again, and carboxylic acid, but no absorption at 805 cm.$^{-1}$. Analysis suggested the presence of difficulty removable water of hydration.

Anal. Calcd. for $C_5H_7N_5O_2S \cdot H_2O$: equiv. wt., 219; C, 27.39; H, 4.14; N, 31.95; O, 21.90; S, 14.63. Found: equiv. wt., 212; C, 27.93, 27.80; H, 4.22, 4.09; N, 32.21; O, 17.72, 17.45; S, 14.03.

To prepare **S-(2-cyanoethyl)thioammeline** a mixture of 28 g. (0.20 mole) of thioammeline, 120 ml. of water, 10 ml. (0.005 mole) of 0.5 *N* sodium hydroxide, 0.2 g. of cupric sulfate and 11 g. (0.20 mole) of acrylonitrile was heated at 82° for 1.5 hr., then cooled. The yellowish crystalline product weighed 34 g. (87%). It was soluble in hot ethylene glycol monoethyl ether, 1:1 aqueous ethylene glycol monoethyl ether (1 g./19 ml.), slightly soluble in hot water, acetonitrile (1 g./150 ml.), methanol, ethanol and acetone, and insoluble in hot benzene; m.p. 248–250°. Its infrared spectrum showed the expected absorption at 806 cm.$^{-1}$, and an aliphatic nitrile, with no absorption at 775 cm.$^{-1}$, and had a strong resemblance to the spectrum of S-methylthioammeline.

Anal. Calcd. for $C_6H_8N_6S$: S, 16.34. Found: S, 16.06.

S-Methylthioammeline[13,14] was similarly prepared from the sodium salt of thioammeline and dimethyl sulfate in 94% yield. It was soluble in hot ethylene glycol monoethyl ether and hot 1:1 aqueous ethylene glycol monoethyl ether (1 g./40 ml.), slightly soluble in hot water, methanol, ethanol, acetone and acetonitrile, and insoluble in hot benzene, diethyl ether, hexane and chloroform; m.p. 270–272° dec.; sharp infrared absorption at 812 cm.$^{-1}$.

Anal. Calcd. for $C_4H_7N_5S$: N, 44.56. Found: N, 44.04 (by Kjeldahl method); N, 44.92, 45.11 (by pressure Kjeldahl method); use of the Dumas method consistently gave low values for nitrogen.

S-Methallylthioammeline[15] was prepared from the sodium salt of thioammeline and methallyl chloride, in 92% yield. It was soluble in hot acetone, diethyl ether, methanol, ethanol (1 g./3 ml.) and acetonitrile (1 g./25 ml.), slightly soluble in hot benzene and hexane, and insoluble in hot water, m.p. 132–132.5°; sharp infrared band at 808 cm.$^{-1}$.

Anal. Calcd. for $C_7H_{11}N_5S$: C, 42.62; H, 5.62; N, 35.51; S, 16.25. Found: C, 42.73; H, 5.66; N, 35.21; S, 16.03.

S-Benzylthioammeline, prepared in 93% yield from thioammeline and benzyl chloride by the reported procedure,[14] was soluble in hot acetone, methanol and ethanol (1 g./15 ml.), slightly soluble in hot acetonitrile, and insoluble in hot benzene and hexane; m.p. 171–172°; sharp infrared band at 805 cm.$^{-1}$.

Acknowledgments.—We express our thanks to Elspeth C. Eberlin, N. Colthup, R. C. Gore and J. E. Lancaster for their assistance in determining and interpreting the infrared spectra of these compounds, to R. C. Hirt and R. G. Schmitt for their similar assistance with the ultraviolet spectra, and to Elizabeth C. Grim and Patricia Lentz for analytical assistance.

STAMFORD, CONN.

