Chem.*, **33**, 390 (1968).

(4) C. K. Bradsher and F. H. Day, *Tetrahedron Lett.*, 409 (1971).

(5) The numbering for **3** is that recommended by Dr. Kurt L. Loening of *Chemical Abstracts* for the 6,11-*o*-benzene-7,10-methanobenzo[*b*]quinolizinium system. Our decision to use the same numbering system for adducts obtained from all norbornene derivatives was made to facilitate tabulation of the nmr data.

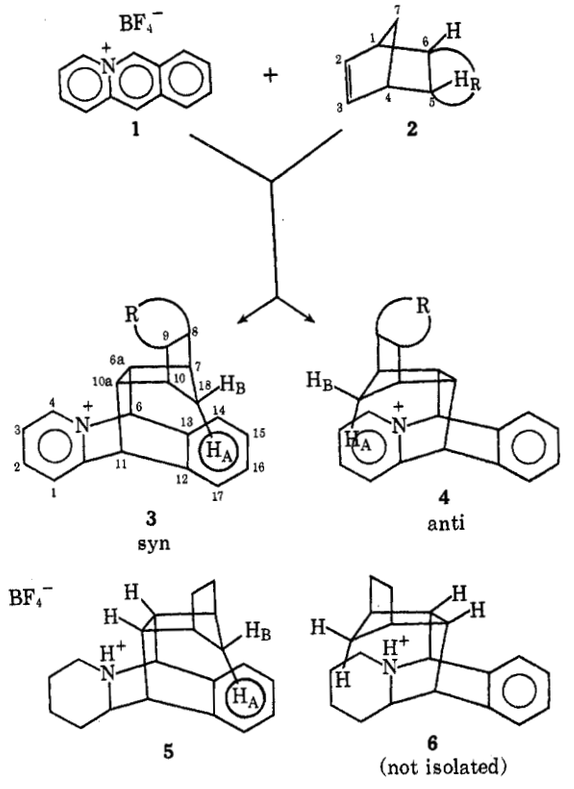
(6) S. B. Soloway, *J. Amer. Chem. Soc.*, **74**, 1027 (1942).

(7) Since some of the signals from the products of norbornene derivatives fell into the region of a tetramethylsilane signal, the primary internal standard for our measurements was the chloroform signal. This signal was set at δ 7.30 to put our results on approximately the usual TMS scale.

(8) C. K. Bradsher and L. E. Beavers, *J. Amer. Chem. Soc.*, **77**, 4812 (1955).

(9) The gradient device used was type E as described in Erich Heftmann, "Chromatography," 2nd ed, Reinhold, New York, N. Y., 1967, p 104.

SCHEME I
ADDITION OF ENDO 5,6-SUBSTITUTED NORBORNENES



correctness of the structural assignments (Table I). In the syn isomer (**3**, R = H_2), protons on carbons 7 and 10 over the uncharged benzene ring are so similar in their environment that they have the same resonance and because of the lack of coupling with protons 6 and 11 and with each other, appear to be magnetically equivalent. On the other hand the bridgehead protons at 6a and 10a project toward the pyridinium ring and appear as quartets with different resonances because of the different distances of the two protons from the positive charge.

The anti isomer (**4**, R = H_2) has bridgehead protons H-10 and H-7 over, and at different distances from, the quaternary nitrogen, and hence have resonances at different fields. On the other hand, the protons at the 10a and 6a bridgehead positions are directed over the uncharged benzene ring and appear as a single singlet.

Definite assignment of the resonances and the nature of the coupling was made possible by means of decoupling experiments. Using the pure syn isomer, when the doublet at δ −0.42 was irradiated, the doublet at δ 0.60 collapsed to a singlet. A similar collapse of the δ −0.42 doublet was observed when the signal at δ 0.60 was irradiated, indicating geminal coupling (J_{AB} = 12 Hz) of the 18A and 18B protons of the methylene group. The bridgehead proton (H-6) adjacent to nitrogen is easily identified because it is so strongly deshielded. With the syn isomer, irradiation of the signal at δ 6.30 due to H-6 caused the collapse of the quartet at δ 2.30 to a doublet, identifying the signal for the proton at 6a. Irradiation of the other easily identifiable protons at position 11 caused a collapse of the quartet at δ 2.18 to a doublet and identified the signal due to the proton at 10a.

