1400, 1290, 1180, 1145, 1095, 1030, 1005, 920, 585, 565, and 545 $cm^{-1}$; nmr $\delta$ 8.0 (d, 2, $J$ = 8 Hz, phenyl CH), 7.8 (d, 1, $J$ = 3 Hz, pyrrolyl CH), 7.6 (d, 2, $J$ = 8 Hz, phenyl CH), 7.2 (d, 1, $J$ = 3 Hz, pyrrolyl CH), 6.7 (t, 1, $J$ = 3 Hz, pyrrolyl CH), and 2.5 (s, 3, $-CH_3$).

*Anal.* Calcd for $C_{13}H_{10}N_2O_4S$: C, 53.78; H, 3.47; N, 9.65. Found: C, 53.62; H, 3.52; N, 9.50.

***N*-Tosylpyrrole-2-carboxamide (13).**—Brief (2–3 min) heating on the steam bath of a mixture of 1 g of **12** with 10 ml of 10% aqueous sodium hydroxide yielded a solution which was filtered cooled, and acidified with dilute hydrochloric acid. There precipitated 0.85 g of **13**: mp 214–218, raised to 224–225° by recrystallization from ethanol; ir (Nujol) 3300, 3275, 1675, 1590, 1550, 1350, 1300, 1190, 1175, 1145, 1120, 1090, 1070, 950, 875, 810, 740, 660, 605, 570, and 540 $cm^{-1}$; nmr $\delta$ 12.0 (s, 1, NH), 11.8 (s, 1, NH), 8.0 (d, 2, $J$ = 8 Hz, phenyl CH), 7.5 (d, 2, $J$ = 8 Hz, phenyl CH), 7.3 (m, 1, pyrrolyl CH), 7.1 (m, 1, pyrrolyl CH), 6.2 (m, 1, pyrrolyl CH), and 2.4 (s, 3, $-CH_3$). The above spectra were identical with the corresponding spectra of the product of the reaction of pyrrole with tosyl isocyanate in dioxane [mp 224–226° (lit.[5] mp 222–224°), mmp 224–226°].

**Registry No.**—**1**, 32846-52-9; **2**, 32846-53-0; **3**, 4551-72-8; **4**, 634-97-9; **5**, 32846-56-3; **6**, 32846-57-4; **7**, 4778-77-2; **8**, 13939-91-8; **10**, 32846-60-9; **11**, 21972-99-6; **12**, 32846-62-1; **13**, 32846-63-2.

**Acknowledgment.**—Financial support from the Research Corporation, the Research Allocations Committee of the University of New Mexico, and the Department of Chemistry of the University of New Mexico is gratefully acknowledged.

# 6,11-Dihydroacridizinium Derivatives Having a 6,11-Etheno Bridge[1]

W. S. BURNHAM AND C. K. BRADSHER*

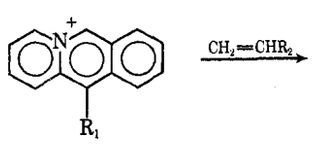
*Department of Chemistry, Paul M. Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706*

*Received June 28, 1971*

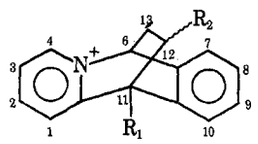
Ethano-bridged derivatives may be made by addition of vinyl alcohol or amine derivatives to the acridizinium ion, but no means has been found for converting these to etheno-bridged derivatives. Etheno-bridged derivatives may be prepared by addition of acetylenic compounds to 11-substituted acridizinium ions, but if no substituent is present at position 11 rearrangement occurs, affording derivatives of 1-(2-pyridyl)naphthalene.

**Cycloaddition Reactions Using Vinyl Derivatives.**—The synthesis of 6,11-dihydroacridizinium compounds having a 6,11-etheno bridge would provide a means for the study of the inductive effect of an adjacent but unconjugated positive charge on the addition reactions of a double bond, as well as an intermediate for the possible synthesis of an azoniajanusene.[2] Our initial plan was to prepare an ethano-bridged compound having a hydroxyl group (or suitable derivative) on the bridge, and to convert this to an etheno-bridged derivative *via* an elimination reaction.

