trated. The residual yellow oil was dissolved in ethanol, a solution of 37 g of maleic acid in ethanol was added, and on addition of ether a crystalline crop of a maleate was obtained which after recrystallization from a mixture of methanol and ether gave 43 g of white prisms. This product was suspended in an ice-cold aqueous solution of potassium carbonate. Extraction with methylene chloride gave a product which after recrystallization from a mixture of benzene and petroleum ether yielded 20.1 g (17%) of white needles melting at 130–132°: uv max (2-propanol) 223 m$\mu$ ($\epsilon$ 9300), infl 245 (4500), shoulder 278 (1300); ir ($CHCl_3$) 1700 cm$^{-1}$ (C=O).

*Anal.* Calcd for $C_{10}H_{10}N_2O$: C, 68.95; H, 5.79; N, 16.08. Found: C, 69.17; H, 5.76; N, 15.99.

**2,3-Dihydro-5H-imidazo[2,1-*a*]isoindol-5-one (XI).**—From a solution of 17.4 g (0.1 mol) of X in 350 ml of benzene 25 ml of solvent was removed by distillation. After cooling 25 g (0.14 mol) of diethylazodicarboxylate was added and the solution was refluxed for 65 hr. The mixture was chilled and the hydrazo ester was removed by filtration. The orange filtrate was concentrated *in vacuo* and the residue was recrystallized from a mixture of tetrahydrofuran and petroleum ether to give 10.6 g (62%) of white needles melting at 139–141°: uv max (2-propanol) 215 m$\mu$ ($\epsilon$ 37,000), 218 (36,900), 252 (12,500), 303 (4300), [infl 246 (11,500), 260 (9500); ir ($CHCl_3$) 1670 (C=N) and 1725 cm$^{-1}$ (C=O).

*Anal.* Calcd for $C_{10}H_8N_2O$: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.49; H, 4.54; N, 15.98.

**2,3-Dihydro-5-methoxy-5-phenyl-5H-imidazo[2,1-*a*]isoindole Hydrochloride (XII·HCl).**—A solution of 5 g of IX hydrochloride in 50 ml of methanol was refluxed for 18 hr. The solution was concentrated *in vacuo* dissolved in 20 ml of methanol and 60 ml of ether was added. Crystals (0.5 g) precipitated and were identified as starting material. The mother liquor was concentrated and the residue was recrystallized from a mixture of methanol, methylene chloride and ether to give 3.1 g (59%) of white prisms melting at 139–141° dec: uv max (2-propanol) 244 m$\mu$ ($\epsilon$ 14,400), 278 (5100); ir (KBr) 1670 cm$^{-1}$ (C=N).

*Anal.* Calcd for $C_{17}H_{16}N_2O \cdot HCl$: C, 67.83; H, 5.70; $OCH_3$, 10.32. Found: C, 67.84; H, 5.63; $OCH_3$, 10.44.

The corresponding base was obtained as a colorless oil on treatment with alkali: uv infl (0.1 *N* KOH) 230 m$\mu$ ($\epsilon$ 14,600), 290 (2700), max 269 (4200), 275 (4600); ir (smear) 1660 cm$^{-1}$ (C=N); nmr ($CDCl_3$) $\delta$ 3.12 (s, 3, $OCH_3$), 2.6–3.5 (m, 2, —N—$CH_2$), 4.2–4.5 (m, 2, =N—$CH_2$), 7.1–8.0 (m, 9).

**Hydrolysis of XII·HCl to IX.**—A solution of 0.2 g of XII·HCl in 10 ml of water was kept at 25° for 48 hr. The solution was basified with 2 *N* aqueous sodium hydroxide and the precipitate (0.14 g, 84%) was collected and identified as IX.

