## Displacement Reactions on 1-Azulylmethyltrimethylammonium Iodide<sup>1,2</sup>

ARTHUR G. ANDERSON, JR.,<sup>3</sup> ROBERT GRIFFIN ANDERSON,<sup>4</sup> AND THOMAS S. FUJITA

Department of Chemistry, University of Washington, Seattle 5, Washington

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Displacements on 1-azulylmethyltrimethylammonium iodide have been effected by a variety of nucleophilic species in good yields. A number of new azulene derivatives have been prepared *via* this method. Two of these, 1-azuleneacetic acid and the corresponding nitrile, were submitted for testing as plant growth regulators and found to be active.

Numerous examples of the aminomethylation of reactive olefins and aromatic compounds with formaldehyde and dimethylamine in the presence of acid are to be found in the literature.<sup>5</sup> Treatment of azulene with N,N,N',N'-tetramethyldiaminomethane, paraformaldehyde, and acetic acid as described by Lindsay and Hauser for the preparation of N,N-dimethylaminoferrocene<sup>5</sup> gave only amorphous, green solids. A modified procedure employing the inverse addition of reagents and much milder conditions was found to be adaptable to the preparation of the monosubstitution product (I) in 96% yield and the disubstitution product (II) in 72% yield.<sup>6</sup> Both I and II were somewhat unstable and were analytically characterized as salt derivatives. In agreement with previous findings<sup>7</sup> the shift in the position of the principal maximum in the visible region caused by the two dimethylaminomethyl groups in the 1- and 3-positions of II was found to be twice that found with the monosubstituted compound.



As nucleophilic displacement of the trimethylamino portion of 1-azulylmethyltrimethylammonium iodide (III) provided a potentially valuable route for the construction of many side chains

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(5) See, for example (a) G. F. Hennion, C. C. Price, and V. C. Wolff, Jr., J. Am. Chem. Soc., 77, 4633 (1955); (b) H. R. Snyder and E. L. Eliel, *ibid.*, 70, 1703 (1948); (c) J. K. Lindsay and C. R. Hauser, J. Org. Chem., 22, 355 (1957).

(6) After the completion of this phase of the present investigation and concurrent with the displacement reaction studies, K. Hafner, *Angew. Chem.*, **70**, 419 (1958), reported monoaminomethylation of azulene by a similar procedure, the displacement on I with piperidine, and the displacement on III with sodiomalonic ester. More recently aminomethylation with dimethylaminomethanol and perchloric acid and the displacement on III with ethoxide have been described by M. Mühlstadt, W. Treibs, and J. Mohr, *Ber.*, **94**, 808 (1961).

(7) A. G. Anderson and B. M. Steckler, J. Am. Chem. Soc., 81, 4941 (1959); A. G. Anderson and R. N. McDonald, *ibid.*, 81, 5669 (1959), and reference therein.

heretofore unknown or formed with difficulty, we investigated a number of reactions of this type. Treatment of III with alcoholic potassium cyanide formed 1-cyanomethylazulene (IV) in 82% yield and hydrolysis of this gave 54% of 1-azuleneacetic acid (V). Interestingly, both IV and V have been found to possess quite high activity as plant growth regulators in promoting cell elongation.<sup>8</sup> Reduction of V with diborane afforded 2-(1-azulyl) ethanol (VI) in 98% yield.

Reaction of III with sodium methoxide produced 91% of 1-methoxymethylazulene (VII), and analogous processes formed the corresponding phenyl ether (VIII), the thiophenyl ether (IX), and 1-mercaptomethylazulene (X) in yields of 84, 75, and 92%, respectively.

The displacement by carbanion species was examined with sodium ethyl acetoacetate and sodium diethylmalonate. The former afforded 61%of ethyl 2-acetyl-3-(1-azulyl)propanoate (XI), the infrared spectrum of which showed the expected doublet in the carbonyl region (ester at 5.76  $\mu$ and ketone at 5.83  $\mu$ ). Saponification of XI in dilute base followed by decarboxylation in acid produced 4-(1-azulyl)butanone-2 (XII) in 60%yield. The infrared spectrum of XII exhibited a single carbonyl peak at 5.85  $\mu$ . The product from the malonic ester alkylation, presumed to be diethyl 1-azulylmethylmalonate (XIII), was saponified and yielded 78% of the corresponding acid (XIV). Decarboxylation of this acid formed 3-(1-azulyl)propanoic acid (XV).