TABLE I
ADDITION OF ENDO 5,6-SUBSTITUTED NORBORNENES (**2**) TO ACRIDIZINIUM FLUOROBORATES (**1**)

Substituent ring R	Time, hr	Temp, °C	Analytical sample, mp, °C	Formula[a]	Syn (**3**): anti (**4**)[b]	Yield,[c] %	Nmr, δ (multiplicity)[d] H-18A	H-18B	H-10	H-7	H-10a	H-6a	H-11	H-6
None	24	82[e]	Syn, 282–284	$C_{20}H_{20}BF_4N$	60:40	82	−0.42 (d)[f]	0.60 (d)[f]	2.27 (s)	2.27 (s)	2.18 (q)[g,h]	2.30 (q)[h,i]	5.05 (d)[g]	6.30 (d)[i]
			Anti, 270–271				−0.85 (d)[f]	0.87 (d)[f]	2.35 (s)	2.47 (s)	2.35 (s)	2.35 (s)	5.10 (s)	6.30 (s)
$(CH_2)_3$	48	82[e]	Mixture, 265–267	$C_{23}H_{24}BF_4N$	85:15	42	−0.32 (d)[f]	0.78 (d)[f]	*j*	*j*	*j*	*j*	5.03 (d)[k]	6.30 (d)[l]
CONHCO	72	82[e]	Syn, 400 dec	$C_{22}H_{19}BF_4N_2O_2$	100:0	62	−0.16 (d)[m]	1.10 (d)[m]	3.0 (m)	3.0 (m)	2.50 (q)[n,o]	2.83 (q)[i,o]	5.20 (d)[n]	6.43 (d)[i]
$CON(CH_3)CO$	120	82[e]	Syn, 375–377 dec	$C_{23}H_{21}BF_4N_2O_2$	100:0	99	−0.10 (d)[f]	1.09 (d)[f]	*j*	*j*	2.27 (q)[g,h]	2.62 (q)[i,h]	5.20 (d)[g]	6.43 (d)[i]
COOCO	96	120[p]	Syn, 300 dec	$C_{22}H_{18}BF_4NO_3$	100:0	25	−0.05 (d)[f]	1.08 (d)[f]	2.97 (s)	2.97 (s)	2.30 (q)[q,r]	2.80 (q)[i,r]	5.20 (d)[g]	6.67 (d)[i]
CH_2OCH_2	24	82[e]	Syn, 298–299	$C_{22}H_{22}BF_4NO$	100:0	53	−0.12 (d)[f]	0.94 (d)[f]	*s*	*s*	*s*	*s*	5.05 (d)[k]	6.30 (d)[t]
							−0.07 (d)[f,w]	1.10 (d)[f]	*s*	*s*	*s*	*s*	5.10 (d)[y]	6.37 (d)[z]
$CH_2NH_2{}^+CH_2$[u]	96	120[p]	Mixture, 325–330[v]	$C_{22}H_{24}B_2F_8N_2$	70:30	22	−0.53 (d)[f,x]	1.30 (d)[f]	*s*	*s*	*s*	*s*	5.10 (d)[y]	6.37 (d)[z]

[a] Satisfactory analyses were submitted for all analytical samples described in this table: Ed. [b] Ratio of syn to anti as determined by nmr on first product isolated. [c] Unless otherwise indicated yields are of total cycloaddition product. [d] For numbering see Scheme I. All signals showed expected integration. [e] Refluxing acetonitrile. [f] J_{AB} = 12 Hz. [g] $J_{10a,11}$ = 3 Hz. [h] $J_{6a,10a}$ = 10 Hz. [i] $J_{6,6a}$ = 4 Hz. [j] Not clearly resolved. [k] $J_{10a,11}$ = 2 Hz. [l] $J_{6,6a}$ = 3 Hz. [m] J_{AB} = 12 Hz. [n] $J_{10a,11}$ = 3 Hz. [o] $J_{6a,10a}$ = 8 Hz. [p] Sealed tube. [q] $J_{10a,11}$ = 4 Hz. [r] $J_{6a,10a}$ = 9 Hz. [s] Not definitely assigned. [t] $J_{6,6a}$ = 2 Hz. [u] Both anions were fluoroborate. [v] This mixture was not separated. The nmr results have been assigned by analogy to the unsubstituted compound. [w] All data on this line assigned to syn isomer. [x] All data on this line assigned to anti isomer. [y] $J_{10a,11}$ = 1 Hz. [z] $J_{6,6a}$ = 1 Hz.