**2-(2-Aminoethyl)-3-hydroxy-4-phenylphthalimidine (XIII).**—A solution of 0.5 g of IX in 50 ml of tetrahydrofuran, 10 ml of methanol and 5 ml of aqueous 2 *N* sodium hydroxide was refluxed for 48 hr. The yellow solution was concentrated, diluted with water, and extracted with methylene chloride. The extract was dried and concentrated to give 0.35 g (65%) of white prisms which after washing with ether melted at 172–176° (lit.[4b] mp 175–176°).

**Registry No.**—II, 16780-82-8; IV·$H_2SO_4$, 16780-83-9; V·$H_2SO_4$, 16780-84-0; V·HCl, 16780-85-1; VI, 16780-86-2; VI·HCl, 16780-87-3; VII, 16780-98-6; VIII, 16780-97-5; IXa, 16780-88-4; IXa·HCl, 16780-89-5; IXa·HBr, 16797-48-1; IXb, 16780-90-8; IXb·HCl, 16780-91-9; IXb·HBr, 16780-92-0; X, 16780-93-1; XI, 16780-94-2; XII, 16780-95-3; XII·HCl, 16780-96-4.

**Acknowledgment.**—We are indebted to Mr. S. Traiman, Dr. F. Vane, and Dr. T. Williams for spectroscopic data and interpretations and to Dr. Al Steyermark and Dr. F. Scheidel for microanalytical data. We wish to thank Professor G. Büchi for valuable advice and stimulating discussions.

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# The Reaction of Active Methylene Compounds with Carbon Disulfide in the Presence of Ammonia. II. The Reaction of Acetone and Methyl Ethyl Ketone

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The title reaction was extended to acetone and methyl ethyl ketone as the active methylene compound. Acetone, in the presence of ammonia, reacted with carbon disulfide to give a series of thiazine and diazine compounds. The most stable compound obtained was 3,4-dihydro-4,4,6-trimethyl-2(1H)-pyrimidinethione (V). Methyl ethyl ketone yielded 2-ethyldihydro-2,5,6-trimethyl-4H-3,1-thiazine-4-thione (X) and 4-ethyl-3,4-dihydro-4,5,6-trimethyl-2(1H)-pyrimidinethione (XI). A dithiole (XII) also was isolated from the reaction products of methyl ethyl ketone. The structures of these new compounds were proposed. The interrelation of a series of compounds which were obtained from the reaction product of acetone was described.

In previous research,[2] it was found that cyclohexanone, in the presence of ammonia and treated with carbon disulfide, gives 4(1H)-thiono-5,6,7,8-tetrahydro-2H-3,1-benzothiazine-2-spirocyclohexane and the related compounds. The reaction has now been extended to acetone and methyl ethyl ketone as the active methylene compound.

First, it was found that acetone, in contrast with cyclohexanone, did not give the corresponding thiazine derivative. Instead, a series of thiazine and diazine compounds of a different type was isolated. For example, when a mixture of acetone, carbon disulfide, and aqueous ammonia was shaken at room temperature for 20 hr, 6-hydroxy-4,4,6-trimethyltetrahydro-2H-1,3-thiazine-2-thione (I), 6-amino-4,4,6-trimethyltetrahydro-2H-1,3-thiazine-2-thione (II), 6-amino-4,4,6-trimethyltetrahydro-2(1H)-pyrimidinethione (III), and 3,4-dihydro-4,4,6-trimethyl-2(1H)-pyrimidinethione (V) were isolated from the reaction mixture.

Among these compounds, V was the most stable and thus could be most easily obtained from the reaction mixture. Compound I proved to be identical with the compound which was synthesized by Jansen and Mathes[3] from diacetonamine and carbon disulfide or from 2-methyl-2-isothiocyano-4-pentanone and dithiocarbamic acid. Compound II also was obtained from the reaction of diacetone alcohol or mesityl oxide.