In continuation of the study of the effects of different groups in the 1-position on the principal maximum in the visible region,<sup>7</sup> the absorption spectra of the new derivatives were recorded and the pertinent data are given in Table I. Some interesting comparisons may be noted. The conversion of the  $-CH_2N(CH_3)_2$  group to  $-CH_2$ - $N(CH_3)_3$  caused a reversal in the sign of the spectral shift in the anticipated direction. Less expected were the relative magnitudes of the bathochromic shifts in the series  $-CH_2OC_6H_5 > --CH_2SC_6H_5$ -CH<sub>2</sub>OCH<sub>3</sub>. Thus in these 1-substituted > azulenes this would appear to be the relative order of stabilization of the excited state by the substituent groups through electron donation, and/or the reverse order of the stabilization of the

(8) R. W. Muir and C. Hansch, Nature, 190, 741 (1961).



TABLE I

Absorption Maxima $(M_{\mu})$ of	1-Substituted	Azulenes
Groups	$\lambda_{max}$	$\Delta \lambda_{max}^{d}$
-CH2-H	$608^{a}$	+28
$-CH_2CH_2CO_2H$	600°	+22
$-CH_2OC_6H_5$	600 <sup>b</sup>	+22
$CH_2CH_2OH$	$598^{a}$	+18
$CH_2CH(CO_2C_2H_5)COCH_3$	$595^{b}$	+17
$-CH_2SH$	$595^{a}$	+15
$CH_2CH(CO_2H)_2$	592°	+14
$-CH_2SC_8H_5$	592 <sup>b</sup>	+14
$-CH_2N(CH_3)_2$	$592^{a}$	+12
$-CH_2CN$	$589^{a}$	+9
$-CH_2CO_2H$	585°	+7
CH <sub>2</sub> OCH <sub>3</sub>	585 <sup>a</sup>	+5
		00
	000°	22

<sup>a</sup> Cyclohexane or *n*-hexane solvent. <sup>b</sup> Methylene chloride solvent. <sup>c</sup> Alcohol solvent. <sup>d</sup> Based on values of 580 m $\mu$ (hexane) and 578 m $\mu$  (methylene chloride or alcohol) for azulene.

ground state by electron attraction<sup>7</sup>; the latter seems less probable.

Treatment of the quaternary salt (III) with either sodium borohydride or sodium hydride gave 1-methylazulene (XVI) in yields of 65 and 92%, respectively. This route to XVI is perhaps easier to carry out than that involving Wolff-Kishner reduction of 1-formylazulene.<sup>6,9</sup> The ac-

(9) W. Treibs, H. Newpert, and J. Hiebsch, Ber., 92, 141 (1959); K. Hafner and C. Bernhard, Ann., 625, 108 (1959). The direct methylation of azulene is unsatisfactory (cf. A. G. Anderson, E. J. Cowles, J. J. Tazuma, and J. A. Nelson, J. Am. Chem. Soc., 77, 623 (1955). tion of sodium hydride as a nucleophile rather than as a base was unexpected.<sup>10</sup> In connection with a study of the n.m.r. spectra of azulene compounds,<sup>11</sup> the spectrum of XVI was examined. Of interest was the observation that the presence of the 1-methyl group had no noticeable effect on the chemical shift of the 8-hydrogen. A doublet centered at  $\tau = 1.91$  p.p.m. (relative to tetramethylsilane as an internal standard) accounted for both the 4- and 8-hydrogens and the splitting of 9.6 c.p.s. was within the range (8.4–10.2 c.p.s.) found for the seven-ring protons in a number of other azulenes.<sup>11</sup>

#### Experimental<sup>12</sup>

1-Dimethylaminomethylazulene (I) and 1-Azulylmethyltrimethylaminomethylazulene (I) and 1-Azulylmethyltrimethylaminomethane (0.233 g., 2.29 mmoles), paraformaldehyde (60 mg., 2.0 mmoles), and 4 ml. of glacial acetic acid was heated until a clear solution was obtained. The solution was cooled and added dropwise to a cold (ice bath) solution of azulene (0.5 g., 3.91 mmoles) in 10 ml. of

<sup>(10)</sup> Current studies include the behavior of III with other bases.