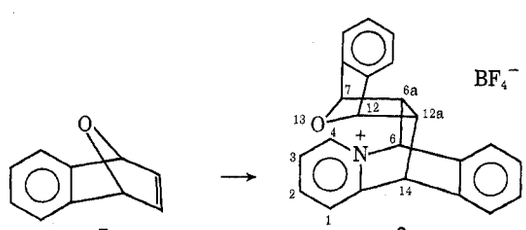
Similar irradiation experiments with the anti isomer (**4**, R = H_2) revealed signals from H-6A and H-10A as one singlet and those from H-7 and H-10 as singlets. It is significant that protons H-6 and H-11 are not coupled.

Hydrogenation of a pure sample of the syn isomer (**3**, R = H_2) afforded **5**, in which the resonances due to the methylene protons appeared at almost the same fields (H_{18A}, δ −0.33, H_B, δ 0.60) as in the starting materials. While there was not enough of the pure anti isomer (**4**, R = H_2) available to permit a similar reduction, reduction of the mixture of syn and anti products had shown the disappearance of signals at δ −0.85 and 0.87.

The remaining compounds in Table I were prepared to study the effect on the stereochemistry of the cycloaddition exerted by rings attached endo at positions 5 and 6 of the norbornene structure (**2**). Only when the ring consisted solely of methylene groups [**2**, R = $(CH_2)_3$] or when there was a positive charge on the ring (**2**, R = $CH_2N^+H_2CH_2$) was there evidence for the formation of any but the syn isomer. While in every case except that affording a 99% yield [**2**, R = $CON(CH_3)_2CO$] it might be presumed that significant quantities of the anti isomer were present, routine observation of the filtrate gave no evidence of the existence of anti isomer, and it is believed that the reaction in these cases does occur exclusively syn.

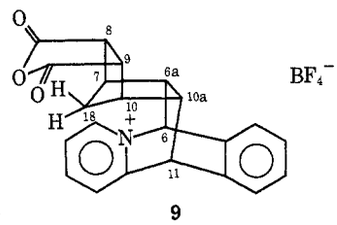
A plausible explanation for this stereoselectivity is that, when unshared electrons are available on the central atom of the endo ring, attraction to the positive charge of the acridizinium nitrogen is a controlling factor. The fact that even without an endo bridge (**2**, R = H_2) more syn then anti addition occurs, suggests that repulsion of the methylene hydrogens by the pyridinium ring may be greater than that by the benzenoid ring.

As a test of the attraction of unshared electrons toward the positive nitrogen, the addition of 1,4-dihydronaphthalene 14-*endo*-oxide (**7**) to the acridizinium nucleus was carried out. The expected product, the anti stereoisomer (**8**), was the only one obtained. Structural assignment was based on the observation that the protons at 6a and 12a are equivalent (hence over the benzenoid ring) while those at C-7 and C-12 were not, indicating that one of the two was significantly closer to the positive charge on nitrogen and hence more deshielded than the other.



7 **8**

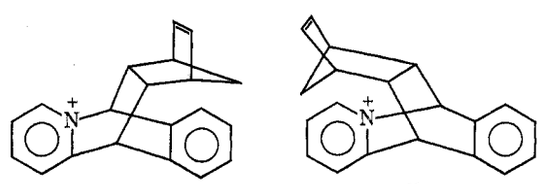
The only cycloaddition with an exo derivative of norbornene used the readily available[10] norbornene-*exo*-5,6-dicarboxylic anhydride. It was found that cycloaddition occurred more readily than with the endo isomer and that the product was a mixture. Interestingly, a single crystallization gave the pure anti adduct (**9**) in an overall yield of 15%. Assignment of



9

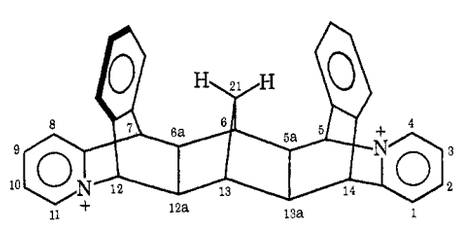
the structure rests on the effect of the positive nitrogen on the bridgehead proton signals in the nmr.