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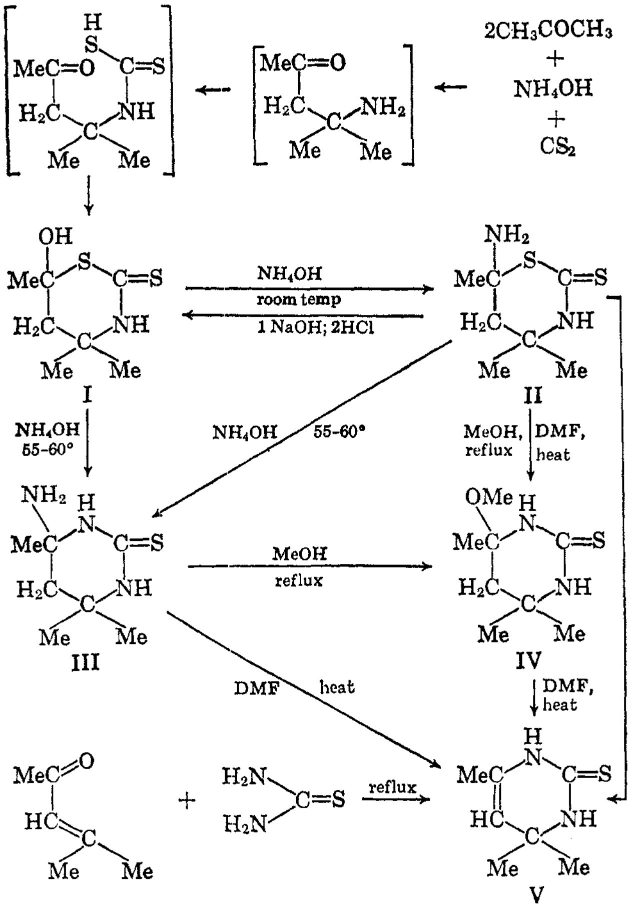
[2] T. Takeskima, T. Hayashi, M. Muraoka, and T. Matsuoka, *J. Org. Chem.*, **32**, 980 (1967).

[3] J. E. Jansen and R. A. Mathes, *J. Amer. Chem. Soc.*, **77**, 5431 (1955).

Interconversion of these compounds are as described in Scheme I (see Experimental Section).

SCHEME I

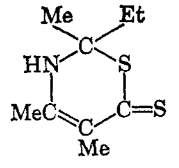


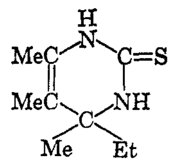
The structure of V was inferred from the following facts. (1) The reaction of mesityl oxide with thiourea gave the compound. (2) It was obtained from I by way of different routes (Scheme I). (3) Upon degradation with hydrochloric acid the compound afforded acetone. (4) Agreement of infrared, ultraviolet, and nmr spectra, the elemental analysis, and the molecular weight measurement. All agreed with the structure formulated for V (consult Experimental Section). The structure of II, III, and IV (see Experimental Section) were inferred from the interrelation between I, II, III, IV, and V, and the absorption spectra.

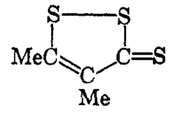
It is of interest that, when I and 6-hydroxy-4,4,6-trimethyltetrahydro-2H-3,1-thiazine-2-thione (VI) were treated with hot morpholine, elimination of the dithiocarboxyl group occurred to give morpholinium morpholine-N-dithiocarboxylate (IX),[4] which is now fully characterized (see Experimental Section).

Second, it was found that methyl ethyl ketone reacted in two ways. When the reaction was conducted below 0°, the main product was 2-ethyldihydro-2,5,6-trimethyl-4H-3,1-thiazine-4-thione (X, the pattern of cyclohexanone); when it was run at or above room temperature (*ca.* 25°), the main product was 4-ethyl-3,4-dihydro-4,5,6-trimethyl-2(1H)-pyrimidinethione (XI, the pattern of acetone). In addition, when the reaction was carried out below 0°, a small amount of 4,5-dimethyl-1,2-dithiole-3-thione (XII) could be isolated. This compound was more readily prepared by adding hydrogen sulfide to the reaction mixture (see Experimental Section).