[CONTRIBUTION NO. 1042 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Chemistry of Pyrazine and Its Derivatives. III. The Synthesis of Carbinols by the Participation of Methylpyrazine in Aldol-type Condensations[1]

BY JOHN D. BEHUN[2] AND ROBERT LEVINE

RECEIVED APRIL 3, 1959

Several aldehydes and ketones have been condensed with pyrazylmethylsodium to give the corresponding pyrazylmethylcarbinols, $PzCH_2C(OH)RR^1$, in fair to excellent yields. Diphenylpyrazylmethylcarbinol was reductively cleaved with ethanolic potassium hydroxide to give methylpyrazine and benzhydrol while its reaction with potassium hydroxide in *t*-butyl alcohol gave methylpyrazine and benzophenone. Benzophenone was also reduced to benzhydrol (90.8%) by ethanolic potassium hydroxide. 1-Pyrazyl-2-phenyl-2-propanol, on reaction with ethanolic potassium hydroxide, was converted to a mixture of methylpyrazine, acetophenone, methylphenylcarbinol (A) and 1,5-diphenyl-3-methylpentane-1,5-dione (B). A mixture of A and B also was obtained when acetophenone was treated similarly.

In the previous paper[3] of this series, we reported that high yields of pyrazyl methyl ketones, $PzCH_2COR$, were obtained by the interaction of a series of aliphatic, aromatic and heterocyclic esters with pyrazylmethylsodium, which was prepared from methylpyrazine and sodium amide in liquid ammonia. The present paper is concerned with the results of a study involving aldol-type reactions between methylpyrazine and several aldehydes and ketones to give a series of carbinols containing the pyrazylmethyl radical.

Prior to our study, aldol-type condensations had been effected between a few aldehydes and ketones and methylpyrazine and 2,5-dimethylpyrazine. Thus, Franke[4] treated 2,5-dimethylpyrazine with several aromatic aldehydes in a bomb at 160–200° for eight hours using zinc chloride as the catalyst. Under these conditions, mono- and disubstituted olefinic products, which resulted from the dehydration of the initially-formed carbinols, were obtained in unreported yields. Also, Kitchen and Hanson[5] obtained a 38% yield of 2-pyrazylethanol by heating methylpyrazine with paraformaldehyde in a stainless steel autoclave for 4.5 hours at 165°. In addition Klein and Spoerri[6] found that the reaction of 2,5-dimethylpyrazine with methyllithium followed by the addition of propionaldehyde gave none of the expected carbinol and instead a 44% yield of the azomethine addition product, 2,3,6-trimethylpyrazine, was obtained. Furthermore, during the course of the present investigation, Zaugg, DeNet and Freifelder[7] reported the synthesis of diphenylpyrazylmethylcarbinol from methylpyrazine and benzophenone using sodium amide as the condensing agent. However, the reaction conditions employed were considerably different from those

(1) This work was performed under Contract No. AT(30-1)-670 between the U. S. Atomic Energy Commission and the University of Pittsburgh.

(2) This paper is based on part of the thesis presented by J. D. B. to the Graduate Faculty of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree.

(3) J. D. Behun and R. Levine, THIS JOURNAL, **81**, 5157 (1959).

(4) R. Franke, *Ber.*, **38**, 3724 (1905).

(5) L. J. Kitchen and E. S. Hanson, THIS JOURNAL, **73**, 1938 (1951).

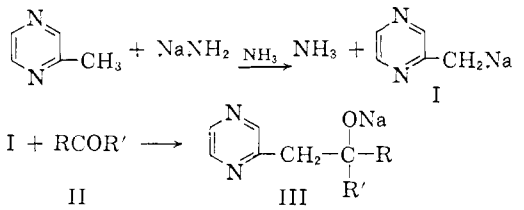
(6) B. Klein and P. E. Spoerri, *ibid.*, **73**, 2949 (1951).

(7) H. E. Zaugg, R. W. DeNet and M. Freifelder, *ibid.*, **80**, 2773 (1958).

which were used in the present study and a much lower yield (23%) was obtained by these workers than was obtained (98.6%) in the present investigation.

