(11.25 g, 0.104 mole) was introduced through a vacuum manifold system. The reactor was then set aside and allowed to stand overnight at ambient temperature. At the end of this period (about 16 hr), the excess pressure in the reactor was released and the liquid contents were slurried with sodium fluoride, filtered, and distilled. There was obtained 9.0 g of a water-white liquid, bp 34°, which was shown to be 1,1,1,4-tetrafluoro-2-trifluoromethyl-2,3-butadiene.

This procedure was used to prepare all the compounds listed in Table II.[13]

(13) NOTE ADDED IN PROOF:—C. Woolf and B. Lichstein, Central Research Laboratory, Allied Chemical Corp., have noted a reaction similar to that described in this paper.

$$(F_3C)_2C(OH)CH{=}CH_2 \xrightarrow{SF_4} (F_3C)_2C{=}CHCH_2F$$

Registry No.—Ia, 646-72-0; Ib, 15052-50-3; Ic, 5714-47-6; Id, 15052-52-5; Ie, 15052-53-6; If, 15052-54-7; IId, 15052-55-8; IIe, 15052-56-9; IIf, 15052-57-0; IIIa, 15052-58-1; IIIb, 15052-59-2; IIIc, 15052-60-5; IIId, 15052-61-6; IIIe, 15052-62-7; IIIf, 15052-63-8; VIII, 15052-64-9; IX, 15052-65-0; X, 15052-66-1; XI, 15052-67-2; XII, 15052-68-3; $F_2C{=}C(CF_3)CCl{=}CFH$, 15052-69-4.

Acknowledgment.—We are grateful to Dr. B. B. Stewart, Dr. R. Ettinger, and Mr. R. J. Tepper for assistance with the nmr spectra, and to Professor Jerrold Meinwald for helpful discussions of the theoretical aspects of the work.

Notes

Azuleno[1,8-*bc*]thiapyran and Azuleno[1,8-*cd*]azepine[1]

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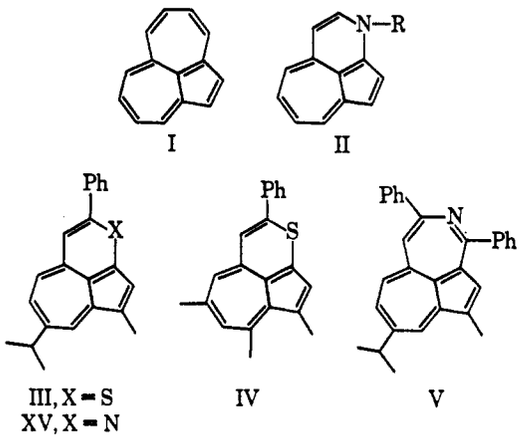
There has been much interest recently in heterocyclic analogs of nonbenzenoid aromatic hydrocarbons. Both π-excessive[2] and π-equivalent[3] heteroanalogs of azulene have been reported.

We have been interested in new heterocycles which are iso-π-electronic with the interesting, nonbenzenoid aromatic hydrocarbon cyclopenta[*e,f*]heptalene (I)[4] prepared by Hafner and Schneider. The first π-excessive[5] heteroanalog of I to be prepared[6] was 1H-cyclohepta[*d,e*]-1-pyrindine (II). Its absorption spectra were found to be quite similar to those of I.

In this paper we wish to report the syntheses of two new heteroanalogs of I. Two derivatives, III and IV, of the azuleno[1,8-*bc*]thiapyran structure have been prepared. A nitrogen heterocycle obtained during the synthesis of III has been identified as 1,3-diphenyl-7-isopropyl-9-methylazuleno[1,8-*cd*]azepine (V). Compound V is the first π-equivalent[7] heteroanalog of I to be reported.



I II III, X = S XV, X = N IV V

Azuleno[1,8-*bc*]thiapyran.—Guaiazulene (1,4-dimethyl-7-isopropylazulene) was selected initially as the starting material since it had the desired structural features. That is, a functional group can be introduced at the 4-methyl carbon *via* base-induced condensation reactions,[8] and electrophilic substitution, which can occur only at the 3 position, can be used to introduce a sulfur-containing functional group at that position.