The structures of X, XI, and XII were inferred mainly from the infrared and ultraviolet spectra. The features of infrared and ultraviolet spectra of X was quite identical with those of 4(1H)-thiono-5,6,7,8-tetrahydro-2H-3,1-benzothiazine-2-spirocyclohexane.[2] Likewise, the spectrum of XI was similar to that of V. The features of the ultraviolet spectrum of XII were identical with those of 5-phenyl-1,2-dithiole-3-thione.[5]


X


XI


XII

## Experimental Section

**6-Hydroxy-4,4,6-trimethyltetrahydro-2H-1,3-thiazine-2-thione (I).**—To a mixture of acetone (58 g, 1 mol) and carbon disulfide (152 g, 2 mol) was gently passed dry ammonia gas for *ca.* 30 hr with shaking at room temperature (*ca.* 17°), and the mixture was allowed to stand overnight. Water (50 ml) was added to this reaction mixture to dissolve ammonium dithiocarbamate produced. The solid product was collected, washed with water, and dried: yield 32 g (34%). The crude crop (I) was recrystallized from acetone or methanol or DMF. The recrystallization also was effected by adding twice the volume of water to a saturated solution of the crude substance in pyridine: colorless prisms (20 g); mp 114–115° dec (slow heating) and 122–126° dec (rapid heating); the compound produced yellowish green or light green coloration toward Grote reagent;[6] uv max (99% EtOH) 241 mμ (log ε 3.85), 286 (4.11); ir (KBr) 3350 (m), 3174 (m), 1536 (s), 1012 (s), 958 cm$^{-1}$ (s).

*Anal.* Calcd for $C_7H_{13}NOS_2$: C, 43.94; H, 6.85; N, 7.32; S, 33.52; mol wt (vapor pressure osmometer), 191.3. Found: C, 44.35; H, 6.82; N, 7.39; S, 33.08; mol wt, 214 (in acetone).

The melting point and the infrared spectrum of this compound were in good agreement with the ones reported by Jansen and Mathes[3] (reported mp 114° dec).

**Conversion of 6-Amino-4,4,6-trimethyltetrahydro-2H-1,3-thiazine-2-thione (II) into I.**—Compound II (1 g), which is described below, was dissolved in 6 *N* aqueous sodium hydroxide and kept for 10 hr. The solution was acidified by adding 7 ml of 6 *N* hydrochloric acid while cooling with ice. The white precipitate produced was collected, washed with water, dried, and recrystallized as above: yield 0.86 g. The substance was identified with I by mixture melting point and infrared and ultraviolet spectra.

In accordance with Jansen and Mathes,[3] I upon treatment with 70% sulfuric acid at 85° was dehydrated to give VII, mp 121–122°.

Compound I (3.5 g) was dissolved in 10 ml of 14% aqueous sodium hydroxide and kept for several hours at *ca.* 25°, and then made acidic with 2 *N* hydrochloric acid. The original compound could be nearly quantitatively recovered. The compound thus seemed to be considerably stable toward caustic alkali. Compound I was indifferent toward sodium nitroprusside.

**6-Amino-4,4,6-trimethyltetrahydro-2H-1,3-thiazine-2-thione (II).**—A mixture of acetone (20.3 g, 0.35 mol), carbon disulfide (100 g, 1.3 mol), and 73 ml of aqueous ammonia (28%) was reacted in a manner similar to that described.[2] The yellow needles produced were collected, washed with water and ether, and dried to yield 14 g (42%).

The crude crop was dissolved in a minimal amount of cold DMF until saturation. To this was added an equal volume of water, and the crystals which separated were collected: yield 9.5 g. Recrystallization also was carried out from ethanol or,

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[4] Refer to the paper (p 980) cited in ref 2.

[5] H. Behringer and D. Deichmann, *Tetrahedron Lett.*, No. 11, 1013 (1967).