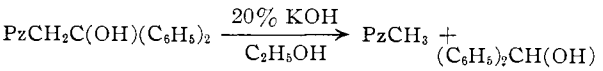
As in the acylation of methylpyrazine,[3] the condensation of methylpyrazine with aldehydes and ketones proceeded very readily, when sodium amide in liquid ammonia was used as the condensing agent, to give the corresponding secondary and tertiary alcohols which are listed in Table I.

With the exception of the reaction with isobutyraldehyde, which gave only a 21.0% yield of isopropylpyrazylmethylcarbinol, good to excellent yields (53.7–98.6%) of the alcohols were obtained. A 2:2:1 molar ratio of methylpyrazine:sodium amide:carbonyl compound was used in effecting all the reactions which appear in Table I. Thus, while a 2:2:1 molar ratio of reactants, using benzaldehyde as the carbonyl compound, gave a 67.0% yield of 1-phenyl-2-pyrazylethanol, the yield dropped to 43.0% when a 1:1:1 molar ratio of reactants was employed. The course of these condensations is believed to involve the addition of pyrazylmethylsodium across the carbonyl group of the aldehyde or ketone as shown in the following scheme. Although it appears probable that the excess pyrazylmethylsodium (I) increases the yields of the products by the operation of a mass action effect, there is the possibility that some of I may react with III to convert it to its disodium derivative by metalating the methylene group and thus additional I would be required for this purpose.



Next, the structures of three representative carbinols were elucidated. That the compound obtained from the reaction of pyrazylmethylsodium with benzaldehyde is indeed 1-phenyl-2-pyrazylethanol was shown by a modified Oppenauer oxidation to the known phenacylpyrazine.[3]

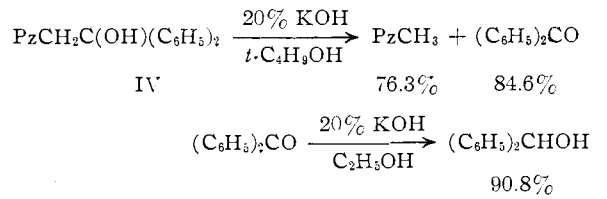
Somewhat unanticipated results were obtained when diphenylpyrazylmethylcarbinol (IV) was treated with ethanolic potassium hydroxide in an attempt to reverse the aldol-type reaction by which it was formed. From this reaction, a mixture of methylpyrazine (88.5%) and benzhydrol (93.2%, V) rather then the expected benzophenone was isolated. Apparently reductive cleavage rather



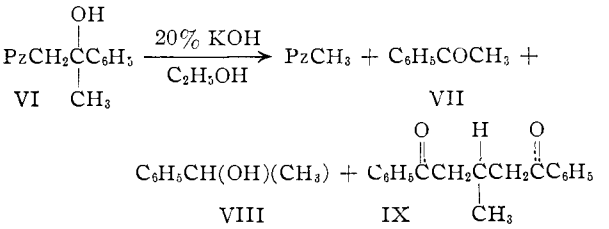
Pz = pyrazyl radical

than simple cleavage of IV occurred. The reductive cleavage apparently results from a Meerwein–Ponndorf–Verley type reaction in which the ethanol serves as a hydrogen donor and reduces the initially-formed benzophenone.

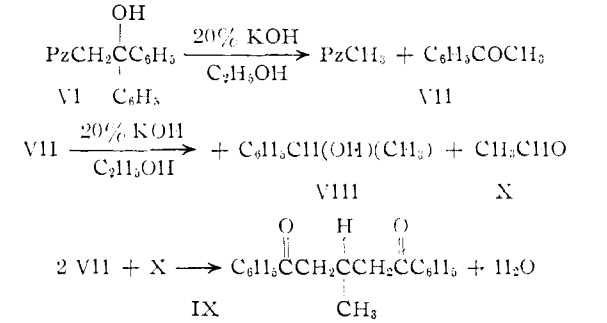
In support of this argument, two experiments were performed. It was found that when IV was treated with potassium hydroxide in *t*-butyl alcohol (which cannot function as a hydrogen donor) a mixture of methylpyrazine (76.3%) and benzophenone (84.6%) was obtained. In addition, it was found that benzophenone can be reduced in 90.8% yield to benzhydrol on treatment with ethanolic potassium hydroxide. This last reaction has been effected previously[8] in unreported yield. The over-all reactions involved are