The sodium salt of guaiazulene VI, generated[8] by the reaction of guaiazulene with sodium N-methylanilide was treated with benzonitrile to give, after acid hydrolysis, 7-isopropyl-1-methyl-4-phenacylazulene (VII), mp 116–117°, in 58% yield. This ketone had a carbonyl band at 5.90 μ in the infrared, and showed a λ_{max} of 608 mμ in the visible region. Treatment of VII with thiocyanogen[9] gave a 92% yield of the 3-thiocyano derivative VIII. This derivative had a band at 4.64 μ ascribed to the –SCN group,[10] as well as the carbonyl band at 5.88 μ, in its infrared spectrum and a visible λ_{max} at 583 mμ. When VIII was treated with zinc and acetic acid, the thiocyano

(1) (a) Supported in part by a grant (GP-250) from the National Science Foundation. (b) Previously reported as a communication to *Tetrahedron Letters*, No. 23, 1877 (1965).

(2) (a) A. G. Anderson, Jr., W. F. Harrison, and R. G. Anderson, *J. Am. Chem. Soc.*, **85**, 3448 (1963). (b) G. V. Boyd and F. W. Clark, *J. Chem. Soc.*, 859 (1966). (c) R. Mayer, J. Franke, V. Horak, I. Hanker, and R. Zharadnik, *Tetrahedron Letters*, 289 (1961).

(3) T. Nozoe, in "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 7; K. Hafner and M. Kreuder, *Angew. Chem.*, **73**, 657, (1961).

(4) K. Hafner and J. Schneider, *Ann.*, **624**, 37 (1959).

(5) A. Albert, "Heterocyclic Chemistry. An Introduction," Oxford University Press, Inc., Essential Books Division, New York, N. Y., 1959.

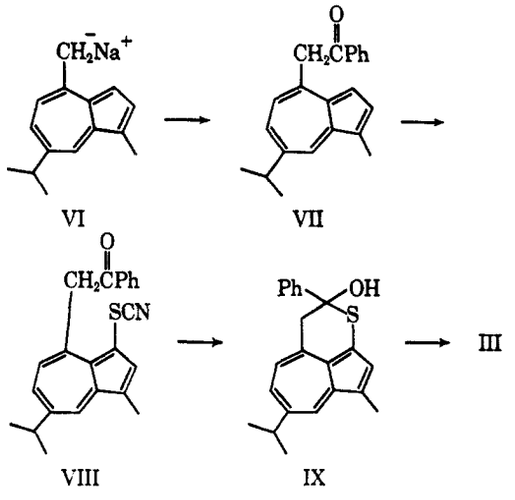
(6) L. L. Replogle, *J. Am. Chem. Soc.*, **86**, 3137 (1964).

(7) See ref. 2a; *cf.* footnote 9.

(8) K. Hafner, H. Pelster, and H. Patzelt, *Ann.*, **650**, 80 (1961).

(9) A. G. Anderson, Jr., and R. N. McDonald, *J. Am. Chem. Soc.*, **81**, 5669 (1959).

(10) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 28.

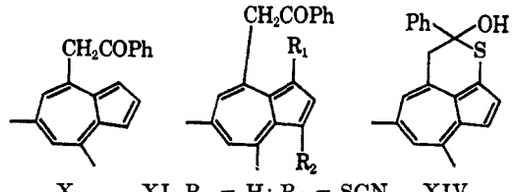


group was reduced to a mercapto group which then added, intramolecularly, to the carbonyl function to give the presumed cyclic hemimercaptol IX.

Since IX was a rather unstable green oil, it was not completely characterized, but it did show the expected spectral features. Its infrared spectrum had a new band at 2.95 μ (–OH) and the bands at 4.6 and 5.9 μ had disappeared. Also it had a λ_{max} in the visible region at *ca.* 680 mμ, which would be consistent with the bathochromic shift expected for an azulene bearing a 1-alkylthio group.[11] Dehydration of IX with phosphoric acid in acetic acid yielded 6-isopropyl-8-methyl-2-phenylazuleno[1,8-*bc*]thiapyran as a reddish brown, crystalline solid, mp 88.5–89.5°. The conversion of VIII to III occurred in 93% yield.