The addition of 2 mol of acridizinium ion to norbornadiene was carried out with the hope of creating an adduct in which both of the methylene protons would appear at negative values on the TMS scale. The reaction was carried out stepwise, the first addition taking place in refluxing acetonitrile and yielding a mixture consisting of approximately 73% syn (**10**) and 27% anti (**11**) isomers. Fractional crystallization of the mixture did not result in a useful change in isomer ratio, so the final step in the synthesis was carried out using the mixture. When heated with acridizinium fluoroborate in a sealed tube at 120°, the mixture reacted to afford the diadduct **12** in 51% yield.



10 **11**

(not separated)



12

The problem of regioisomerism in the second cycloaddition seems more difficult to resolve than problems of stereoisomerism. The formulation of the second azonia group as being at 11a rather than 7a rests only on the principle of maximum separation of like charges. Despite this uncertainty it is still possible to draw some interesting conclusions with regard to the stereochemistry of the system. Even if one assumes that there is no deviation from the usual preference for exo addition, there remain three possibilities for the structure: syn,syn; syn,anti; and anti,anti. It is easy to eliminate the possibility of endo addition and/or that the structure is syn,anti, for the data in Table I make it quite clear that under those circumstances the methylene protons should give rise to two distinct sets of doublets. Actually the product shows a singlet at δ −0.80 corresponding to two protons, evidence that the methylene protons have a symmetrical environment, eliminating every possibility except an exo,exo–syn,syn or exo,exo–anti,anti configuration. The possibility that the product is anti,anti is appealing, be-

(10) D. Craig, *J. Amer. Chem. Soc.*, **73**, 4889 (1951).

cause the field at which the two-proton singlet appears is matched in Table I only by the H_A proton of an anti derivative, but this line of reasoning does not take into account the effect of overlapping fields which arises from the aromatic ring facing the *vicinal* proton of the methylene group. Decisive in our assignment of the diadduct as syn,syn was the yield (51%) of diadduct observed, for, barring rearrangements or dissociation–recombination, such a yield of anti,anti product would be impossible with a starting material that was only 27% anti. In addition, decoupling experiments indicate that protons 6 and 13 occur as a singlet as do H-7 and H-10 in syn isomer **3**. Likewise protons at 5 and 12 and 7 and 14 are split by protons at 5a and 6a and 12a and 13a, respectively, again corresponding with the pattern observed in syn isomer **3**.

Experimental Section

Methods.—All nmr data were obtained by use of a Varian T-60 spectrometer and, unless otherwise specified, using trifluoroacetic acid as solvent and chloroform (δ 7.30) as an internal standard. The melting points were determined in capillaries using a Thomas-Hoover apparatus. All analyses were by Janssen Pharmaceutica Research Laboratories, Beerse, Belgium, or M-H-W Laboratories, Garden City, Mich.

Materials.—*endo*-1,2-Dihydrodicyclopentadiene,[11] *endo*-*N*-methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboximide,[12] 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene,[13] and *endo*-2-aza-1,2-dihydrodicyclopentadiene[13] were prepared according to published directions. A quantity of *endo*-5-norbornene-2,3-dicarboximide was obtained from Professor Pelham Wilder, Jr. Except as noted, other norbornene derivatives were purchased.

6,11[1′,2′]Cyclohexeno-6,11-dihydroacridizinium.—A solution of 0.95 g of freshly distilled cyclohexene and 0.3 g of acridizinium tetrafluoroborate[14] in 3 ml of dry acetonitrile was heated for 2 days at 120° in a sealed tube. The reaction mixture was poured into ether, affording 0.35 g (94%) of a colorless powder, mp 261–262°. Recrystallization from methanol gave yellowish crystals, mp 267°.