When 1-pyrazyl-2-phenyl-2-propanol (VI) (the product obtained from the reaction of acetophenone with methylpyrazine) was cleaved with ethanolic potassium hydroxide, four compounds were isolated: methylpyrazine, acetophenone (VII), methylphenylcarbinol (VIII) and 1,5-diphenyl-3-methylpentane-1,5-dione (IX).



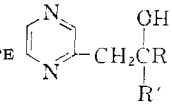
It is apparent that the methylpyrazine and acetophenone (VII) are formed by the normal cleavage of VI. The methylphenylcarbinol (VIII) apparently is formed by the reduction of part of the acetophenone (VII) with ethanol functioning as the hydrogen donor. Finally, the diketone (IX) appears to arise by a loss of one molecule of water between two molecules of VII and one of acetaldehyde, which would be formed in the reduction of acetophenone by the ethanolic potassium hydroxide. The over-all reactions are



In support of this scheme it has been found that the reaction of acetophenone with alcoholic potassium hydroxide solution gives a mixture of recovered acetophenone, methylphenylcarbinol (VIII) and the diketone (IX).

(8) M. P. J. Montagne, *Rec. trav. chim.*, **27**, 334 (1908).

TABLE I

CARBINOLS OF THE TYPE 

R	R′	Yield, %	M.p. or b.p. °C.	Mm.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
i-C_3H_7	H	21.0	111.0–112.0	2.5	$C_9H_{14}N_2O$	65.03	65.13	8.49	8.15
C_6H_5	H	67.0	88.2–88.8[a]		$C_{12}H_{12}N_2O$	71.98	72.22	6.04	6.00
CH_3	C_2H_5	66.8	117.0–118.0	5.5	$C_9H_{14}N_2O$	65.03	65.46	8.49	8.19
CH_3	*i*-C_3H_7	55.3	121.0–123.0	5	$C_{10}H_{16}N_2O$	66.62	66.98	8.95	8.84
C_6H_5	CH_3	54.2	159.0–161.0	3					
			59.5–60.2[a]		$C_{13}H_{14}N_2O$	72.88	72.52	6.29	6.56
C_6H_5	C_2H_5	53.7	142.0–143.0	2	$C_{14}H_{16}N_2O$	73.65	73.48	7.05	6.96
C_6H_5	C_6H_5	98.6	148.0–148.8[b,c]		$C_{18}H_{16}N_2O$	78.24	77.87	5.84	5.61
Cyclohexanone		66.0	152.0–155.0	9					
			84.6–85.2[a]		$C_{11}H_{17}N_2O$	68.34	68.22	8.87	8.46

[a] Recrystallized from 60–70° petroleum ether. [b] Recrystallized from methanol. [c] See ref. 7.

Experimental[9]