Another derivative of the azuleno[1,8-*bc*]thiapyran system was prepared starting from 4,6,8-trimethylazulene. This trimethylazulene was converted to 6,8-dimethyl-4-phenacylazulene (X) in low yield using the same method employed for the preparation of VII. This ketone (X) had a carbonyl band at 6.0 μ in its infrared spectrum, and it also had the anticipated nmr spectrum with the α-methylene signal at τ 5.25. However, a satisfactory elemental analysis could not be obtained. Reduction of this ketone to the known alcohol β-[4-(6,8-dimethylazulyl)]-α-phenylethyl alcohol provided additional evidence of its structure.

Both the reactive 1 and 3 positions of X are available for attack; so one would expect thiocyanation of X to yield two monothiocyano derivatives, *viz.*, 6,8-dimethyl-4-phenacyl-1-thiocyanoazulene (XI) and 4,6-dimethyl-8-phenacyl-1-thiocyanoazulene (XII). A 62% yield of a mixture of XI and XII, as well as a 3% yield of the disubstituted product 6,8-dimethyl-4-phenacyl-1,3-dithiocyanoazulene (XIII), was obtained from the reaction of X with thiocyanogen. The mixture of XI and XII had λ_{max} 532 mμ and melted over a wide range of approximately 120–145°.



XI, R_1 = H; R_2 = SCN
XII, R_1 = SCN; R_2 = H
XIII, R_1 = R_2 = SCN

An nmr analysis of this mixture indicated that XII was the major component and that the ratio of XII to XI was approximately 3:2. This analysis was based on the ratio of the peak areas of the methylene groups α to the carbonyl group. The spectrum showed two broad singlets, the larger one at τ 4.68 and the smaller one at 5.28, which could be due only to the α-methylene groups. The α-methylene group of the ketone X appears at τ 5.25 whereas that of VIII, which has the thiocyano and phenacyl groups *peri* to one another, is at 4.70. Therefore, the peak at τ 4.68 in the spectrum of the mixture must be due to XII and the peak at 5.28 is due to XI.

It was not found possible to separate the mixture of XI and XII by chromatography. Even tlc using a variety of conditions showed only one spot. However, fractional crystallization of the mixture from ethanol afforded a product melting at 153–155°. Since the nmr spectrum of this material had a peak at τ 5.22, it is believed to be XI.

The dithiocyano derivative XIII can exist in two crystalline modifications, red needles or purple needles, just like the closely related compound 1,3-dithiocyano-4,6,8-trimethylazulene.[11]

The mixture of thiocyano ketones was reduced with zinc and acetic acid in ethanol solution. It was difficult to separate the components of this reaction mixture. Repeated chromatographies, including a preparative tlc, finally afforded a 26% yield of 5,7-dimethyl-2-hydroxy-2-phenyl-2,3-dihydroazuleno[1,8-*bc*]thiapyran (XIV), mp 119–121°. This derivative had a visible maximum at 622 mμ and an OH band at 2.9 μ in its infrared spectrum.

When a greater amount of acetic acid was used in the reduction of the mixture and the reaction time extended, the major product was the completely conjugated heterocycle 5,7-dimethyl-2-phenylazuleno[1,8-*bc*]thiapyran (IV). A small amount of the hemimercaptol XIV was also isolated, and this was converted to IV by acid. The total yield of IV was 38%. The reduction conditions also caused some cleavage of the sulfur functional group from the ring as the ketone X was isolated in 20% yield.

This sulfur heterocycle appears to be quite stable. It is more stable than the corresponding nitrogen heterocyclic system II, whose derivatives slowly decompose.[6] Further, III and IV can be chromatographed on activated alumina without decomposition, while derivatives of II can only be chromatographed safely on deactivated (grade IV or V) alumina.