[6] The color was observed within several minutes after the reagent was applied. It was used merely for reference purpose (test for SH, CS, and CSSH).

better, from acetone below 55°; higher temperature caused partial conversion of II into V and another substance. The compound formed colorless prisms: mp 146–147° dec (slow heating) and 150–157° dec (rapid heating); Grote test, light green tinged with ochre; uv max (99% EtOH) 245 m$\mu$ (log $\epsilon$ 3.81), 289 (4.11); ir (KBr) 3372 (m), 3300 (m), 3150 (s), 1620 (m), 1524 (s), 1008 (s), 964 cm$^{-1}$ (s); ir ($CHCl_3$) 3400 (w), 3340 (s), 3150 (m), 1620 (m), 1485 (s), 1004 (s), 965 cm$^{-1}$ (s).

*Anal.* Calcd for $C_7H_{14}N_2S_2$: C, 44.17; H, 7.42; N, 14.72; S, 33.69; mol wt (vapor pressure osmometer), 190.3. Found: C, 44.22; H, 7.23; N, 14.37; S, 33.59; mol wt, 187 (in acetone).

**Conversion of I into II.**—A suspension of I (7 g, 0.037 mol) in 15 ml of aqueous ammonia (28%) was shaken at room temperature for 8 hr. The crystals (needles) which separated were collected, washed with water, and dried to yield 4.1 g (59%). Recrystallization gave colorless prisms (*ca.* 3 g) which agreed with II in all respects.

The hydrochloride of II was prepared as follows. Compound II (1 g) was dissolved in 5 ml of 6 *N* hydrochloric acid. The white precipitate produced was collected and recrystallized from aqueous acetone to give colorless crystals, melting above 250°.

*Anal.* Calcd for $C_7H_{15}N_2S_2Cl$: C, 37.07; H, 6.67; N, 12.35; Cl, 15.63. Found: C, 36.68; H, 6.31; N, 12.31; Cl, 15.41.

Upon refluxing in ethanol or recrystallization from acetic acid or DMF, II was converted into V.

Upon treatment with aqueous ammonia (28%) at room temperature for 3 to 4 days or at 55° for 1 hr, II was converted into III.

Compound II, added to ammoniacal sodium nitroprusside, produced at first yellow coloration and the whole then gradually turned pink-purple.

When refluxed with methanol II yield IV in addition to V (see below). A saturated solution of II in methanol on standing at room temperature for 3 to 4 days afforded IV.

Treatment of II with sodium methoxide in methanol at room temperature likewise gave IV and V.

**6-Amino-4,4,6-trimethyltetrahydro-2(1H)-pyrimidinethione (III).**—A solution of I (15 g) in 150 ml of aqueous ammonia (28%) was warmed at 55–60° for 1 hr. Colorless prisms separated from the solution. After the mixture cooled, the crystals were collected, washed with 10% aqueous ammonia, and dried: yield 9.8 g (72%). The compound (III) formed colorless prisms, mp 256–258° dec and 251–252° dec (in sealed tube), which cracked near 200° especially when the measurement of melting point was conducted in an open tube. Recrystallization from methanol was not achieved. Upon recrystallization III converted partly into IV and V thereby lowering the purity: Grote test, greenish blue; uv max (99% EtOH) 248 m$\mu$ (log $\epsilon$ 4.15); ir (KBr) 3335 (m), 3200 (s, br), 1568 (s), 1535 (s), 1012 cm$^{-1}$ (m); ir ($CHCl_3$) 3404 (s), 3200 (m, br), 1565 (m), 1525 (m), 1002 cm$^{-1}$ (m).

*Anal.* Calcd for $C_7H_{15}N_3S$: C, 48.52; H, 8.73; N, 24.25; S, 18.51. Found: C, 48.51; H, 8.60; N, 22.79; S, 18.63. The analysis was repeated several times, but the nitrogen content measured was always lower than the calculated value. This may be due to the nature of the compound which was likely to liberate ammonia.