1. **Synthesis of 1-Phenyl-2-pyrazylethanol.**—Methylpyrazine (0.4 mole, 37.6 g.) was added to sodium amide (0.4 mole), prepared from 0.4 mole (9.2 g.) of sodium) in 250–300 ml. of anhydrous liquid ammonia and the mixture was stirred for 0.5 hour. Then, benzaldehyde (0.2 mole, 21.2 g.) dissolved in an equal volume of anhydrous ether was added. The mixture was stirred for one hour and then the reaction was quenched by the addition of 25.0 g. of solid ammonium chloride. The liquid ammonia was replaced by 200 ml. of ether and then the mixture was poured onto 100 g. of ice and neutralized with concentrated hydrochloric acid. The white solid (20.1 g. of 1-phenyl-2-pyrazylethanol) which was present was filtered and the filtrate was made strongly acidic with concentrated hydrochloric acid and was extracted with several portions of ether. The remaining aqueous solution was made strongly basic with aqueous sodium hydroxide solution and was extracted with several portions of chloroform. Additional quantities of carbinol, 4.4 and 2.3 g., respectively, were obtained from the ether and chloroform extracts. The total yield of carbinol was 26.8 g. (67.0%), m.p. 88.2–88.8° (from 60–70° petroleum ether). There were also recovered 3.2 g. of benzaldehyde, b.p. 70–75° at 20 mm., from the ether extracts and 14.9 g. of methylpyrazine, b.p. 70–75° at 100 mm., from the chloroform extracts. The other carbinols in Table I were prepared similarly.

2. **Oppenauer Oxidation of 1-Phenyl-2-pyrazylethanol.**—The method employed was similar to that used by Woodward, *et al.*,[10] for the oxidation of quinine to quinonine.

A mixture of 1-phenyl-2-pyrazylethanol (0.04 mole, 8.0 g.), benzophenone (0.2 mole, 35.0 g.) and potassium *t*-butoxide (0.1 mole, 11.2 g.) was suspended in 200 ml. of benzene and was refluxed for 22 hours. The reaction mixture was cooled to room temperature, was poured onto ice and was made acidic with concentrated hydrochloric acid. The crude phenacylpyrazine (1.4 g., 17.7%) which precipitated was filtered and was identified as its 2,4-dinitrophenylhydrazone, m.p. 180.0–182.5° alone and when mixed the 2,4-dinitrophenylhydrazone of an authentic sample of phenacylpyrazine.[3]

3. **Reductive Cleavage of Diphenylpyrazylmethylcarbinol by Ethanolic Potassium Hydroxide.**—Diphenylpyrazylmethylcarbinol (0.036 mole, 10.0 g.) in 200 ml. of 20% ethanolic potassium hydroxide (95% ethanol) was refluxed for two hours. The mixture was poured onto ice and was extracted with chloroform. Distillation of the chloroform extracts gave 3.0 g. (88.5%) of methylpyrazine, b.p. 75–76° at 100 mm. (picrate, m.p. 126.5–127.5° alone and when mixed with an authentic sample), and 6.2 g. (93.2%) of benzhydrol, b.p. 139–143° at 3.5 mm. and m.p. 67.0–68.0 (from 60–70° petroleum ether) alone and when mixed with an authentic sample.

4. **Reduction of Benzophenone with Ethanolic Potassium Hydroxide.**—Benzophenone (0.05 mole, 9.1 g.) in 225 ml. of 20% ethanolic potassium hydroxide was refluxed for two hours and the mixture was processed as described in the last experiment to give 8.3 g. (90.8%) of benzhydrol, m.p. 67.5–68.5° alone and when mixed with an authentic sample.

5. **Cleavage of Diphenylpyrazylmethylcarbinol by Potassium Hydroxide in *t*-Butyl Alcohol.**—Diphenylpyrazylmethylcarbinol (0.018 mole, 5.0 g.), *t*-butyl alcohol (100 ml.), potassium hydroxide (20.0 g.) and water (5.0 ml.) was refluxed for two hours and was processed as described in experiment 3 to give 1.3 g. (76.3%) of methylpyrazine, b.p. 75–76° at 100 mm. (picrate, m.p. 126.5–127.5° alone and when mixed with an authentic sample), and 2.8 g. (84.6%) of benzophenone, b.p. 128–130° at 3.5 mm., m.p. 48.0–48.6° (from 60–70° petroleum ether) alone and when mixed with an authentic sample.