It was found that ethyl vinyl ether, butyl vinyl ether, and vinyl acetate all added to the acridizinium ion in good yield (Table I). As would be expected from the strong polarization of such vinyl derivatives, the orientation in each case was that with the oxy function at position 12. Acid-catalyzed cleavage of the ether or ester linkages gave the same alcohol (**3**, $R_1$ = H; $R_2$ = OH). Acetylation of this hydroxyl derivative gave the acetate **7**, identical with that obtained in the cycloaddition reaction with vinyl acetate. It was also possible to convert the hydroxyl compound (**3**, $R_1$ = H; $R_2$ = OH) to the tosylate (**3**, R = H; $R_2$ = Tos) by action of tosyl chloride and pyridine.




**1**, $R_1$ = H
**2**, $R_1$ = Ph




**3**

**4**, $R_1$ = H; $R_2$ = OEt
**5**, $R_1$ = Ph; $R_2$ = OEt
**6**, $R_1$ = H; $R_2$ = OBu
**7**, $R_1$ = H; $R_2$ = OAc
**8**, $R_1$ = H; $R_2$ = *N*-carbazyl
**9**, $R_1$ = H; $R_2$ = 1-pyrrolidin-2-one

The alcohol (**3**, $R_1$ = H; $R_2$ = OH) was not dehydrated when allowed to stand in concentrated sulfuric acid for 24 hr. The acetate **7** survived heating in a sealed tube at 210°, refluxing for 10 hr in dimethylformamide, or refluxing for 24 hr in pyridine. The tosylate was recovered (95%) after refluxing for 20 hr in pyridine and after refluxing in diglyme (162°) for 11 hr. It also resisted for 86 hr solvolysis in refluxing acetic acid containing sodium acetate.[3]

The addition of *trans*-1,2-dichloroethylene to acridizinium fluoroborate at 130° gave the expected 12,13-dichloro-6,11-dihydro-6,11-ethanoacridizinium fluoroborate. An attempt to remove the chlorine by the action of a zinc–copper couple[4] yielded a substance which was not a quaternary salt.

The addition of *N*-vinylcarbazole and *N*-vinyl-2-pyrrolidone to the acridizinium nucleus occurs quite readily but neither of the resulting bases (**8** or **9**) was suitable for a Cope elimination reaction.

**Cycloaddition Reactions Using Acetylenic Derivatives.**—Due to the lack of promise shown by these indirect approaches to the synthesis of etheno-bridged compounds, the addition of acetylenic derivatives to the acridizinium nucleus (Table II) was reexamined.

(1) This research was supported by Public Health Service Research Grant No. HE-02170 of the National Heart Institute of the National Institutes of Health.

(2) *Cf.* S. J. Cristol, and D. C. Lewis, *J. Amer. Chem. Soc.*, **89**, 1476 (1967).

(3) On the basis of subsequent experiments (*vide infra*) it would seem probable that decomposition products obtained in these and more drastic elimination attempts may have contained some salts of 1-(2-pyridyl)naphthalene.

(4) *Cf.* S. J. Cristol and W. Y. Lim, *J. Org. Chem.*, **34**, 1 (1969).