The ultraviolet and visible spectra[12] of III are quite similar to those of the corresponding nitrogen heterocycle, 6-isopropyl-1,2,8-trimethylcyclohepta[*d*,*e*]-1-pyrindine (XV). A ring proton nmr spectrum of III was consistent with the proposed structure.[12]

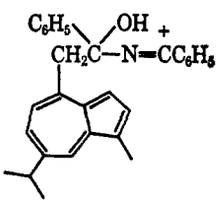
Azuleno[1,8-*cd*]azepine.—In some preparations of the ketone VII, small amounts of a golden brown, crystalline solid had been isolated from the acid extract. From one of these preparations, when a large excess of benzonitrile was mistakenly used, a significant amount (*ca.* 10%) of this solid was obtained. It was recrystallized from ethanol to give golden

(11) L. L. Replogle, R. M. Arluck, and J. R. Maynard, *J. Org. Chem.*, **30**, 2715 (1965).

(12) See ref 1b for figures of the spectra and a discussion of them.

brown needles, mp 152.5–153.5°. The absorption spectra[12] were similar to those of III, including the band in the 700–1100-mμ region which is characteristic of cyclopenta[*e,f*]heptalene[4] (I) and its heterocyclic analogs II and III. It gave an elemental analysis and molecular weight determination consistent with the molecular formula $C_{29}H_{25}N$. On the basis of these data, its nmr spectrum,[12] and its genesis, this compound is believed to be 7-isopropyl-9-methyl-1,3-diphenylazuleno[1,8-*cd*]azepine (V). Like the thiapyran derivative III, this new nitrogen heterocycle also is a stable compound.

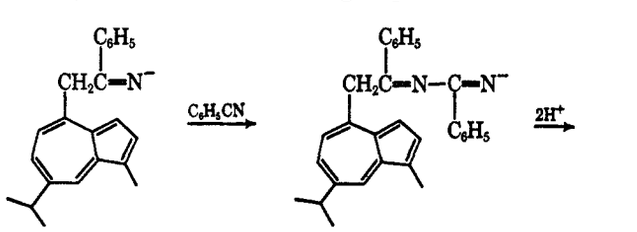
The unexpected formation of the azuleno[1,8-*cd*]-azepine ring system from VI and benzonitrile raises the question of the mechanism involved. Apparently two molecules of benzonitrile are being incorporated in this reaction. One mechanism which was considered was the acid-catalyzed nucleophilic attack by the nitrogen atom of benzonitrile on the ketone VII (or its imine precursor) to give the intermediate XVI.



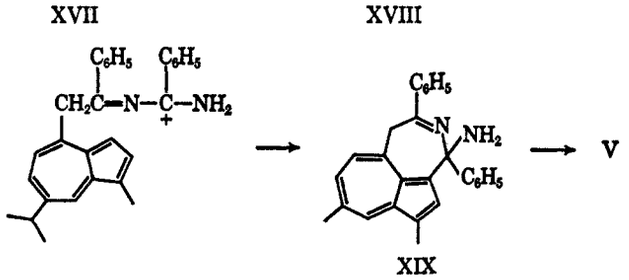
XVI

This adduct (XVI) could then undergo cyclization *via* electrophilic attack at the 1 position; subsequent dehydration would yield V. However, when the ketone VII and an excess of benzonitrile were treated with aqueous hydrochloric acid, no reaction occurred even after heating.

A more likely mechanism is that shown below. The imine salt (XVII) initially formed by reaction of VI with benzonitrile could attack another molecule of benzonitrile to produce the diadduct XVIII. An analogy for this step is provided by the base-catalyzed trimerization of nitriles to 2,5,6-trialkyl-4-aminopyrimidines (Frankland–Kolbe synthesis). It is proposed[13] that the ring nitrogens result from attack by an imine anion, resulting from anionic addition to a nitrile, on another nitrile group. Under the acid conditions of the work-up procedure, the diadduct could cyclize by electrophilic substitution to give XIX which could then be transformed to the product by loss of ammonia.



XVII XVIII



XIX

(13) G. W. Kenner and A. Todd, in "Heterocyclic Compounds," Vol. 6, R. C. Elderfield, Ed., John Wiley and Sons, Inc., New York, N. Y., 1957, p 248.