<sup>(11)</sup> A. G. Anderson, L. L. Replogle, and W. F. Harrison, unpublished results.

<sup>(12)</sup> Melting points are uncorrected and were taken on a Fisher-Johns apparatus. Ultraviolet and visible spectra were recorded on a Model 115 or Model 14 Cary spectrophotometer. Infrared spectra were taken on a Ferkin-Elmer Model 21 spectrophotometer. Nuclear magnetic resonance absorption was recorded by B. J. Nist with a 60-Me. Varian high resolution spectrometer with tetramethylsilane as an internal standard. Microanalyses were performed by G. Weiler and F. B. Strauss, Oxford, England, A. Bernhardt, Max Planck Institute, Mulheim (Ruhr), or by A. Kuo, L. Ho, and B. J. Nist.

methylene chloride. The mixture was swirled occasionally with continued cooling for 1 hr. and then allowed to stand in a refrigerator overnight. After dilution with 20 ml. of water and then 10 ml. of 5% hydrochloric acid, the mixture was shaken and the separated aqueous layer was washed with four 20-ml. portions of methylene chloride. The combined organic extracts were washed once with water. The combined aqueous layers were then made alkaline with 10% sodium hydroxide and twice extracted with ether. The combined ethereal extracts were washed with water until the washings were neutral to pH paper, and then were dried over sodium sulfate. Most of the solvent was removed and the residue was chromatographed on basic alumina. Ether eluted an intense blue band which gave 0.694 g. (96%) of 1-dimethylaminomethylazulene (I) as a blue oil which decomposed on standing. It was converted to the quaternary salt (III) for analysis. A cyclohexane solution of I showed  $\lambda_{max}$  in  $m_{\mu}$  ( $D_{max}$ ) in the ultraviolet at 238 (0.55), 278 (1.56), 283 (1.47), 346 (0.16). Absorption was observed in the visible at 570 (1.21), 592 (1.47), 618 (1.29), 648 (1.31), and 718 (0.53).

A solution of I (0.492 g., 2.66 mmoles) in 25 ml. of absolute ethanol was treated with a slight excess of methyl iodide. The reaction mixture was allowed to stand at room temperature for 30 min., then cooled (ice bath) and the crystals which had separated were collected. The purple needles (0.652 g., 75%) of 1-azulylmethyltrimethylammonium iodide did not melt below 300°. A 95% ethanol solution exhibited maxima in m $\mu$  (D<sub>max</sub>) at 556 (1.37) and 597 (1.20).

Anal. Caled. for  $C_{14}H_{18}NI$ : C, 51.38; H, 5.50; N, 4.28. Found: C, 51.18; H, 5.46; N, 4.39.

The picrate of I crystallized from methanol as dark brown needles and was recrystallized from the same solvent; m.p. 120-122°.

Anal. Calcd. for  $C_{10}H_{18}O_7N_4$ : C, 55.07; H, 4.38. Found: C, 55.03; H, 4.08.

1,3-Bis(dimethylaminomethyl)azulene (II).-A solution N,N,N',N'-tetramethyldiaminomethane (0.4 g., of mmoles), paraformaldehyde (1 g., 3.3 mmoles), and 5 ml. of glacial acetic acid was formed and allowed to react with a solution of azulene (0.43 g., 3.6 mmoles) in 5 ml. of methylene chloride as described in the preparation of 1-dimethylaminoazulene (I) above except that the reaction was carried out at room temperature and the mixture allowed to stand for 4 days before being diluted with 25 ml. of water. The product was isolated as described for the preparation of I except that methylene chloride was the eluent. The single blue band which developed yielded 0.582 g. (71.7%)of 1,3-bis(dimethylaminomethyl)azulene as a blue oil which was somewhat unstable and was converted to a salt derivative for analysis (an n-hexane solution showed maxima in  $m_{\mu}$  (D<sub>max</sub>) in the visible at 583 (1.05), 608 (1.23), shoulder at 633 (1.07), 662 (1.04), and 733 (0.37).