TABLE I

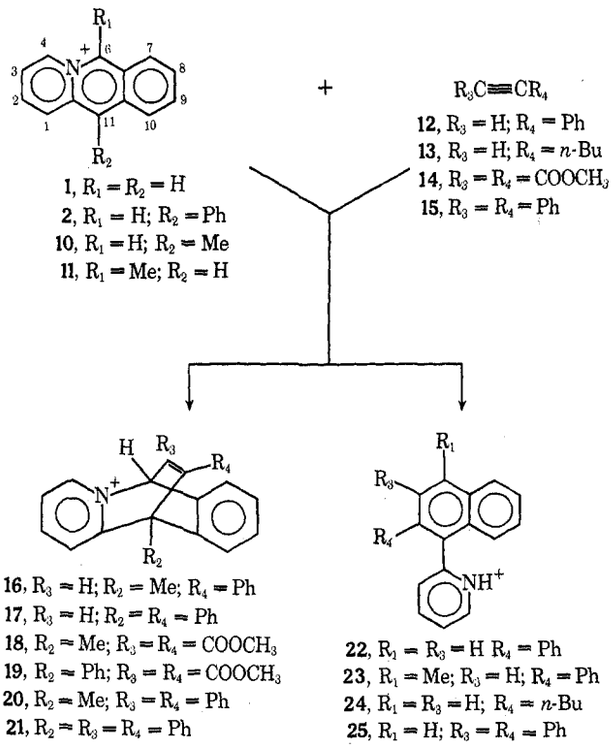
ADDITION OF VINYL DERIVATIVES TO ACRIDIZINIUM BROMIDE SALTS

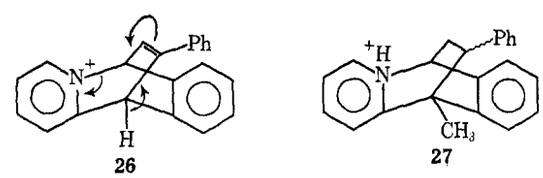
| Vinyl derivative | Acridizinium[a] | Temp, °C | Time, hr | Product | Method[b] | Mp, °C | Yield, % | Formula[c] |
|---|---|---|---|---|---|---|---|---|
| OEt | 1 | 20 | 72 | 4 | A | 206–206.5[d] | 91 | $C_{17}H_{18}ClNO_5$ |
| OEt | 2 | 20 | 72 | 5 | A | 138–144[e] | 33 | $C_{23}H_{22}ClNO_5$ |
| OBu | 1 | 82 | 12 | 6 | B | 90–94[f,g] | 64 | $C_{19}H_{22}BrNO \cdot 0.5H_2O$ |
| OAc | 1[h] | 65 | 72 | 7 | A | 215–217[e] | 89 | $C_{17}H_{16}ClNO_6$ |
| *N*-Carbazyl | 1[i,g] | 20 | 15 | 8 | B | 227–230[d] | 68 | $C_{27}H_{21}ClN_2O_4$ |
| 1-Pyrr[j] | 1[k,l] | 20 | 12 | 9 | B | 214–216.5[f] | 50 | $C_{19}H_{19}ClN_2O_5$ |

[a] Except as noted the starting material was the bromide salt. [b] See Experimental Section. Note that all products except 6 were isolated as perchlorate salts. [c] Satisfactory analytical data (C, H, N) were presented for all compounds in this table: Ed. [d] Recrystallized from MeCN–$Et_2O$; nmr ($CF_3CO_3H$, aliphatic protons only) δ 6.48 (broad s, 1, C-6 H), 5.53 (d, 1, $J$ = 3 Hz, C-11 H), 4.4–4.7 (m, 1, C-12 H), 3.7–4.4 (m, $CH_2CH_3$), 2.8–3.3 (m, 1, C-13 H), 1.32 (t, 3, $CH_3$). [e] Recrystallized from MeOH. [f] Recrystallized from MeOH–$Et_2O$. [g] Note that this product is the bromide salt. [h] Cycloaddition carried out in methanol. [i] Reaction carried out in MeCN–MeOH (1:2). [j] 1-Pyrrolidin-2-one. [k] Acridizinium perchlorate was the starting material. [l] Reaction carried out in MeCN–$MeNO_2$ (1:1).

Fields, *et al.*,[5] had reported that they had been unable to effect the addition of dimethyl acetylenedicarboxylate to the acridizinium ion. It appeared possible, however, that such an addition could be made to succeed by use of higher temperatures and of less electron-deficient acetylene derivatives.

As expected, phenylacetylene reacted with the acridizinium ion much more slowly than did styrene and the reaction was best accomplished in a sealed tube at 135–140°. At this temperature acridizinium perchlorate would occasionally explode and the tetrafluoroborate anion was found more satisfactory. The reaction product proved not to be the simple cycloaddition product **26**, since nmr showed no bridgehead hydrogens, but is without doubt 1-(2-pyridyl)-2-phenylnaphthalene (**22**) as the tetrafluoroboric acid salt. This rearrangement of **26** is readily understandable if it is recalled that scission of a carbon–nitrogen bond could lead to the formation of a cinnamyl-type carbonium ion which could aromatize by elimination of a proton. A parallel aromatization leading to 2-morpholino-1-(2-pyridyl)naphthalene was observed by Fields, *et al.*,[5] when an attempted addition of 1,1-dimorpholinoethylene to the acridizinium ion occurred with elimination. Such elimination–rearrangements have been made the subject of a recent study.[6]




Rearrangement was also observed when the acridizinium ion was allowed to react with 1-hexyne or diphenylacetylene.

