after removal of solvent, afforded another 7 mg of product, mp 111.5–113°. The combined yield of IV was 36 mg (38%).

A cyclohexane solution of IV showed in the ultraviolet, λ_{max} in mμ (log ε) at 231 (4.38), 256 (4.31), 300 (4.65), shoulder at 313 (4.50), 353 (3.55), 409 (3.42), 434 (3.49), and 462 (3.38), and in the infrared in mμ (ε), 747 (664), 823 (751), and 910 (425), with a shoulder at 683 (424). An nmr spectrum in deuteriochloroform showed H-8 and H-9 as doublets (J = 4 cps) at τ 2.98 and 2.88, H-3 a singlet at 3.65, H-4 (6) and H-6 (4) as singlets at 4.12 and 4.18, a complex multiplet for the phenyl protons at 2.4–2.8, and the 5- and 7-methyls at 7.73 and 7.92.

Anal. Calcd for $C_{20}H_{16}S$: C, 83.29; H, 5.59. Found: C, 83.14; H, 5.87.

Reaction of the Sodium Salt of Guaiazulene (VI) with an Excess of Benzonitrile.—A reaction similar to the one above was performed except that 3.244 g (16.4 mmoles) of guaiazulene, 25.0 ml of 0.67 *N* solution of sodium N-methylanilide in ether, and 16.0 ml (155 mmoles) of benzonitrile were used. After acid hydrolysis the solution was green instead of blue. Ether was added and the ethereal layer was extracted with 5% hydrochloric acid until the acid extract was no longer strongly colored (5 or 6 times). The yellowish green extracts were combined and neutralized with solid sodium carbonate to approximately pH 7; the resulting mixture was extracted with ether. The solvent was removed and the N-methylaniline was removed *in vacuo* using a vacuum pump as the mixture was heated. The crystalline residue, 627 mg (9.9%) was recrystallized from ethanol to give 7-isopropyl-9-methyl-1,3-diphenylazuleno[1,8-*cd*]azepine as golden brown needles, mp 152.5–153.5°. A cyclohexane solution had λ_{max} in the ultraviolet in mμ (log ε) at 255 (4.36), 307 (4.59), shoulders at 333 (4.36) and 389 (4.18), 398 (4.22), 459 (3.22), 490 (3.31), and in the near-infrared in mμ (ε) at 730 (98), 800 (122), 890 (113), and a shoulder at 1010 (59).

Anal. Calcd for $C_{29}H_{25}N$: C, 89.88; H, 6.50; N, 3.61; mol wt, 387.5. Found: C, 89.80; H, 6.64; N, 3.58; mol wt, 366.

Registry No.—III, 2054-29-7; IV, 14908-08-8; V, 2229-10-9; VII, 2054-32-2; VIII, 2054-31-1; X, 14908-03-3; XI, 14908-04-4; XII, 14908-05-5; XIII, 15215-92-6; XIV, 15038-91-2; azuleno[1,8-*bc*]thiapyran, 3759-04-4; azuleno[1,8-*cd*]azepine, 3573-45-3.

The Reaction of an Azirine with Anilinium Perchlorate. A Method of Obtaining α-Ammonium Anils[1]