Experimental Section[14]

7-Isopropyl-1-methyl-4-phenacylazulene (VII).—To a mixture of 1.33 g (6.72 mmoles) of guaiazulene, dissolved in dry ether and kept under a dry nitrogen atmosphere, was added 9.7 ml of a 0.69 *N* solution of sodium N-methylanilide in ether. The green mixture was stirred for about 10 min, and 0.70 ml (0.70 g, 6.8 mmoles) of benzonitrile was added slowly from a syringe. The reaction mixture which had become dark maroon was stirred for 30 min, and 40 ml of 1 *N* hydrochloric acid was added, whereupon the mixture turned blue, and stirring was continued for 15 min. The mixture was extracted with ether. The residue remaining after removal of solvent was recrystallized from Skellysolve B to give 1.173 g (58%) of the ketone VII as blue needles, mp 116.5–117°.

Solvent was removed from the mother liquor and the residue was chromatographed on acid-washed alumina. A large blue band was eluted with petroleum ether (30–60°). This band contained a considerable amount of unreacted guaiazulene, but also some benzonitrile.

An infrared spectrum of VII in carbon tetrachloride showed a carbonyl peak at 5.90 μ. A cyclohexane solution of VII showed λ_{max} in mμ (log ε) in the ultraviolet at 248 (4.56), 285 (4.63), shoulder at 287 (4.63), shoulder at 343 (3.56), 352 (3.66), and 368 (3.54). There was a single maximum in the visible at 608 mμ (ε 516), with shoulders at 590 (453), 629 (472), and 663 (418).

Anal. Calcd for $C_{22}H_{22}O$: C, 87.37; H, 7.33. Found: C, 87.10; H, 7.29.

7-Isopropyl-1-methyl-3-thiocyano-4-phenacylazulene (VIII).—Thiocyanogen was prepared from a mixture of 2.42 g (7.50 mmoles) of lead thiocyanate in 20 ml of dry dichloromethane, cooled in an ice–salt bath, and the requisite amount (*ca.* 6.2 ml) of 1.2 *M* bromine in carbon tetrachloride solution. This thiocyanogen solution was added in portions to a flask cooled by an ice–salt bath containing 2.114 g (7.00 mmoles) of 7-isopropyl-1-methyl-4-phenacylazulene in 25 ml of dry dichloromethane, with stirring over a period of about 20 min. Water was added and the organic phase was separated. Solvent was removed *in vacuo*, and the solid residue was recrystallized from Skellysolve B giving 2.102 g of VIII as dark bluish purple needles, mp 125–126.5°. A second crop consisting of 0.203 g with mp 122.5–124° was obtained. The combined yield was 92%.

An infrared spectrum of VIII showed —SC=N and C=O peaks at 4.64 and 5.88 μ, respectively. A cyclohexane solution of VIII exhibited λ_{max} in mμ (log ε) in the ultraviolet at 247 (4.53), shoulder at 262 (4.44), 294 (4.59), shoulder at 352 (3.60), 360 (3.68), and 376 (3.78). There was a single maximum in the visible at 583 mμ (ε 520) with a shoulder at 618 mμ (ε 460).

Anal. Calcd for $C_{23}H_{21}ONS$: C, 76.84; H, 5.98; N, 3.90. Found: C, 76.93; H, 5.79; N, 4.1.

6-Isopropyl-8-methyl-2-phenylazuleno[1,8-*bc*]thiapyran (III).—A mixture of 288 mg (0.805 mmole) of thiocyano ketone VIII, 50 ml of absolute ethanol, 12 ml of glacial acetic acid, and 800 mg of zinc dust was stirred for 8 hr and then filtered to remove the excess zinc. Water was added and the mixture was extracted with petroleum ether. The solvent was removed *in vacuo* and the oily, blue-green residue (presumably the hemimercaptol IX) was dissolved in 5 ml of glacial acetic acid. One-half of a milliliter of 85% phosphoric acid was added. After the yellow-green mixture was stirred for 5 min, 50 ml of saturated sodium bicarbonate solution was added, and the mixture was extracted with petroleum ether. Solvent was removed from the green petroleum ether extract, and the resi-

