which was again suspended in 200 ml. of 15% ammonia solution and stirred overnight. Filtration yielded 1.76 g. of crude undissolved ester as a tan solid, m.p. 230–235°.

(*b*) *From the acid via the silver salt.* The ammonia extract obtained above (400 ml.) was added with stirring to a solution formed by dissolving 2 g. of silver nitrate in 40 ml. of concentrated ammonium hydroxide. The solution was heated in the steam bath for 2.5 hr. and then stirred overnight at room temperature. The chocolate powder was collected and dried; yield 0.56 g. The silver salt was suspended in 60 ml. of methanol containing 1 g. of ethyl iodide and the mixture refluxed for 4 hr. After removal of the silver iodide by filtration, the ester was isolated and recrystallized from ethanol, yielding 0.2 g. of long yellow needles, m.p. 230–234°. The analytical sample (procedure b) melted at 237–239°.

Anal. Calcd. for $C_{18}H_{14}N_2O_6$: C, 61.01; H, 3.98. Found: C, 61.11; H, 4.28.

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Photodimerization of Acridizinium Salts

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Crystalline acridizinium bromide monohydrate[2] (I) when exposed to irradiation by sunlight or from a sun lamp is converted to a higher melting, less soluble compound lacking the yellow color and the fluorescence characteristic of the starting material. The ultraviolet absorption spectrum of the new compound (Fig. 1) makes it clear that the irradiation has destroyed the conjugation characteristic of the acridizinium system. The possibility that photooxidation has taken place is easily eliminated by the observation that there is no change in weight during irradiation. Analysis indicates that the new product (II) has approximately the same composition as the starting material.

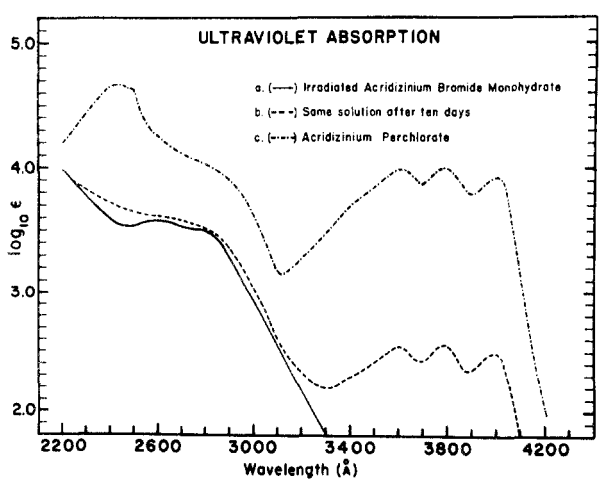
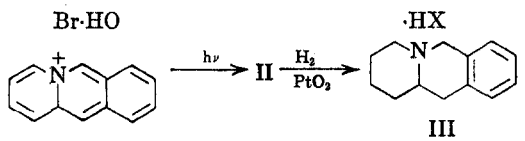


FIGURE 1.

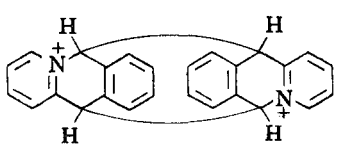
The irradiation product is a salt and can be converted to a picrate and a perchlorate having the composition expected for the acridizinium analog. The bromide (II) was unaffected by refluxing for two hours in 48% hydrobromic acid and when heated at 100° with 6*N* nitric acid it was merely converted to the nitrate salt. When the bromide II



was reduced catalytically in the presence of platinum oxide the only product identified was a salt of benzo[c]azabicyclo[4.4.0]decane (III).

An interesting observation was that a solution of the nonfluorescent irradiated bromide (II), in 95% ethanol, after standing at room temperature for ten days became faintly fluorescent. Spectroscopic examination of the solution showed a definite indication of the presence of a small quantity of the acridizinium ion. When the irradiation product (II) in 95% ethanol solution was refluxed for 18 hours it afforded acridizinium bromide in 82% yield. If this is a simple thermal dissociation it occurs more readily in solution since a sample of crystalline irradiated bromide II was unchanged after heating in a drying oven at 75° for 24 hours.