Compound III upon recrystallization from acetic acid, DMF, or morpholine was converted into V. When refluxed with methanol for 1 hr III yielded IV in addition to V (see below).

Compound III, on standing, gradually liberated ammonia and was converted into V. The abortive attempt to prepare the hydrochloride of III may be due to this nature of the compound.

**Conversion of II into 6-Methoxy-4,4,6-trimethyltetrahydro-2(1H)-pyrimidinethione (IV).**—Compound II (4 g) was dissolved in 40 ml of hot methanol and refluxed for 1 hr. After being cooled, colorless prisms which separated were collected, washed with methanol, and dried: yield 1.8 g (51%). The crude crop was dissolved in a minimal quantity of cold DMF, and to this was added an equal volume of water. The crystals which separated were collected: colorless prisms or cubes (yield, 1.2 g); mp 267° dec and 241–242° dec (in sealed tube); the crystal cracked near 200° before it had melted; Grote test, light green tinged with ochre; uv max (99% EtOH) 249 m$\mu$ (log $\epsilon$ 4.08); ir (KBr) 3200 (s, br), 1565 (s), 1510 (s), 1182 (s), 1086 cm$^{-1}$ (m); ir ($CHCl_3$) 3400 (s), 1530 (s, br), 1495 (s), 1152 (s), 1084 cm$^{-1}$ (m).

*Anal.* Calcd for $C_8H_{16}N_2OS$: C, 51.05; H, 8.57; N, 14.88; S, 17.00; mol wt (Rast), 188.2. Found: C, 51.30; H, 8.27; N, 15.25; S, 17.41; mol wt, 180.

**Conversion of III into IV.**—Compound III (0.5 g) was suspended in 5 ml of methanol and refluxed for 1 hr. The crystalline product was collected, washed with methanol, and dried to yield 0.4 g (74%).

The product obtained by this or preceding method was contaminated by V.

**Conversion of II into IV.**—Compound IV also was obtained from II by treating the latter with sodium methoxide in methanol at *ca.* 25° for several hours. In this case contamination by V also was inevitable.

When a saturated solution of II in methanol was allowed to stand at room temperature for 2 to 3 days, a small amount of IV separated from the solution. This specimen consisted of almost pure IV.

Upon recrystallization from DMF or morpholine IV was converted into V.

**Conversion of III into 3,4-Dihydro-4,4,6-trimethyl-2(1H)-pyrimidinethione (V).**—Compound III (2 g) was refluxed with 4 ml of DMF for 10 min (considerable amount of ammonia gas evolved) and then allowed to stand. Long needles separated from the solution, and at the same time, the color of the solution turned greenish blue. When the whole was cooled to room temperature, the color turned ochre yellow. To the reaction mixture was added 10 ml of water and the whole then was filtered. The crystalline product obtained was washed with water and dried: yield 1.75 g (97%). Recrystallization from ethanol gave colorless needles (*ca.* 1 g): mp 266–267° dec (slow heating) and 274–276° dec (rapid heating); Grote test, light green tinged with ochre; uv max (99% EtOH) 269 m$\mu$ (log $\epsilon$ 4.08); ir (KBr) ~3200 (s, br), 1704 (m), 1658 (m), 1578 (s), 1493 cm$^{-1}$ (m); ir ($CHCl_3$) 3428 (s), 3400 (s), 1700 (m), 1650 (w), 1535 cm$^{-1}$ (s); nmr ($CF_3CO_2H$) $\delta$ 8.89 [s, 1, N(3)H], 8.07 [s, 1, N(1)H], 4.95 (s, 1, CH), 1.94 (s, 3, $CH_3$), 1.49 (s, 6, $2CH_3$).

*Anal.* Calcd for $C_7H_{12}N_2S$: C, 53.81; H, 7.74; N, 17.93; S, 20.52; mol wt (Rast), 156.2. Found: C, 53.75; H, 7.66; N, 17.57; S, 20.44; mol wt, 180.