(14) Melting points were taken on a calibrated Fisher-Johns apparatus. Infrared spectra were taken on a Beckman IR-4 or IR-5; ultraviolet and visible spectra were taken on a Cary 14. Nuclear magnetic resonance spectra were taken in deuteriochloroform solution with tetramethylsilane as the internal marker, using a Varian A-60 spectrometer; chemical shifts are reported as τ values. Coupling constants were taken directly from the spectra and are apparent values. Microanalyses were performed by Dr. A. Bernhardt, Max Planck Institute, Mülheim, Germany, or by Berkeley Analytical Laboratories, Berkeley, Calif.

due was chromatographed on basic (Merck) alumina with 1:1 petroleum ether–carbon tetrachloride as the eluent. A large yellow-green band was eluted followed by a small blue band. The residue from the yellow-green eluate was rechromatographed using a 3:2 petroleum ether–carbon tetrachloride eluent and this yielded 235 mg (93%) of the heterocycle III as a reddish brown crystalline solid, mp 88.5–89.5°.

A cyclohexane solution of III showed λ_{max} in mμ (log ε) in the ultraviolet at 220 (4.41), 260 (4.37), 297 (4.64), 364 (4.09), 420 (3.55), 450 (3.51), and 480 (3.40), and in the near-infrared in mμ (ε) at 823 (493) and 925 (573), with a shoulder at 1030 (323). An infrared spectrum showed no absorption corresponding to –SCN, C=O, or –OH groups.

Anal. Calcd for $C_{22}H_{20}S$: C, 83.50; H, 6.37. Found: C, 83.76; H, 6.35.

In a different experiment, some of the intermediate hemimercaptol IX was isolated as a blue-green oil and partially characterized. A visible spectrum showed a maximum at *ca.* 680 mμ. An infrared spectrum indicated the disappearance of the SCN and —C=O groups, and a new band at 2.95 μ indicated an —OH group.

6,8-Dimethyl-4-phenacylazulene (X).—To 7.390 g (0.043 mole) of 4,6,8-trimethylazulene in a flask cooled by an ice bath was added 60 ml of 0.82 *N* ethereal solution of sodium N-methylanilide. This red-brown mixture was stirred for 40 min and then 4.8 ml (0.047 mole) of benzonitrile was added. The mixture was warmed and stirred for 60 min, and then it was hydrolyzed with 1 *N* hydrochloric acid. Ether was added, and the ethereal solution was extracted many times with 6 *N* hydrochloric acid until the acid extracts were no longer colored. Solvent was removed and the residue was chromatographed over acid-washed alumina with 2:1 petroleum ether–dichloromethane. The large purple band which was eluted contained both unreacted trimethylazulene and the product ketone. Removal of solvent from the eluate left a purple solid which was triturated several times with portions of petroleum ether. The residue was recrystallized from ethanol to give 2.82 g (25%) of 6,8-dimethyl-4-phenacylazulene, mp 162–165° (after drying *in vacuo* over P_2O_5). An additional 0.50 g of less pure ketone, mp 155–162°, and 1.31 g of starting material were obtained from the combined petroleum ether triturates plus the mother liquor by chromatography followed by several recrystallizations. An infrared spectrum (nujol) of X showed a C=O band at 6.0 μ. A cyclohexane solution of X showed maxima in the ultraviolet in mμ (log ε) at 283 (4.65), 287 (4.69), 292 (4.70), and 352 (3.88). There was a single maximum in the visible at 550 mμ (ε 588) for a chloroform solution of X. The nmr spectrum of X in deuteriochloroform showed the *ortho* protons at *ca.* τ 2.8, H-2 as a triplet at 2.35, a complex multiplet at 2.5–2.8, H-5 and H-7 as overlapping singlets at 2.95 and 3.00, the methylene protons at 5.25, and 8-methyl and 6-methyl at 7.19 and 7.43.

Anal. Calcd for $C_{20}H_{18}O$: C, 87.55; H, 6.61. Found: C, 86.52; H, 6.72.