6. **Cleavage of 1-Pyrazyl-2-phenyl-2-propanol with Ethanolic Potassium Hydroxide.**—1-Pyrazyl-2-phenyl-2-propanol (0.032 mole, 6.8 g.) was added to 100 ml. of 20% ethanolic potassium hydroxide and the resulting solution was refluxed for two hours. The mixture then was processed as described in experiment 3 to give 3.8 g. (99.5%) of methylpyrazine, b.p. 75–78° at 100 mm.; 2.8 g. of a mixture of acetophenone and methylphenylcarbinol, b.p. 130–135° at 98 mm. (see experiment 7) and 0.8 g. (19.0%) of 1,5-diphenyl-3-methylpentane-1,5-dione, b.p. 190–200° at 2.5 mm., m.p. 71–72° (from an ether–60–70° petroleum ether mixture, see experiment 7).

7. **Reaction of Acetophenone with Ethanolic Potassium Hydroxide.**—Acetophenone (0.1 mole, 12.0 g.) was added to 200 ml. of 20% ethanolic potassium hydroxide solution and the mixture was refluxed for two hours. The reaction mixture then was poured onto ice, was salted out with sodium chloride and was extracted with several portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate and the solvent was removed at atmospheric pressure. Distillation of the residue in vacuum gave 4.9 g. of material (fraction A), b.p. 130–135° at 2.5 mm., and 5.8 g. (39%) of material (fraction B), b.p. 190–200° at 2.5 mm., m.p. 71–72° (from an ether–60–70° petroleum ether mixture) alone and when mixed with the material which was obtained in experiment 6.

Fraction A was chromatographed on a column filled with Merck acid-treated alumina which was moistened with 30–60° petroleum ether. By eluting with 30–60° petroleum ether, containing up to 20% benzene, 3.4 g. of acetophenone was isolated. Further elution with a 30% ethyl ether solution in benzene gave 1.5 g. of methylphenylcarbinol. The infrared spectra of the ketone and carbinol were identical with those of authentic samples. The infrared spectrum of fraction B and that of the material of the same boiling point and melting point which was obtained in experiment 6 are identical. The spectrum of fraction B has the following bands: (a) 1680 cm.$^{-1}$, which is characteristic of phenyl ketones,[11] (b) 1375 cm.$^{-1}$, which is characteristic of the methyl group,[12] and (c) 1410 cm.$^{-1}$, which is characteristic

(9) The methylpyrazine used in this investigation was supplied through the courtesy of Wyandotte Chemicals Corporation.

(10) R. B. Woodward, N. L. Wendler and J. F. Brutschy, THIS JOURNAL, **67**, 1428 (1945).

(11) L. J. Bellamy, "Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 114.

(12) See ref. 11, p. 13.

of the $-CH_2CO-$group.[13,14] The spectral data and the elemental analysis of fraction B indicate that the compound is 1,5-diphenyl-3-methylpentane-1,5-dione. *Anal.* Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.33; H, 6.88. The diketone gave a dioxime, m.p. 177–178° (from an ethanol–water mixture). *Anal.* Calcd. for $C_{18}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.46. Found: C, 73.06; H, 6.89; N, 9.42.

PITTSBURGH 13, PENNA.

(13) N. B. Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950).
(14) S. J. Francis, *J. Chem. Phys.*, **19**, 942 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Azulene. IX. Synthesis of Some Derivatives of 1-Azulenethiol and 1,3-Azulenedithiol[1-3]

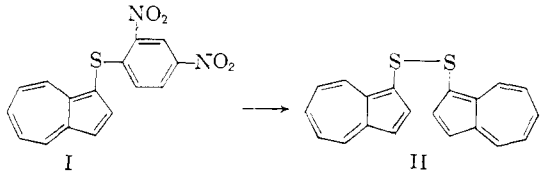
BY ARTHUR G. ANDERSON, JR., AND RICHARD N. MCDONALD

RECEIVED APRIL 24, 1959

Azulene has been found to react with 2,4-dinitrobenzenesulfenyl chloride and with thiocyanogen in the absence of catalysts. From the substitution products obtained a number of new derivatives of 1-azulenethiol and 1,3-azulenedithiol have been synthesized. Efforts to prepare the unsubstituted thiol compounds were unsuccessful.