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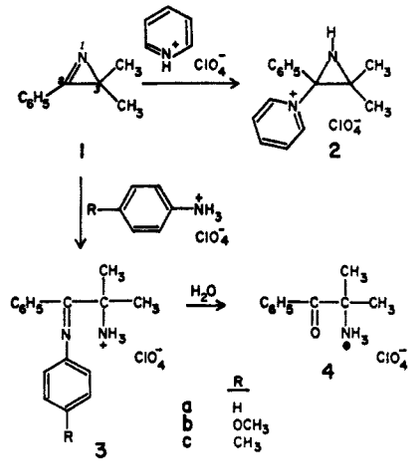
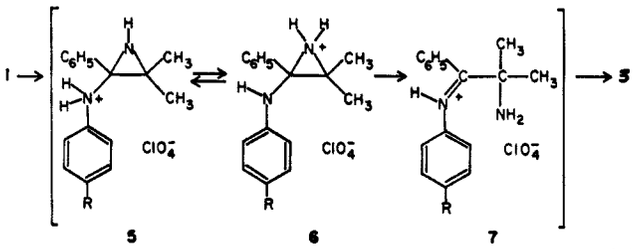
Under acidic conditions the π bond of an azirine is the locus of reaction with tertiary aromatic bases. First evidence for this came from the report of Neber and Burgard[2] that pyridine hydrochloride formed a stable adduct with 2-(2,4-dinitrophenyl)-3-methyl-1-azirine, for which a structure was proposed by Hatch and Cram.[3] The preparation of a similar compound, 3,3-dimethyl-2-phenyl-2-N′-pyridiniumaziridine perchlorate (2) from 3,3-dimethyl-2-phenyl-1-azirine (1) and pyridine perchlorate in either pyridine or acetonitrile was reported recently from this laboratory.[4] It was of interest to determine the course of the reaction of the representative azirine 1 with primary aromatic amines.

Treatment of 1 with anilinium (or aniline) perchlorate in acetonitrile gave α-ammoniumisobutyrophenone anil perchlorate (**3a**) (see eq 1) instead of an adduct analogous to 2. By analogy with the pyridine



(1)

example, however, the probable first step in the conversion to **3a** is the transfer of a proton to 3,3-dimethyl-2-phenyl-1-azirine and attack by aniline on the iminium bond to give **5**. A second proton transfer from anilinium to the more strongly basic aziridine nitrogen would lead to the intermediate **6** (eq 2). Cleavage at the 1,2 bond of the strained ring to give the resonance-stabilized carbonium–iminium ion **7** would be followed by a final proton transfer to yield the product **3a**. An intriguing feature of the mechanistic sequence



(2)

is the effective transfer of all three protons from one nitrogen to the other. A practical feature of the reaction lies in the nearly quantitative yield of α-ammoniumisobutyrophenone anil perchlorate (**3a**) obtainable *via* this route, whereas attempts to prepare the compound by direct combination of the perchlorate salt (**4**) of α-aminoisobutyrophenone with aniline under a variety of conditions were unsuccessful. The lower reactivity of ketones toward anil formation and the steric hindrance of **4** to nucleophilic attack[5] combine to make **3a** inaccessible by the direct condensation route. The structure of the anil **3a** was established by the correct analysis for $C_{16}H_{19}ClN_2O_4$, the $-N^+H_3$ and C=N stretching bands at 3125 and 3050 and at 1650 cm^{-1}, respectively, in the infrared, and the nmr signals (acetone-d_6) at τ 8.20 (s, 6 H) for two methyls and 2.71 (s) and 2.34–2.37 (m) for the thirteen protons of $^+NH_3$ and the aromatic rings. Hydrolysis of **3a** in water

(1) The support of this work by a research grant (GP-2012) from the National Science Foundation is gratefully acknowledged.

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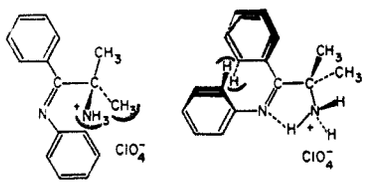
(3) M. J. Hatch and D. J. Cram, *J. Am. Chem. Soc.*, **75**, 38 (1953).

(4) N. J. Leonard and B. Zwanenburg, *ibid.*, **89**, 4456 (1967).

(5) H. H. Strain, *ibid.*, **52**, 820 (1930).

yielded α-ammoniumisobutyrophenone perchlorate (**4**) (or α-aminoisobutyrophenone perchlorate).