When phenylacetylene (**12**) was allowed to react with 11-methylacridizinium ion (**10**), no rearrangement occurred and the adduct **16** could be hydrogenated to a derivative **27** in which both the ethylene bridge and the pyridinium ring had been saturated. The identical derivative **27** could be prepared by addition of styrene to 11-methylacridizinium ion followed by catalytic reduction. This demonstrates that phenylacetylene adds to the 11-methylacridizinium ion with the same *regiospecificity*[7] as does styrene. Unrearranged addition products of 11-methyl- (**10**) and 11-phenylacridizinium ions with phenylacetylene (**12**), dicarbomethoxyacetylene (**14**), and diphenylacetylene (**15**) are recorded in Table II.

## Experimental Section

Melting points were taken in capillaries using a Thomas–Hoover apparatus and are uncorrected. All nmr data were obtained using 60-megacycle instruments. Elemental analyses were by Janssen Pharmaceutica Research Laboratories, Beerse, Belgium, or by N-H-W Laboratories, Garden City, Mich. Mass spectra were taken at low resolution at the Research Triangle Center for Mass Spectrometry using the MS 902 spectrometer.

**Fluoroborate Salts.**—The fluoroborate salts were prepared either by (A) addition of fluoroboric acid to the known[8] bromide or (B) by substitution of 48% fluoroboric acid for perchloric acid in the isolation of the cation from polyphosphoric acid cyclization mixtures.[9–11] Results are summarized in Table III.

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

(6) D. L. Fields and T. H. Regan, *ibid.*, **35**, 1870 (1970).

(7) *Cf.* A. Hassner, *J. Amer. Chem. Soc.*, **90**, 216 (1968).

(8) C. K. Bradsher and L. E. Beavers, *ibid.*, **77**, 4812 (1955).

(9) C. K. Bradsher and J. C. Parham, *J. Heterocycl. Chem.*, **1**, 121 (1964).

(10) C. K. Bradsher and J. C. Parham, *J. Org. Chem.*, **28**, 83 (1963).

(11) C. K. Bradsher and T. W. G. Solomons, *J. Amer. Chem. Soc.*, **81**, 2550 (1959).

TABLE II

PRODUCTS OF THE REACTION OF SOME ACRIDIZINIUM FLUOROBORATES WITH DERIVATIVES OF ACETYLENE AT 135–140°

| Substituents | | | | | | |
|---|---|---|---|---|---|---|
| Acetylene | Acridizinium | Time, hr | Yield, % | Mp, °C[a,b] | Formula | Product[c] |
| Ph | | 3 | 70 | 191–193 | $C_{21}H_{16}NBF_4$ | R 22[d] |
| Ph | 6-Me | 8 | 80 | 156–157[e] | $C_{22}H_{17}N$ | R 23 |
| Ph | 11-Me | 0.75 | 62 | 229–230[f] | $C_{22}H_{18}NBF_4$ | U 16[g] |
| Ph | 11-Ph | 0.75[i] | 50 | 240[f,h] | $C_{27}H_{20}NBF_4$ | U 17 |
| *n*-Bu | | 12 | 78 | 164.5–165.5[j] | $C_{25}H_{22}N_4O_7$ | R 24 |
| $(COOCH_3)_2$ | 11-Me | 0.10 | 93 | 230.5–231[f] | $C_{20}H_{18}BF_4NO_4$ | U 18 |
| $(COOCH_3)_2$ | 11-Ph | 1.75[i] | 30 | 198–199[f] | $C_{25}H_{20}BF_4NO_4$ | U 19 |
| $Ph_2$ | | 250[k] | 30 | 265–270[f] | $C_{27}H_{20}BF_4N$ | R 25 |
| $Ph_2$ | 11-Me | 40 | 85 | 269–269.5 | $C_{28}H_{22}BF_4N$ | U 20 |
| $Ph_2$ | 11-Ph | 239 | 40 | 264[f,l] | $C_{33}H_{24}BF_4N$ | U 21 |