The literature on the chemistry of azulenes includes only one report of the attachment of a sulfur atom to the aromatic nucleus. Treibs and Schroth[4] accomplished the sulfonation of guaiazulene with dioxane–sulfur trioxide and conversion of the sulfonic acid to the corresponding acid chloride and amide. The present investigation was directed initially toward the synthesis of 1-azulenethiol and 1,3-azulenedithiol. The isolation of these compounds has not been achieved but a number of derivatives of them have been prepared.

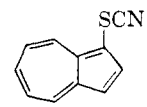
Buess and Kharasch[5] have described the preparation of thiophenols through electrophilic substitution with 2,4-dinitrobenzenesulfenyl chloride and cleavage of the aryl 2,4-dinitrophenyl sulfide with alkali. Treatment of azulene with the sulfenyl chloride in the presence of aluminum chloride or stannic chloride gave only a low yield of the desired product I. It was apparent that the complexes formed by azulene and the Lewis acid catalysts were quite insoluble in the reaction mixture. Kharasch and co-workers[5,6] had found that activated benzene systems (dialkylanilines) required no catalyst. When the sulfenyl chloride and azulene were brought together in a dichloromethane solution a spontaneous reaction began at once and an 82% yield of 2,4-dinitrophenyl azulyl sulfide (I) resulted. Treatment of this product with methanolic alkali afforded a low yield of di-1-azulyl disulfide (II) but none of the desired 1-azulenethiol. All attempts to prepare the latter from I failed.



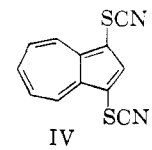
I II

Reductive cleavage of II represented another possible route to 1-azulenethiol and the preparation of the former from azulene and sulfur monochloride was tried. The reaction was run with excess azulene to minimize polymeric disulfide formation, but only gummy mixtures were obtained. The single pure substance isolated after treatment of the gummy product with lithium aluminum hydride was not a thiol and was not identified. A 1-substituted azulene would not be expected to form polymeric products. Reaction of 1-nitroazulene with sulfur monochloride and aluminum chloride gave a dark red substance thought to be bis-(3-nitroazulyl) disulfide which was not obtained analytically pure, a smaller quantity of a product identical with 1-nitro-3-chloroazulene prepared by the chlorination of 1-nitroazulene with N-chlorosuccinimide, and a small amount of a rather unexpected product, 1,3-dinitroazulene. The difficulty in the purification of the main product led to the examination of other reactions for the introduction of a sulfur atom onto the azulene nucleus.

The use of thiocyanogen to form aromatic thiocyanates has been described by Wood and Fieser,[7] and by Brewster and Schroeder.[8] Reaction of equimolar amounts of azulene and thiocyanogen at 0–5° gave a 93.5% net yield of 1-thiocyanoazulene (III). The same proportions at room temperature gave a mixture of III (45%) and 43% of 1,3-dithiocyanoazulene (IV). When two equivalents of thiocyanogen were used at 0–5°, 23% of III and 77% of IV were formed. The infrared spectrum of III showed a sharp peak at 4.65 μ. Miller,[9] reports a value of 4.63 μ for the thiocyano group.



III



IV

(1) From the Ph.D. thesis of Richard N. McDonald, University of Washington, 1957.
(2) Support for a part of this work by contracts DA-04-200-ORD-235 and DA-04-200-ORD-601 with the Office of Ordnance Research, U. S. Army, is gratefully acknowledged.
(3) Presented in part at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.
(4) W. Treibs and W. Schroth, *Ann.*, **586**, 202 (1954).
(5) C. M. Buess and N. Kharasch, THIS JOURNAL, **72**, 3529 (1950).
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(7) J. L. Wood and L. F. Fieser, *ibid.*, **63**, 2323 (1941).
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