The dipicrate crystallized from methanol as dark brown needles, m.p. 172-175°.

Anal. Calcd. for  $C_{28}H_{28}O_{14}N_8$ : C, 48.00; H, 4.03. Found: C, 47.98; H, 4.02.

1-Cyanomethylazulene (IV).—A solution of 1-azulylmethyltrimethylammonium iodide (0.109 g., 0.33 mmole) and potassium cyanide (65 mg., 1.0 mmole) in 10 ml. of absolute ethanol was heated under reflux for 2 hr., then cooled and 50 ml. of water added. The blue mixture was extracted with ether and the ether extract was washed twice with 20-ml. portions of water and then dried over sodium sulfate. After removal of the solvent the residue was chromatographed on basic alumina. Benzene eluted a bright blue band which gave 45 mg. (81.6%) of 1-cyanomethylazulene as a viscous blue oil which on standing crystallized as blue needles, m.p. 43-44°. An *n*-hexane solution showed  $\lambda_{max}$  in m $\mu$  (D<sub>max</sub>) in the ultraviolet at 237 (0.46), 276 (1.35), 282 (1.22), 342 (0.11), and 356 (0.06). Absorption was observed in the visible at 589 (1.06), 637 (0.90), and 703 (0.34). The infrared spectrum (chloroform) showed a peak for the cyano group at 4.48  $\mu$ .

Anal. Calcd. for C<sub>12</sub>H<sub>9</sub>N: C, 86.25; H, 5.42. Found: C, 86.39; H, 5.54.

1-Azuleneacetic Acid (V).-A solution of 1-cyanomethylazulene (0.15 g., 0.9 mmole) in 15 ml. of 50% aqueous ethanol 0.6 M in sodium hydroxide was heated under reflux for 2.5 hr. and then cooled and diluted with 75 ml. of water. The mixture was extracted with ether and concentration of the dried ether layer followed by chromatography of the concentrate on basic alumina gave 45 mg. of unreacted 1cyanomethylazulene. The aqueous phase was acidified with 5% hydrochloric acid solution and extracted three times with ether. The combined ethereal extracts were washed with water, dried over sodium sulfate, and concentrated. The residue was chromatographed on acid-washed alumina and elution with solvents less polar than methanol removed only a very small amount of a green material which was discarded. Glacial acetic acid removed a blue band which was flooded with water and the whole was then extracted with ether. The organic laver was exhaustively extracted with water and dried over sodium sulfate. After removal of the solvent the blue residue was chromatographed on silicic acid. From the last colored band eluted with methylene chloride was obtained 90 mg. (53.9%; 76.9% net) of 1-azuleneacetic acid as blue needles, m.p. 92-93°, which could be sublimed without decomposition at 105° and 0.5 mm. A methylene chloride solution showed  $\lambda_{max}$  in m $\mu$  (D<sub>max</sub> in the ultraviolet at 237 (0.51), 278 (1.44), 284 (1.33), 389 (1.26), 342 (0.18), and 357 (0.07). Absorption was observed in the visible at 585 (1.04), 633 (0.91), and 700 (0.32). The infrared spectrum (chloroform) exhibited peaks at 585 and 2.9 µ.

Anal. Caled. for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>: C, 77.42; H, 5.38. Found: C, 77.52; H, 5.64.