[a] Satisfactory analyses (±0.4% for C, H, N) were submitted for all products in this table: Ed. [b] All salts are tetrafluoroborates. [c] R = rearranged, U = unrearranged. [d] The free base, mp 106.5–107.5°, crystallized from ethanol–water, mass spectrum parent peak at *m/e* 281. *Anal.* Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.83; H, 5.26; N, 4.93. [e] The yield and melting point reported are those of the free base; nmr ($CD_3CN$) δ 2.90 (s, 3, $ArCH_3$), 7.1–8.7 (m, 15, ArH). [f] With decomposition. [g] Nmr ($CD_3CN$) δ 2.20 (s, 3, $CH_3$), 6.9–9.2 (m, 15, ArH). [h] C, calcd 72.83; found, 73.25. [i] It is important that the reaction time not be extended and that the temperature be kept at almost exactly 140°. [j] The yield and melting point are of the picrate, obtained by the action of ethanolic picric acid solution on the free base; recrystallized from ethyl acetate. [k] A second 0.5-g portion of phenylacetylene was added after 80 hr. [l] C, calcd 76.02; found, 76.45.

TABLE III

ACRIDIZINIUM TETRAFLUOROBORATES

| No. | Substituent | Method[a] of prepn | Mp, °C | Recrystn solvent | Formula[b] |
|---|---|---|---|---|---|
| 1 | | A | 184.5–185 | MeOH | $C_{13}H_{10}BF_4N$ |
| 11 | 6-Me | B | 200–201 | HOH | $C_{14}H_{12}BF_4N$ |
| 10 | 11-Me | B | 219–220 | MeOH–EtOAc | $C_{14}H_{12}BF_4N$ |
| 2 | 11-Ph | B | 234–235 | MeOH | $C_{19}H_{14}BF_4N$ |

[a] Methods A and B refer to methods in paragraph on fluoroborate salts. [b] Data indicating satisfactory carbon, hydrogen, and nitrogen analyses for these compounds were submitted: Ed.

**Addition of Vinyl Derivatives to Acridizinium Salts (Table I).**—Unless otherwise indicated, the acridizinium derivative (**1** or **2**) as the bromide salt was dissolved or suspended in acetonitrile which had been dried by distilling it from phosphorus pentoxide. The volume of solvent varied from 25 to 100 ml per 1 g of salt. The vinyl derivative was added in 3–10 molar excess and the reaction was followed by disappearance of the long-wavelength absorptions characteristic of the acridizinium uv spectrum. The volume of solution was reduced to about one-third in a rotary evaporator and the product was isolated by (A) addition of water and sodium perchlorate to precipitate the perchlorate salt or (B) by addition of anhydrous ether to precipitate the salt without change in anion. Recrystallization solvents are indicated in the footnotes to Table I.

**12-Hydroxy-6,11-dihydro-6,11-ethanoacridizinium Perchlorate (3, $R_1$ = H; $R_2$ = OH). A. By Hydrolysis of the 12-Ethoxy Adduct (4).**—The cleavage of the ethoxy linkage could be accomplished by the use of hydriodic hydrobromic, or hydrochloric acid, all yielding the same perchlorate salt on addition of sodium perchlorate. Five grams of the adduct **4** as the bromide salt was refluxed for 5 hr with a mixture of 50 ml of 47% hydrobromic acid and 10 ml of concentrated sulfuric acid. The hydrobromic acid was evaporated under reduced pressure, then 30 ml of water followed by an excess of sodium perchlorate was added. The resulting precipitate, mp 157–162.5°, yield 4.3 g (93%), was quite pure.

**B. By Hydrolysis of the 12-Butoxy Adduct (6).**—This could be effected by heating 0.5 g of the adduct **6** for 22 hr at 110° with 10 ml of 57% hydriodic acid. The product which separated appeared from its brown color to be a triiodide salt and addition of iodine caused precipitation of additional product. The combined precipitates (0.8 g) were stirred with silver chloride. The resulting chloride was, in turn, converted to the perchlorate identical with the product obtained by procedure A.