The ring opening reaction was extended to other examples by using the perchlorates of *p*-anisidine and *p*-toluidine with 3,3-dimethyl-2-phenyl-1-azirine (**1**) in anhydrous acetonitrile below 0°, which yielded α-ammoniumisobutyrophenone *p*-methoxyanil perchlorate (**3b**) and α-ammoniumisobutyrophenone *p*-methylanil perchlorate (**3c**), respectively. The structures were assigned by analogy, elemental analysis, and ir and nmr spectra. The assignment of the stereochemistry of the anils requires a decision between the *trans* (with respect to the two phenyl groups) form of **3**, in which there is unfavorable interaction between the ammoniumisopropyl group and the N-phenyl ring, and the *cis* form, in which the unfavorable steric interaction between the two phenyl rings may be relieved to some extent by twisting of a phenyl ring slightly out of coplanarity with the C=N bond[6]



3 (*trans*) **3** (*cis*)

and may be balanced by the intramolecular hydrogen bonding[7] which is possible in this geometric isomer. However, the relative stability of the two forms can be a function of the state and, in solution, of the solvent. A clear decision has not been reached on the basis of the evidence available at this time, but the ultraviolet spectra of these and related compounds in absolute ethanol suggest that the *cis* form of **3** is favored in this solvent.

Experimental Section

Aniline Salts.—A chilled solution of 1.0 g of aniline, *p*-anisidine, or *p*-toluidine in 10 ml of water was treated with 1.4 g of commercial 70% perchloric acid at −20°. After 15 min the reaction mixture was treated with 50 ml of ether. The white solid was collected and recrystallized from ethylene chloride or ethylene chloride–*n*-pentane. The yields varied from 81 to 94%.

Anilinium perchlorate had mp 259–260° dec (*caution:* explodes just above the melting point!).

Anal. Calcd for $C_6H_8ClNO_4$: C, 37.23; H, 4.17. Found: C, 37.62; H, 4.17.

***p*-Methoxyanilinium perchlorate** had mp 189–190° dec.

Anal. Calcd for $C_7H_{10}ClNO_5$: C, 37.60; H, 4.51. Found: C, 37.90; H, 4.65.

***p*-Methylanilinium perchlorate** had mp 254–255° dec.

Anal. Calcd for $C_7H_{10}ClNO_4$: C, 40.50; H, 4.86; N, 6.75. Found: C, 40.75; H, 4.86; N, 6.64.

Reaction of 3,3-Dimethyl-2-phenyl-1-azirine (1) with Anilinium Perchlorates. Formation of α-Ammoniumisobutyrophenone Anil Perchlorates (3).—A solution of 0.75 g (0.005 mole) of 3,3-dimethyl-2-phenyl-1-azirine,[4,8] $n^{22.5}D$ 1.5237, in 5 ml of acetonitrile was stirred at −10° while a solution of 1 g (0.005 mole) of anilinium perchlorate in 25 ml of acetonitrile was added dropwise over a period of 30 min. The pale yellow reaction mixture was allowed to stand at −10° for 64 hr, and the precipitated crystalline material (0.99 g), mp 161°, was collected by filtration. The filtrate was concentrated *in vacuo* to about half of its volume, cooled to −10°, and diluted by dropwise addition of ether, which caused the precipitation of shiny white crystals (0.65 g). The *final* total yield of product was 1.68 g (96%). Crystallization from ethylene chloride gave **α-ammoniumisobutyrophenone anil perchlorate (3a)** as shiny white prisms (1.05 g): mp 161.5–162.5°; ν_{max}^{Nujol} 3180, 1660 cm^{-1}; ν_{max}^{KBr} 3125, 3050, 1650 cm^{-1}; $\nu_{max}^{ClCH_2CH_2Cl}$ (0.01 *M*) 3050–3250 (w, br), 1650 cm^{-1} (w); (0.1 *M*) 3050–3250 (s, br), 1650 cm^{-1} (s); nmr τ (acetone-d_6), 8.20 (s, 6 H), 2.71 (s), and 2.34 to 3.37 (m, 13 H); λ_{max}^{EtOH} 293 mμ (ε 1630).

Anal. Calcd for $C_{16}H_{19}ClN_2O_4$: C, 56.72; H, 5.63; N, 8.27; Cl, 10.47. Found: C, 56.81; H, 5.80; N, 8.54; Cl, 10.65.