Anal. Calcd for $C_{19}H_{20}BF_4N$: C, 65.35; H, 5.77; N, 4.01. Found: C, 65.59; H, 5.79; N, 3.85.

Cycloaddition of Acridizinium Fluoroborate (1) with Norbornene Derivatives (2). A. In Refluxing Acetonitrile.—To the acridizinium fluoroborate suspended in anhydrous acetonitrile (7 ml/g 1) 2 or 3 equiv of the norbornene derivative was added and the mixture was refluxed until the uv absorption of a sample showed that absorption in the 399-mμ region was absent. The recovery of the product was made either by pouring the mixture into dry ether or by evaporating the solvent and triturating the residue with acetone or methanol. In every case the product was recrystallized from acetonitrile.

B. In a Sealed Tube.—The sealed tube reactions were carried out similarly except that the solutions were more concentrated (1.5 ml CH_3CN/g 1) and the tubes were heated at 120°. The adduct (**3** and **4**, R = $CH_2N^+H_2CH_2$) obtained from *endo*-2-aza-1,2-dihydrodicyclopentadiene was crystallized from acetonitrile–ethyl acetate to which a few drops of fluoroboric acid had been added.

Separation of *syn*- and *anti*-Norbornene Adducts (3 and 4, R = H_2).—From 13 g of the 60:40 mixed product in two recrystallizations from acetonitrile, 1.7 g of pure syn isomer was obtained. The mother liquors from the crystallization were concentrated, 5 g of alumina was added, and the solvent was removed under reduced pressure. This material was placed at the top of an alumina column (4 × 100 cm) of Merck 80–200 mesh alumina packed by the slurry method using methylene chloride. Elution was by the gradient method[9] with 33% acetonitrile–67% methylene chloride as the polar solvent and methylene chloride as the nonpolar solvent. Progress of the elution could be followed by fluorescence under uv light. Only a partial separation was obtained but the first fractions contained 0.08 g of pure anti isomer.

1,2,3,4,5,6,6a,7,8,9,10,10a,11,11a-Tetradecahydro-6,11-*o*-benzeno-7,10-methanoacridizinium Fluoroborate (5).—A suspension of 0.9 g of pure *syn*-6,6a,7,8,9,10,10a,11-octahydro-6,11-benzeno-7,10-methanoacridizinium fluoroborate (**3**, R = H_2) was suspended in 100 ml of ethanol and 0.1 g of platinum oxide catalyst was added. The mixture was hydrogenated at atmospheric pressure until slightly more than the theoretical quantity of hydrogen had been absorbed. The tan product (0.9 g) was recrystallized from acetonitrile affording colorless crystals: mp 292°; nmr δ −0.33 (d, 1, J_{AB} = 12 Hz, H_A-18), 0.60 (d, 1, J_{AB} = 12 Hz, H_B-18), 4.57 (d, 1, $J_{6,6a}$ = 3 Hz, H-6).

Anal. Calcd for $C_{20}H_{26}BF_4N$: C, 65.41; H, 6.86; N, 3.81. Found: C, 65.24; H, 6.93; N, 3.78.

6,7,12,14-Tetrahydro-6,14-*o*-benzenobenz[*i*]acridizinium 7,12-Oxide Fluoroborate (8).—The addition of 1,4-dihydronaphthalene 1,4-*endo*-oxide (**7**)[15] to acridizinium fluoroborate was carried out in acetonitrile by heating at 50° for 12–14 hr. After removal of the solvent, ether trituration of the residue afforded crystals which were recrystallized from acetone and then from methanol: yield 1 g (43%); mp 230° dec; nmr δ 2.80 (s, 2, H-6a,12a), 5.40 (s, 1, H-14), 5.60 (s, 1, H-12), 5.77 (s, 1, H-7), 6.66 (s, 1, H-6).

Anal. Calcd for $C_{23}H_{18}BF_4NO$: C, 67.18; H, 4.41; N, 3.41. Found: C, 67.21; H, 4.57; N, 3.41.