**C. By Hydrolysis of the 12-Acetoxy Adduct (7).**—Two grams of the perchlorate of vinyl acetate adduct **7** was refluxed for 2 hr in 50 ml of 1% hydrobromic acid solution. On cooling and collecting, 1.6 g (93%) of the product, mp 163.5–167.5°, was obtained. Preparation A, B, and C gave identical ir and nmr spectra.

The analytical sample, mp 159–162°, was crystallized from methanol as colorless needles.

*Anal.* Calcd for $C_{15}H_{14}ClNO_5$: C, 55.65; H, 4.36; N, 4.33. Found: C, 55.99; H, 4.49; N, 4.38.

The corresponding iodide, mp 196–199°, was crystallized from ethanol–ether as fine pale yellow needles.

*Anal.* Calcd for $C_{15}H_{14}INO$: C, 51.30; H, 4.02; N, 3.99. Found C, 51.01; H, 3.96; N, 4.02.

**Acetylation of 12-Hydroxy-6,11-dihydro-6,11-ethanoacridizinium Perchlorate (3, $R_1$ = H; $R_2$ = OH).**—A small portion of the named salt was acetylated with a mixture of equal parts of acetic anhydride and acetyl chloride by heating the mixture at 50° for 3 hr. The liquid was evaporated under a stream of air and the residue was recrystallized from methanol. The product, mp 215–217°, was identical (ir) with the vinyl acetate adduct (**7**).

**Tosylate of 12-Hydroxy-6,11-dihydro-6,11-ethanoacridizinium Perchlorate (3, $R_1$ = H; $R_2$ = *p*-$CH_3C_6H_4SO_2O$).**—One gram of the perchlorate salt of the 12-hydroxy derivative (**3**, $R_1$ = H, $R_2$ = OH) was ground together in a mortar with 1.2 g of purified *p*-toluenesulfonyl chloride. The mixture was placed in 10 ml of purified pyridine and after 1 min the mixture was cooled and placed in a refrigerator for 24 hr. The product obtained by pouring the mixture on ice was recrystallized from methanol, affording 0.9 g (61%) of colorless needle clusters of analytical purity, mp 185–187°.

*Anal.* Calcd for $C_{22}H_{20}ClNO_7S$: C, 55.29; H, 4.21; N, 2.93. Found: C, 55.30; H, 4.10; N, 3.02.

**12,13-Dichloro-6,11-dihydro-6,11-ethanoacridizinium Tetrafluoroborate.**—In each of ten 16 × 125 mm ignition tubes, 0.3 g of acridizinium tetrafluoroborate, 5 ml of dry acetonitrile, and 1.5 g of *trans*-dichloroethylene were placed and the tubes were sealed under nitrogen. The sealed tubes were heated at 130° for 90 hr. After cooling, the contents of all tubes were poured into 1 l. of anhydrous ether to which 100 ml of petroleum ether (bp 30–60°) had been added. The ether mixture was decanted from the precipitate, which was crystallized from methanol–ether (Norit) as pale yellow aggregates, yield 1.9 g (46%), mp 221–226°.

*Anal.* Calcd for $C_{15}H_{12}BCl_2F_4N$: C, 49.50; H, 3.32; N, 3.85. Found: C, 50.04; H, 3.05; N, 3.76.

**Addition of Acetylene Derivatives to Acridizinium Derivatives (Table II).**—The technique was essentially the same as that used in making 12,13-dichloro-6,11-dihydro-6,11-ethanoacridizinium tetrafluoroborate except that 0.5 g of the appropriate acetylenic compound was substituted for the *trans*-dichloroethylene. Progress of the reaction was followed by opening a tube and measuring, by means of uv spectroscopy, the amount of the unreacted acridizinium ion remaining. When the reaction was complete, the mixture was poured into ether–hexane (2:1) and the resulting precipitate was recrystallized from acetonitrile–ether.

**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*

*Received June 28, 1971*

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.