Analogy between the acridizinium ion and anthracene[3] suggested that the new product might be a photodimer. Anthracene[4] and many of its derivatives[5] dimerize when irradiated in *solution*, and the dimers are known to dissociate[5] on heating. Since the acridizinium ion is unsymmetrical, several isomeric forms of the meso-connected ion are theoretically possible. Structure II seems most likely[6] in that it permits maximum separation between the like charges.



II

Observations concerning boiling point elevation of ethanol solutions, although complicated by the

(1) Public Health Service Research Fellow of the National Institutes of Health, 1952–1954. This investigation was supported in part by a research grant (G-2364) of the National Science Foundation.

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

(3) A subsequent communication will describe another anthracene-type reaction of the acridizinium ion.

(4) J. Fritzsche, *J. Prakt. Chem.*, 101, 333 (1867).

(5) F. D. Greene, S. L. Misrock, and J. R. Wolfe, Jr., *J. Am. Chem. Soc.*, 77, 3852 (1955).

(6) It is possible that a detailed picture of the structure of II will be provided by the methods of x-ray crystallography. Professor J. M. Robertson has indicated his interest in the problem.

possibility for ionization, make it clear that II is not an isomer of I and afford a strong indication that it is a dimer.

EXPERIMENTAL[7]

Photodimerization of acridizinium bromide. One gram of crystalline acridizinium bromide monohydrate I was irradiated under a General Electric sunlamp for about 5.5 hr. with occasional stirring to ensure complete exposure. As the reaction progressed, the color of the material changed from yellow to light tan and the crystals disintegrated. Recrystallization from ethanol-ether yielded .96 g. (93%) of colorless prisms, m.p. 260–263°.

Similar results may be obtained by the use of direct sunlight. In one experiment it was demonstrated that irradiation in a stoppered glass vial for a total of 16 hr. produced no detectable change in weight although conversion was practically complete.

An analytical sample was prepared by recrystallization from ethanol-ether, m.p. 260–264°.[8]

Anal. Calcd. for $(C_{13}H_{10}NBr \cdot 3/2\ H_2O)_2$: C, 54.51; H, 4.22; N, 4.89. Found: C, 54.86; H, 4.03; N, 4.70.

Properties of irradiated acridizinium bromide. The new product (II) is less soluble in water and ethanol than is the starting material I, and the solutions lack the fluorescence characteristic of the acridizinium ion.

The irradiation product was unaffected by drying at 75° for 24 hr. or refluxing in 48% hydrobromic acid for 2 hr.

When 0.23 g. of the irradiation product (II) was refluxed for 18 hr. in 15 ml. of 95% ethanol it yielded 0.19 g. (82.5%) of acridizinium bromide, m.p. 236–237° (lit.[2] 239–240°). The identity of the product was established by means of the ultraviolet absorption spectrum.

Hydrogenolysis of the irradiation product. Hydrogenation of 0.5 g. of irradiated acridizinium bromide was carried out in about 50 ml. of ethanol using Adams' catalyst, a little more than eight molar equivalents of hydrogen being absorbed. The solution was filtered and concentrated yielding 0.3 g. of fine white crystals m.p. 200–228°. These were converted to the picrate in ethanol yielding yellow needles m.p. 160° (lit.[9] 161–162°) of benzo[c]azabicyclo[4.4.0]decane picrate (III) identified by a mixed melting point determination with an authentic sample.

Boiling-point elevation in ethanol. The boiling point elevation caused by solution of 0.300 g. of the bromide in 10 ml. of absolute ethanol was observed and compared with a value calculated on the assumption that no ionization had occurred, and using 1.2° as the molal boiling point elevation constant for ethanol.

Acridizinium bromide (278). Observed, 0.180°; Calcd. 0.162°. Irradiated acridizinium bromide (574). Observed 0.068°, 0.078°. Calcd. 0.078°.

In the first of the two determinations on irradiated acridizinium bromide (II), refluxing in the molecular weight apparatus was continued for 3 hr., during which the boiling-point elevation rose to 0.133°. There was no indication that a maximum in boiling-point had been reached.

The picrate of the irradiation product II was prepared in ethanol as yellow crystals, m.p. 280–283°.