The ketone X was reduced with sodium borohydride in an aqueous THF–sodium hydroxide solution to the corresponding alcohol, β-[4-(6,8-dimethylazulyl)]-α-phenylethyl alcohol in 66% yield. The product was isolated by chromatography over acid-washed alumina (chloroform eluent), followed by recrystallization from petroleum ether, and it had mp 77.5–78.5° (lit.[8] 78°) and λ_{max} (cyclohexane solution) in mμ (ε) at 551 (530), 586 (460), and 644 (167) (lit.[8] 550 (563), 587 (473), and 640 (192).

Thiocyanation of 6,8-dimethyl-4-phenacylazulene.—To an ice-cooled solution of 548 mg (2.00 mmoles) of 6,8-dimethyl-4-phenacylazulene in 10 ml of dry dichloromethane was added the ice-cooled, stirred thiocyanogen solution, prepared from 646 mg (2.00 mmoles) of lead thiocyanate and the requisite amount of 10% bromine in carbon tetrachloride solution, in portions over a period of *ca.* 20 min. The reaction mixture was stirred for another 90 min as the ice melted, and then the solvent was removed *in vacuo*. The crystalline residue was chromatographed over Mallinckrodt CC-7 silica gel. A small purple band was eluted with 3:1 petroleum ether–dichloromethane and the main red band with a 1:1 mixture of those solvents; a following small red-orange band was eluted with dichloromethane. The purple eluate yielded 40 mg of the starting ketone, while the red eluate gave 409 mg (62%) of a mixture of 6,8-dimethyl-4-phenacyl-1-thiocyanoazulene (XI) and 4,6-dimethyl-8-phenacyl-1-thiocyanoazulene (XII). This mixture had $\lambda_{max}^{CHCl_3}$ 532 mμ, a broad mp 120–144°, and an infrared spectrum (carbon tetrachloride) showing peaks at 4.67 (SCN) and 5.93 μ (C=O).

A portion of the mixture was fractionally crystallized from ethanol giving purple crystals, mp 153–155°. The nmr spectrum of this material showed the α-methylene protons signal at τ 5.22, and it is presumed to be 6,8-dimethyl-4-phenacyl-1-thiocyanoazulene (XI). An analytical sample recrystallized from ligroin had mp 155.5–156.5°. A chloroform solution of XI showed λ_{max} in mμ (log ε) in the ultraviolet at 250 (4.55), 306 (4.63), and 350 (3.84). There was a single maximum in the visible at 535 mμ (ε 703).

Anal. Calcd for $C_{21}H_{17}ONS$: C, 76.10; H, 5.17; N, 4.23. Found: C, 76.03; H, 5.19; N, 4.11.

The residue from the red-orange eluate was recrystallized from carbon tetrachloride to give 21 mg (2.7%) of 6,8-dimethyl-4-phenacyl-1,3-dithiocyanoazulene (XIII) as red needles containing a few purple needles. Upon heating, the red needles were converted to the purple form, and this melted at 149–151° dec. An infrared spectrum (KBr) showed peaks at 4.69 (SCN) and 5.96 μ (C=O). A chloroform solution of XIII showed λ_{max} in mμ (log ε) in the ultraviolet at 248 (4.58), 310 (4.59) and 348 (3.91); there was a single maximum in the visible at 517 mμ (ε 915).

Anal. Calcd for $C_{22}H_{16}ON_2S_2$: C, 68.01; H, 4.15; N, 7.21. Found: C, 67.82; H, 4.20; N, 7.06.