***anti*-6,6a,7,8,9,10,10a,11-octahydro-6,11-*o*-benzeno-7,10-methanoacridizinium-*exo*-8,9-carboxylic Acid Anhydride Fluoroborate (9).**—The refluxing acetonitrile procedure was used with *exo*-5,6-norbornenedicarboxylic acid anhydride[10] as in procedure A, the reaction taking 4 days. The product crystallized from acetonitrile, affording the pure anti adduct in 15% yield: mp >360 nmr δ −0.60 (d, 1, J_{AB} = 12 Hz, H_A-18), 0.94 (d, 1, J_{AB} = 12 Hz, H_B-18), 2.65 (s, 2, H-6a,10a), 3.16 (s, 1, H-10), 3.28 (s, 1, H-7), 3.33 (s, 2, H-8,9), 5.26 (s, 1, H-11), 6.50 (s, 1, H-6).

Anal. Calcd for $C_{22}H_{18}BF_4NO_3$: C, 61.28; H, 4.21; N, 3.25. Found: C, 61.36; H, 3.98; N, 3.16.

6,6a,7,10,10a,11-Hexahydro-6,11-*o*-benzeno-7,10-methanoacridizinium Fluoroborate (10 and 11).—In refluxing acetonitrile 1 reacted with excess norbornadiene in 24 hr to afford a 90% yield of a mixture of syn (**10**) and anti (**11**) isomers, mp *ca.* 280°. Although it was not practicable to effect separation by recrystallization, the presence of 73% *syn*-**10** and 27% *anti*-**11** was evidenced by nmr: syn, δ −0.23 (d, 1, J_{AB} = 12 Hz, H-18$_A$), 0.85 (d, 1, J_{AB} = 12 Hz, H-18$_B$); anti, −0.73 (d, 1, J_{AB} = 12 Hz, H-18$_A$), 1.25 (d, 1, J_{AB} = 12 Hz, H-18$_B$); syn and anti, 5.06 (d, 1, $J_{11,10a}$ = 3 Hz, H-11), 6.37 (m, 3, H-6,8,9).

Anal. Calcd for $C_{20}H_{18}BF_4N$: C, 66.88; H, 5.05; N, 3.90. Found: C, 66.95; H, 5.13; N, 3.75.

***syn,syn*-5,5a,6,6a,7,12,12a,13,13a,14-Decahydro-5,14,:7,12-bis-*o*-benzeno-6,13-methano-4a,11a-diazonia Fluoroborate (12).**—A solution of 0.67 g of the monoadduct (10 + 11) and 0.5 g of acridizinium fluoroborate (1) was heated at 120° for 4 days in a sealed tube. The highly insoluble product crystallized on the walls of the tube and the solvent containing any unreacted material was decanted, yield 0.6 g (51%). The product was crystallized, mp >360°, from a large quantity of acetonitrile: nmr δ −0.80 (s, 2, CH_2), 2.4–2.6 (m, 6, H-5a,6,6a,12a,13,13a), 5.13 (d, 2, $J_{6a,7} = J_{13a,14}$ = 2Hz, H-7,14), 6.38(d, 2, $J_{5,5a} = J_{12,12a}$ = 3 Hz, H-5,12).

Anal. Calcd for $C_{33}H_{28}B_2F_8N_2$: C, 63.29; H, 4.51; N, 4.47. Found: C, 63.52; H, 4.42; N, 4.36.

Registry No.—**1**, 32865-43-3; **3** (R = H), 32958-93-3; **3** [R = $(CH_2)_3$], 32865-49-9; **3** (R = CONHCO), 32865-50-2; **3** [R = CON(CH_3)CO], 32865-51-3; **3** (R = COOCO), 32865-52-4; **3** (R = CH_2OCH_2), 32865-53-5; **3** (R = $CH_2NH_2^+CH_2$), 32839-12-6; **4** (R = H), 32865-54-6; **4** [R = $(CH_2)_3$], 32865-55-7; **4** (R = $CH_2NH_2^+CH_2$), 32839-13-7; **5**, 32839-14-8; **8**, 32865-56-8; **9**, 32958-94-4; **10**, 32865-57-9; **11**, 32865-58-0; **12**, 32981-44-5; 6,11[1′,2′]cyclohexeno-6,11-dihydroacridizinium, 32865-60-4.