2-(1-Azulyl)ethanol (VI).-Sodium borohydride (0.228 g., 6.0 mmoles) was added under anhydrous conditions to a solution of 0.147 g. (0.79 mmole) of 1-azuleneacetic acid in 25 ml. of dry tetrahydrofuran. When the evolution of hydrogen (which was exited through a tube ending just below the level of acetone in an adjoining flask) had ceased, 20 ml. of dry tetrahydrofuran containing 3 ml. of boron trifluoride etherate was added dropwise over a period of 20 min. to the stirred reaction mixture. Stirring was continued for an additional 1.5 hr. and then 20 ml. of 5% hydrochloric acid was added to destroy excess diborane and to make the solution acidic. Water (100 ml.) was added, the mixture was extracted several times with ether, and the combined organic extracts were washed with water, 5% sodium bicarbonate, and again with water. The separated, dried (sodium sulfate) ethereal solution was concentrated and the residue was chromatographed on basic alumina. Methanol eluted an intense blue band and the blue oil obtained from this was rechromatographed on silicic acid and eluted with methylene chloride. The blue eluate yielded 0.133 g. (97.8%) of 2-(1-azulyl)ethanol as blue needles, m.p. 59-60°. A cyclohexane solution showed  $\lambda_{max}$  in m $\mu$  (D<sub>max</sub>) in the ultraviolet at 240 (0.67), 274 (1.76), 278 (2.08), 284 (1.90), 288 (1.34), 298 (0.23), 343 (0.21), and 358 (0.12). Absorption was observed in the visible at 575 (0.97), 598 (1.17), 624 (1.01), 653 (1.03), and 725 (0.39). The infrared spectrum (chloroform) showed a peak at 2.82  $\mu.$ 

Anal. Caled. for C<sub>12</sub>H<sub>12</sub>O: C, 83.72; H, 6.98. Found: C, 83.38; H, 6.84.

1-Methoxymethylazulene (VII).—To a solution formed by the reaction of 0.23 g. (10 mmoles) of sodium with 20 ml. of dry methanol was added under anhydrous conditions 0.327 g. (1 mmole) of 1-azulylmethyltrimethylammonium iodide and the mixture was heated under reflux for 1 hr. Water (100 ml.) was then added and the blue suspension was extracted several times with ether. The combined organic extracts were washed twice with water and dried over sodium sulfate. The solvent was removed and the residue was chromatographed over basic alumina. Elution with methylene chloride removed a blue band which yielded 0.157 g. (91.3%) of 1-methoxymethylazulene as a blue oil. A cyclohexane solution showed  $\lambda_{max}$  in m $\mu$  (D<sub>max</sub>) in the ultraviolet at 238 (0.46) 277 (1.44), 284 (1.36), 342 (0.15), and 359 (0.10). Absorption was observed in the visible at 585 (1.23), 637 (1.09), and 705 (0.42) with shoulders at 565 (1.03) and 607 (1.12). The infrared spectrum was recorded. The analytical sample was prepared by molecular distillation at 50° and 0.1 mm.

Anal. Caled. for  $C_{12}H_{12}O$ : C, 83.72; H, 6.98. Found: C, 83.70; H, 6.89.

1-Phenoxymethylazulene (VIII). To a solution formed from the reaction of 92 mg. (4 mmoles) or sodium with 20 ml. of dry methanol was added 0.47 g. (5 mmoles) of phenol under anhydrous conditions. After 10 min., 0.327 g. (1 mmole) of 1-azulylmethyltrimethylammonium iodide was added and the mixture was heated under reflux for 1 hr. The work-up was the same as that described above for 1-methoxymethylazulene except that the ethereal extracts were also washed with 10% sodium hydroxide to remove excess phenol. The crude product was chromatographed on basic alumina and the blue band which was eluted with methanol yielded a viscous blue oil which was chromatographed on silicic acid. The blue fraction eluted with methylene chloride gave 0.197 g. (84.2%) of 1-phenoxymethylazulene as a blue oil. A methylene chloride solution showed  $\lambda_{\max}$  in  $m\mu$  ( $D_{\max}$ ) in the ultraviolet at 236 (0.50), 280 (1.29), 345 (0.14), and 360 (0.08) with shoulders at 284 (1.23) and 2.90 (1.06). Absorption was observed in the visible at 600 (1.22) with shoulders at 647 (1.04) and 717 (0.37).

Anal. Caled. for C<sub>17</sub>H<sub>14</sub>O: C, 87.18; H, 5.98. Found: C, 86.92; H, 6.02.