Anal. Calcd. for $(C_{19}H_{12}N_4O_7 \cdot 1/2\ H_2O)_2$: C, 54.71; H, 3.14; N, 13.42. Found: C, 54.65; H, 3.06; N, 13.21.

The nitrate of the irradiation product II was formed when a small quantity of II was heated on the steam bath for 15 min with 6*N* nitric acid in an attempt to bring about oxidation. The salt, recovered by pouring the solution on ice, was recrystallized from alcohol-ether as colorless needles, m.p. 228–230°.

Anal. Calcd. for $C_{26}H_{20}N_4O_6 \cdot 3/2\ H_2O$: C, 61.00; H, 4.53; N, 10.84. Found: C. 60.84; H, 4.28; N, 10.55.

The perchlorate of the irradiation product II was prepared by addition of perchloric acid to a water solution of the bromide and recrystallized from water as colorless needles, m.p. 294°.

Anal. Calcd. for $(C_{13}H_{10}NClO_4)_2$: C, 55.79; H, 3.60; N, 5.01. Found: C, 55.66; H, 3.85; N, 4.97.

A 0.15 g. sample of the perchlorate (m.p. 290°) was refluxed overnight in 95% ethanol. The solution was concentrated and cooled yielding 0.1 g. (67%) of yellow needles, m.p. 205°. This was identified as acridizinium perchlorate (lit.[2] 205–206.2°) by means of the ultraviolet absorption spectrum.

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(7) All melting points were taken on a Fisher-Johns apparatus and are uncorrected. Ultraviolet absorption spectra were measured in 95% ethanol (1 cm. silica cells). Analyses are by Micro-Tech Laboratories, Skokie, Ill.

(8) Melting point obtained with fairly rapid heating. If the compound is heated very slowly it turns yellow, melting at 238°. It is noteworthy that acridizinium bromide melts at 239–240° (ref. 2).

(9) N. J. Leonard, S. Swann, Jr., and G. Fuller, *J. Am. Chem. Soc.*, **76**, 3193 (1954).

Base-Catalyzed Cleavage of β-Hydroxy Acids and Their Esters

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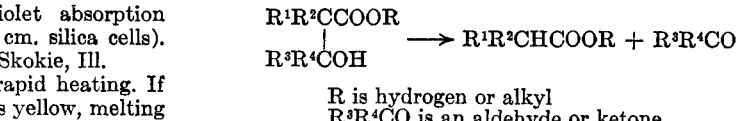
The cleavage of a β-hydroxy acid or ester, in the manner indicated *below*, has been described frequently in the literature.[3]

The effect of molecular structure on base-catalyzed decomposition of β-hydroxy acids and esters was investigated rather extensively by Ivanov and coworkers.[4] All of the β,β-disubstituted α-aryl-β-hydroxypropionic acids studied by them were decomposed readily into arylacetic acids and ketones.



R is hydrogen or alkyl
R^3R^4CO is an aldehyde or ketone

(1) This paper represents part of a dissertation submitted by R. H. Cox in partial fulfillment of the requirements for for the Ph.D. degree in the University of Michigan, 1954.

(2) Sterling-Winthrop Fellow.

(3) In 1880, H. Schnapp [*Ann.*, **201**, 62 (1880)] observed that α,α-diethyl-β-hydroxybutyric acid decomposed, under the influence of heat, into diethylacetic acid and acetaldehyde. Subsequently, a number of similar decompositions have been reported; in most instances the cleavage was catalyzed by a base. Of practical interest is the cleavage of β,β-disubstituted α-phenyl-β-hydroxypropionic acids which has been observed in several instances during the attempted preparation of basic esters of these acids [A. W. Weston and R. W. DeNet, *J. Am. Chem. Soc.*, **73**, 4221 (1951); F. F. Blicke and H. Raffelson, *J. Am. Chem. Soc.*, **74**, 1730 (1952); F. F. Blicke and R. H. Cox, *J. Am. Chem. Soc.*, **77**, 5401 (1955)].

(4) D. Ivanov and J. Popov, *Bull. soc. chim.*, [5] 49, 1547 (1931); D. Ivanov, M. Mihova, and T. Christova, *Bull. soc. chim.*, [4] **51**, 1321 (1932).