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Bromohydrin Formation in Dimethyl Sulfoxide. V.[1] The Reaction of Norbornene

D. R. DALTON,* [2] RONALD K. RODEBAUGH,[2,3] AND CHARLES W. JEFFORD[4]

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122, and Université de Genève, Ecole di Chimie, Genève, Switzerland

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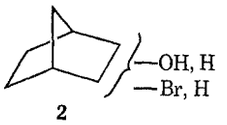
The reaction of bicyclo[2.1.1]heptene (norbornene) with *N*-bromosuccinimide (NBS) in moist dimethyl sulfoxide (DMSO) has been examined in detail. The structures of the products have been elucidated and it has been shown (contrary to an earlier report) that no 2,3-bromohydrin products are obtained. In addition, bromohydrins which were not obtained, but which might have been, *a priori*, expected, were synthesized and shown to be stable to the reaction conditions. The products which were obtained, also stable to the reaction conditions, are accounted for on the basis of ionic and free-radical processes.

We have demonstrated[1,5] that a wide variety of olefins react with *N*-bromosuccinimide (NBS) in moist dimethyl sulfoxide (DMSO) to generate, without rearrangement, stereo- and regiospecifically, the corresponding bromohydrins. Unique among all olefins we have examined, in that rearrangement occurs, is bicyclo[2.2.1]heptene (norbornene) (**1**).

In our initial report[5] concerning the results of the reaction of norbornene (**1**) with NBS in moist DMSO we indicated that 3-bromobicyclo[2.2.1]heptan-2-ol (geometry unspecified) (**2**), *syn*-7-bromobicyclo[2.2.1]-



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heptan-2-*exo*-ol (**3**), and nortricyclene bromide (**4**) were formed in the ratio 3:3:1. This result was based solely upon gas–liquid partition chromatography (glpc) comparison of the products obtained in the NBS–DMSO system with those obtained in *tert*-butyl alcohol–water–sulfuric acid by earlier workers.[6]

Since positive halogen reagents usually do not provide unrearranged material in large amounts when permitted to react with norbornene,[7] and since the geometry of the 2,3 product could potentially provide insight into the reason for the lack of rearrangement, we felt that a thorough investigation of this system merited our attention.

Results and Discussion

When norbornene (**1**) is permitted to react with NBS in moist DMSO six products (99.2%) are, in fact, formed. These products and the relative per cent yields in which they were obtained are shown in Table I

TABLE I

Product	Yield, %
Nortricyclene bromide (**4**)	61.8
syn-7-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (**3**)	21.7
exo-syn-2,7-Dibromobicyclo[2.2.1]heptane (**11**)	8.3
anti-7-Bromobicyclo[2.2.1]heptan-2-*exo*-ol (**8**)	4.4
syn-7-Bromobicyclo[2.2.1]heptan-2-one (**7**)	2.2
endo-exo-2,3-Dibromobicyclo[2.2.1]heptene (**10**)	1.6

and can be accounted for by the species shown in Scheme I.

Thus, **1** is converted (perhaps after initial complexation)[8] into a bromocation which can be represented as the α-bromocarbonium ion A, the bromonium ion B, or some other positive species for which these structures (Scheme I) represent idealized constructions.[9] In either ion A or B the bulk of the bromine atom would presumably preclude exo attack by DMSO[7b,10] but not endo attack by this nucleophilic reagent.

Indeed, formation of the ultimate product of endo attack [*i.e.*, *exo*-3-bromobicyclo[2.2.1]heptan-2-*endo*-ol (**5**)] would be expected either from attack on the first ion or a rearrangement product of this ion resulting from 6,1-hydride migration in the nonclassical ion C (Scheme I).[11] Nevertheless, this product, although sought, is not found and we attribute its absence to the bulky nature of the solvated nucleophile and the requirement that it attack the endo face of the system. Thus, the major product (nortricyclene bromide) (**4**) derives simply from loss of a proton, presumably to succinimide anion.

Transformation of the first ion A or B into C, through σ bond delocalization, or D by a Wagner–Meerwein rearrangement, followed by attack of solvent at C_1 (norbornene numbering) in C or at the positive charge in D from the exo direction results in formation of *syn*-7-

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(2) Department of Chemistry, Temple University, Philadelphia, Pa. 19122.

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(4) Université de Genève, Ecole de Chimie, Genève, Switzerland.

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