1-Thiophenoxymethylazulene (IX).-To a solution formed from the reaction of 0.4 g. (17.4 mmoles) of sodium and 25 ml. of dry ethanol was added 2 g. (18.2 mmoles) of freshly distilled thiophenol under anhydrous conditions. After a few minutes 0.327 g. (1 mmole) of 1-azulylmethyltrimethylammonium iodide was added and the mixture was heated under reflux for 45 min. and then worked up as described above for 1-phenoxymethylazulene. The crude product was chromatographed on basic alumina. The blue band eluted with methylene chloride yielded 0.186 g. (74.5%) of 1-thiophenoxymethylazulene as a blue oil which crystallized on standing as blue needles, m.p. 34-36°. A methylene chloride solution showed  $\lambda_{max}$  in  $m\mu$  ( $D_{max}$ ) in the ultraviolet at 240 (0.66), 280 (1.33), 285 (1.31), 346 (0.18), and 362 (0.12). Absorption was observed in the visible at 592(0.95) with shoulders at 636 (0.83) and 695 (0.31). The infrared spectrum was recorded.

Anal. Calcd. for  $C_{17}H_{14}S$ : C, 81.60; H, 5.60. Found: C, 81.69; H, 5.81.

A trinitrobenzene derivative formed in ethanol solution and recrystallized twice from the same solvent saturated with trinitrobenzene was obtained as red needles, m.p. 100-101°.

1-Mercaptomethylazulene (X).—A solution of potassium hydroxide (0.5 g., 8.8 mmoles) in 20 ml. of dry ethanol was saturated with hydrogen sulfide. 1-Azulylmethyltrimethylammonium iodide (0.327 g., 1 mmole) was added and the mixture was heated under reflux for 1 hr. The solution was diluted with 100 ml. of water, the whole was extracted several times with ether, and the combined ether extracts were washed with water and dried over sodium sulfate. The solvent was removed and the residue was chromatographed on acid-washed alumina. A 3:1 methylene chloride-pentane mixture eluted a blue band which yielded 0.166 g. (92%) of 1-mercaptomethylazulene as a blue oil which had an odor typical of thiols. A cyclohexane solution exhibited  $\lambda_{max}$  (D<sub>max</sub>) in mµ in the ultraviolet at 238 (0.5), 282 (1.34), 346 (0.17), and 362 (0.12). Absorption was observed in the visible at 572 (0.80), 595 (0.96), 620 (0.85), 650 (0.83), and 720 (0.31). The infrared spectrum was recorded. An analytical sample was obtained by molecular distillation at 80° and 0.2 mm.

Anal. Caled. for  $C_{11}H_{10}S$ : C, 75.86; H, 5.75. Found: C, 75.74; H, 5.48.

Ethyl 2-Acetyl-3-(1-azulyl)propanoate (XI).-To 20 ml. (80.7 mmoles) of freshly distilled ethyl acetoacetate in a 50-ml. three-necked round-bottomed flask fitted with a stirrer, reflux condenser, and nitrogen inlet were added, with stirring, 0.4 g. (9.05 mmoles) of a 52% suspension of sodium hydride in oil and then 0.327 g. (1 mmole) of 1-azulyltrimethylammonium iodide. The solution was stirred and heated on a steam bath for 1 hr. (at the end of which time the color was dark green), then placed in a separatory funnel. Ether (50 ml.) and water (100 ml.) were added, the mixture was shaken, and the separated ether layer was exhaustively extracted with water. The blue ether phase was dried over sodium sulfate, the solvent was removed, and the residue was chromatographed on acid-washed alumina. Methylene chloride removed a blue fraction which yielded a blue oil which partially crystallized on standing. Trituration with a small volume of pentane left a small amount of colorless needles undissolved. The mixture was filtered, the filtrate was concentrated, and the residue was chromatographed on neutral alumina. The blue band eluted with ether gave 0.165 g. (61.1%) of ethyl 2-acetyl-3-(1-azulyl)propanoate as a blue oil. A methylene chloride solution showed  $\lambda_{\max}$  in m $\mu$  (D<sub>max</sub>) in the ultraviolet at 237 (0.56), 279 (1.61), 284 (1.47), 289 (1.25), 343 (0.16), and 358 (0.08). Absorption in the visible was observed at 595(0.67), 642 (0.58), and 710 (0.20). The infrared spectrum (chloroform) showed a doublet at 5.76  $\mu$  (ester) and 5.83  $\mu$ (ketone).