α-Ammoniumisobutyrophenone *p*-methoxyanil perchlorate (3b) was prepared from **1** and *p*-anisidine: mp 168–169°; ν_{max}^{Nujol} 3200, 1640 cm^{-1}; $\nu_{max}^{ClCH_2CH_2Cl}$ 3050–3250 (s, br), 1650 cm^{-1} (s); nmr τ ($CDCl_3$), 8.42 (s, 6 H, *gem* CH_3's), 6.42 (s, 3 H, OCH_3), 2.78 (s, br) and 2.5-3.8 (m, 12 H); λ_{max}^{EtOH} 292 mμ (ε 4220).

Anal. Calcd for $C_{17}H_{21}ClN_2O_5$: C, 55.36; H, 5.74; N, 7.60. Found: C, 55.29; H, 5.90; N, 7.49.

α-Ammoniumisobutyrophenone *p*-methylanil perchlorate (3c) was prepared from **1** and *p*-toluidine: mp 167–168°; ν_{max}^{Nujol} 3250, 1640 cm^{-1}; $\nu_{max}^{ClCH_2CH_2Cl}$ 3050–3250 (s, br), 1650 cm^{-1} (s); nmr τ (acetone-d_6), 8.21 (s, 6 H, *gem* CH_3's), 7.87 (s, 3 H, $ArCH_3$), 2.71 (s) and 2.6–3.7 (m, 12 H); λ_{max}^{EtOH} 293 mμ (ε 2290).

Anal. Calcd for $C_{17}H_{21}ClN_2O_4$: C, 57.87; H, 6.00; N, 7.94. Found: C, 58.05; H, 5.93; N, 7.87.

α-Ammoniumisobutyrophenone Perchlorate (4).—A solution of 0.20 g of the anil **3a** in 10 ml of water was heated at 80° for 2 hr. Removal of the water *in vacuo* gave 0.15 g of white prisms. Recrystallization from acetone–ether gave the ketone **4**[4] as colorless prisms: mp 253.5–254.5° dec; 0.12 g (73% yield of purified product); ν_{max}^{Nujol} 3150, 1680 cm^{-1}; nmr τ (acetone-d_6), 7.96 (s, 6 H), 1.82–2.50 (m, 5 H), identical with those of an authentic specimen.[4]

Anal. Calcd for $C_{10}H_{14}ClNO_5$: C, 45.54; H, 5.36; N, 5.30. Found: C, 45.26; H, 5.30; N, 5.02.

Composite Spectra.—When *p*-anisidine was added to an equimolar (actually 0.049 m*M*) solution of α-ammoniumisobutyrophenone perchlorate (λ_{max}^{EtOH} 277 mμ (ε 750)) in absolute ethanol, the solution containing both showed a composite λ_{max}^{EtOH} 297 mμ (ε 3220). Accordingly, it was ascertained that **3b** (above) was not hydrolyzed immediately in absolute ethanol to its component parts. The ultraviolet absorption maxima of additional anils in absolute ethanol anils were determined for direct comparison purposes: benzalaniline, 262 mμ (ε 17,000), 308 (8620); benzal-*p*-anisidine, 264 (12,900), 331 (12,650); benzal-*p*-toluidine, 262 (13,900), 318 (8990). All three anils showed ν_{max}^{Nujol} 1620 cm^{-1}.

Registry No.—**1**, 14491-02-2; **3a**, 14796-07-7; **3b**, 14796-08-8; **3c**, 14796-09-9; **4**, 14901-51-0; anilinium perchlorate, 14796-11-3; *p*-methoxyanilinium perchlorate, 14796-12-4; *p*-methylanilinium perchlorate, 14796-13-5.

(6) D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).
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The Rearrangement of a 2-Aminobenzylidenaminoacetic Acid N-Oxide with Ethyl Chloroformate[1]

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In an attempt to find fresh approaches to the preparation of 7-chloro-1,3-dihydro-3-hydroxy-5-phenyl-2H-1,4-benzodiazepin-2-one (I),[2] we have studied the

(1) Reported at the Medicinal Chemistry Symposium, Bloomington, Ind., June 1966.
(2) S. C. Bell and S. J. Childress, *J. Org. Chem.*, **27**, 1691 (1962).