Reduction of Mixture of Thiocyano Ketones XI and XII.—A red reaction mixture consisting of 108 mg (0.326 mmole) of the mixture of XI and XII, 300 mg of zinc dust, 5 ml of acetic acid, and 20 ml of absolute ethanol was stirred under an argon atmosphere for 4 hr. The purple mixture was filtered, water was added, and this mixture was extracted with ether. The ether extract was washed well with water and then saturated sodium bicarbonate solution and dried. The solvent was removed and the residue was chromatographed over silica gel (CC-7). A small green band was eluted with a 4:1 mixture, blue band with a 2:1 mixture, and red band with 1:1 mixture of petroleum ether–dichloromethane. The green eluate afforded 5 mg of the thiapyran and the red band contained 50 mg of the thiocyano ketones (XI and XII). A tlc analysis (silica gel; 1:1 petroleum ether–dichloromethane) of the residue from the blue eluate (about 50 mg) showed two blue spots with a purple front on the first blue spot. An infrared spectrum of this material (neat) showed an OH band at 2.92 and a C=O band at 5.92 μ. It was then chromatographed on a preparative silica gel G plate (20 × 20 cm; 1.5 mm thick). The plate was developed twice (about 2 hr) using a 2:1 petroleum ether–dichloromethane mixture to give a purple band (highest R_f) followed by a small blue band and a large blue band (lowest R_f). The substance in the small blue band discolored and seemed to decompose upon exposure to air. The large blue band was collected and extracted. The residue from the solution was rechromatographed over CC-7 and yielded 26 mg (26%) of the hemimercaptol XIV as blue needles, mp 119–121°.

A cyclohexane solution of XIV showed λ_{max} in mμ (log ε) in the ultraviolet at 249 (4.42), 321 (4.53), 383 (3.68), and 399 (3.81). There was a single maximum in the visible at 622 mμ (ε 405). An infrared spectrum (neat) showed at OH band at 2.9 μ and the absence of thiocyano and carbonyl groups.

Anal. Calcd for $C_{20}H_{18}OS$: C, 78.39; H, 5.92. Found: C, 78.38; H, 5.73.

5,7-Dimethyl-2-phenylazuleno[1,8-*bc*]thiapyran (IV).—A mixture containing 110 mg (0.333 mmole) of the thiocyanoketone mixture, 300 mg of zinc dust, 10 ml of acetic acid, and 20 ml of absolute ethanol was stirred under an argon atmosphere for 7.5 hr and then allowed to stand overnight. The green reaction mixture was treated as in the reaction above and then chromatographed over CC-7. A 3:1 petroleum ether–dichloromethane mixture eluted a green band followed by a very small green band, and a purple band which was overlapped by a blue band. The brown residue from the green eluate was crystallized from petroleum ether to give 29 mg of the sulfur heterocycle IV as red-brown needles, mp 110.5–113°. The purple eluate yielded 19 mg (21%) of the ketone X. The residue from the blue eluate (11 mg) was dissolved in about 10 ml of acetic acid and 1 drop of 85% phosphoric acid was added. The mixture was allowed to stand for about 10 min and then diluted with water. This was extracted with ether; the ether extract was washed with water and saturated sodium bicarbonate solution. Chromatography of the residue, left

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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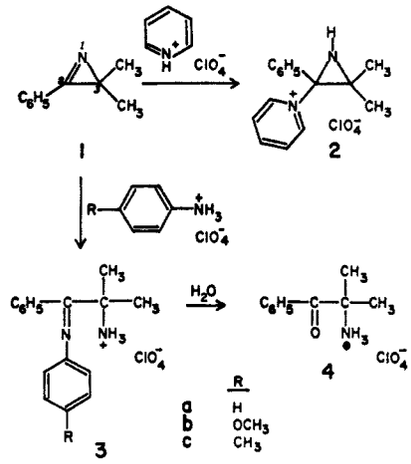
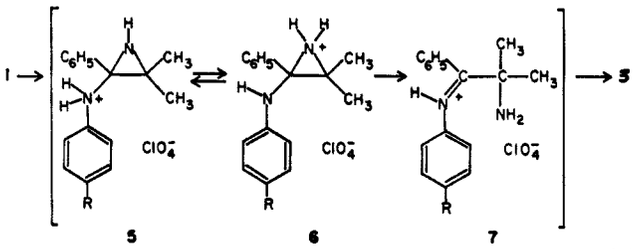
Under acidic conditions the π bond of an azirine is the locus of reaction with tertiary aromatic bases. First evidence for this came from the report of Neber and Burgard[2] that pyridine hydrochloride formed a stable adduct with 2-(2,4-dinitrophenyl)-3-methyl-1-azirine, for which a structure was proposed 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

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

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