The 2,4-dinitrophenylhydrazone crystallized from 95% ethanol as red-brown needles, m.p.  $155-156^{\circ}$ .

Anal. Calcd. for  $C_{23}H_{22}N_4O_6$ : C, 61.33; H, 4.89. Found: C, 61.42; H, 5.10.

4-(1-Azulyl)butanone-2 (XII).—Ethyl 2-acetyl-3-(1-azulyl). propanoate (80 mg., 0.308 mmole) was treated with 20 mlof 5% sodium hydroxide and the mixture was stirred at room temperature for 3 hr., during which time the organic material gradually dissolved. Three milliliters of 50% sulfuric acid was then added and the solution was allowed to stand overnight at room temperature. It was then made slightly alkaline and extracted three times with ether. The combined organic extracts were washed three times with water, dried over sodium sulfate, and the solvent was then removed. The residue was chromatographed on acid-washed alumina. A 1:1 mixture of pentane-methylene chloride developed a blue band which yielded 35 mg. (59.7%) of 4-(1-azulyl)butanone-2 as a blue oil. The infrared spectrum (chloroform) showed only a peak at 5.85  $\mu$  in the carbonyl region.

The 2,4-dinitrophenylhydrazone crystallized from carbon tetrachloride as brown needles, m.p. 186-186.5°.

Anal. Calcd. for  $C_{20}H_{18}N_4O_4$ : C, 63.49; H, 4.76. Found: C, 63.17; H, 4.56.

1-Azulylmethylmalonic Acid (XIV).-To a solution formed from the reaction of 0.23 g. (10 mmoles) of sodium with 25 ml. of absolute ethanol in a 100-ml. three-necked flask set on a steam bath and equipped with a stirrer, reflux condenser, and dropping funnel was added under anhydrous conditions 2 g. (12.5 mmoles) of diethyl malonate. After 10 min., 0.327 g. (1 mmole) of 1-azulylmethyltrimethylammonium iodide was added and the mixture was heated under reflux with stirring for 2 hr. It was then diluted with four volumes of water, neutralized with 5% hydrochloric acid, and extracted twice with ether. The combined organic extracts were washed three times with water, dried over sodium sulfate, and concentrated. The residue was chromatographed on basic alumina and eluted with methylene chloride. Removal of the solvent from the blue eluate fraction gave 0.245 g. (81.6%) of a blue oil presumed to be diethyl 1azulylmethylmalonate (XIII). This material was dissolved in 20 ml. of a 50% ethanol solution 0.6 M in sodium hydroxide. The solution was heated under reflux for 1 hr., then diluted with 100 ml. of water and extracted with 50 ml. of ether. The aqueous phase was acidified with 5% hydrochloric acid and the blue suspension which resulted was extracted with ether. The separated ether layer was washed twice with water and dried over sodium sulfate. The solvent was removed and the residue was chromatographed on silicic acid. Ether removed a blue band which gave 0.155 g. (77.7%) of 1-azulylmethylmalonic acid as blue needles, m.p. 134-135° dec. An ethanol solution showed  $\lambda_{max}$  in m $\mu$  (Dmax) in the ultraviolet at 238 (0.59), 278 (1.88), 284 (1.72), 343 (0.18), and 357 (0.10). Absorption in the visible was observed at 592 (1.20), 643 (1.08), and 710 (0.35).

Anal. Caled. for C14H12O4: C, 68.85; H, 4.92. Found: C, 68.54; H, 5.16.

3-(1-Azulyl)propanoic Acid (XV).—A mixture of potassium acid sulfate (50 mg., 0.365 mmole) and 1-azulylmethylmalonic acid (0.131 g., 0.537 mmole) was heated in a vacuum sublimation apparatus at 150° and 0.5 mm. The evolution of carbon dioxide began immediately and the product was collected on the cold finger (an appreciable amount of material slowly turned brown and remained unsublimed). The sublimate was dissolved in a small volume of benzene and chromatographed on silicic acid. Methylene chloride eluted a blue band which gave 56 mg. (52%) of 3-(1-azulyl)propanoic acid as blue needles, m.p. 89–90°. A methylene chloride solution showed  $\lambda_{max}$  in m $\mu$  (D<sub>max</sub>) in the ultraviolet at 238 (0.40), 279 (1.25), 284 (1.22), and 344 (0.12). Absorption in the visible was observed at 600 m $\mu$ . The infrared spectrum was recorded.

Anal. Caled. for  $C_{13}H_{12}O_2$ : C, 78.00; H, 6.00. Found: C, 77.83; H, 6.32.

1-Methylazulene (XVI). Method A.—A mixture of 15 ml. of absolute ethanol, 1-azulylmethyltrimethylammonium iodide (0.2 g., 0.61 mmole), and an excess of sodium borohydride was heated under reflux for 45 min. and then diluted with 100 ml. of water. The whole was extracted with ether and the separated organic layer was washed with water and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was chromatographed on acid-washed alumina. *n*-Pentane eluted a blue band which gave 56 mg. (64.5%) of 1-methylazulene as a blue oil. The ultraviolet, visible, and infrared spectra of the product were identical with those of an authentic sample.<sup>6</sup>

Method B.—To a suspension of 0.15 g. (0.46 mmole) of 1-azulylmethyltrimethylammonium iodide in 20 ml. of dry benzene was added an excess of a 52% oil dispersion of sodium hydride and the mixture was heated under reflux for 2.5 hr. The solution was then washed thoroughly with water and dried over sodium sulfate. The solvent was removed and the residue was chromatographed over acidwashed alumina as described in method A. There was obtained 60 mg. (92.2%) of 1-methylazulene as a blue oil identical in all respects to the product in Method A.

# The Solvolysis of 2-Iodomercuriethyl Esters<sup>1</sup>

MAURICE M. KREEVOY AND GEORGE B. BODEM

School of Chemistry of the University of Minnesota, Minneapolis 14, Minnesota

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A solvolytic deoxymercuration has been discovered—that of 2-iodomercuriethyl esters. Solvolysis rate constants for the benzoate in mixtures of water with 30% or more of dioxane, ethanol, or acetic acid are linearly related to the Grunwald-Winstein Y's (ref. 8-10). For the acetate, solvolysis rate constants are linearly related to the Grunwald-Winstein Y's in all mixtures of ethanol and dioxane with water, but no linear relation exists over any substantial range of acetic acid-water mixtures. With both compounds a separate slope (m) is obtained for each organic diluent. These results are interpreted in terms of the mechanism of the deoxymercuration reaction and the structure of the transition state.

Some time ago, Sand<sup>2</sup> reported that 2-iodomercuriethyl benzoate (I) is decomposed only slowly by boiling hydrochloric acid. The implications of this report hardly seem credible since halide ion and hydronium ion are now known to catalyze the deoxymercuration reaction, both alone and in combination, quite vigorously around room temperature.<sup>3-6</sup> A re-examination of I was, consequently, undertaken. Compound I, and other 2-iodoethylmercuric esters, react readily in neutral or acid solutions in water or partially aqueous solvents. This paper reports on the neutral solvolysis reactions of I and 2-iodomercuriethyl acetate, II.

Reactions were carried out in dilute, homogeneous solution in water and in mixtures of water with ethanol, acetic acid, and dioxane. The course of the reactions was followed spectrophotometrically by observing the buildup of the mercuric iodide peak around 2800 Å. Compound I has a half-life of around three minutes in dilute aqueous solution at  $25^{\circ}$ .

### Results

Each mole of I solvolyzed yielded one-half mole of mercuric iodide, identified by its ultraviolet spectrum.<sup>5</sup> The solvolysis was also carried out in glacial acetic acid on a larger scale, using a substantially higher concentration of I and a somewhat higher temperature. One-half mole of ethylene, identified by its very characteristic infrared spectrum, was produced per mole of starting material. Ethylene was also identified as a product when II was allowed to solvolyse in water, 20% dioxane, and 20% ethanol. This leads to the overall stoichiometry shown in equation 1.

 $2\text{RCOOCH}_2\text{CH}_2\text{HgI} \longrightarrow \text{RCOO}^- + \text{CH}_2 = \text{CH}_2 + \\ \text{HgI}_2 + \text{RCOOCH}_2\text{CH}_2\text{Hg}^+ \quad (1)$ 

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