**3,4-Dihydro-4,4,6-trimethyl-2(1H)-pyrimidinethione (V).**—A mixture of acetone (29 g, 0.5 mol), carbon disulfide (76 g, 1 mol), and 240 ml of aqueous ammonia (28%) was treated as above: crude crop yield 7 g (18%). Recrystallization from ethanol gave colorless needles (*ca.* 5 g) which were identified with V by mixture melting point, infrared spectrum, and elemental analysis.

Compound V also was prepared as follows. A mixture of thiourea (2 g, 0.026 mol) and mesityl oxide (10 g, 0.1 mol) was refluxed for 8 hr. After the mixture cooled, the crystalline product was collected, washed with ethanol, and dried to yield 2 g (48%). Recrystallization from ethanol gave colorless needles (*ca.* 1.1 g) which were identified with V by the same method as above.

Compound V was rather stable toward acid and alkali. When refluxed with 6 *N* hydrochloric acid for 3 hr or with 12 *N* sulfuric acid for the same period, the compound afforded acetone which was identified by the 2,4-dinitrophenylhydrazone. Compound V was indifferent toward sodium nitroprusside.

**6-Hydroxy-4,4,6-trimethyltetrahydro-2H-3,1-thiazine-2-thione (VI).**—The preparation followed the method described by Jansen and Mathes.[7]

A small amount of the compound was formed in the following reaction in an alkaline medium. A mixture of mesityl oxide (24.5 g, 0.25 mol), carbon disulfide (19 g, 0.25 mol), and 17 ml of aqueous ammonia (28%) was shaken at room temperature for 1 day and then allowed to stand for 10 days. The pasty product which separated was collected, washed with water and ethanol, and dried: yield 2.5 g (5.2%). Recrystallization from benzene gave colorless needles (*ca.* 1.5 g): mp 126–127° (slow heating) and 154–156° (rapid heating) (reported[3] mp 128–129°); ir (KBr) 3320 (s), 3162 (s), 1525 (s), 1008 cm$^{-1}$ (s); ir ($CHCl_3$) 3578 (m), 3340 (m), 1483 (m), 1010 cm$^{-1}$ (s).

*Anal.* Calcd for $C_7H_{13}NOS_2$: C, 43.95; H, 6.85; N, 7.32; S, 33.52. Found: C, 43.85; H, 6.69; N, 7.35; S, 33.47.

The infrared spectrum of this specimen was in good agreement with that of the specimen prepared by the method of Jansen and Mathes.[3]

Compound VI, on treatment with an acid, was easily dehydrated to give 4,4,6-trimethyldihydro-2H-3,1-thiazine-2-thione (VIII) which melted at 95–97° and was considered to be identical with the compound obtained by Jansen and Mathes.[7]

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[7] J. E. Jansen and R. A. Mathes, *J. Amer. Chem. Soc.*, **77**, 2866 (1955).

**Elimination of Dithiocarboxyl Group from I and VI.**—Compound I (2 g) was refluxed with 8 ml of morpholine for several minutes. After being cooled, the separated crystals were collected, washed with ether, and dried to yield 1.9 g (73%). Recrystallization from morpholine gave colorless needles (1.2 g) which were identified with IX by mixture melting point and infrared spectrum.

Compound VI was treated in the same way as above to give IX in 65% yield. It seemed that the reaction of VI was somewhat slow. Further, I, on treatment with piperidine, gave only an oily product.

**Reaction of 3,4-Dihydro-4,4,6-trimethyl-2H-1,3-thiazine-2-thione (VII) and 4,4,6-Trimethyldihydro-2H-3,1-thiazine-2-thione (VIII) with Morpholine.**—Compound VII which was prepared by the method of Jansen and Mathes,[3] on the same treatment as above, yielded an oily product, which was not studied further.

Compound VIII (2 g) was refluxed with 8 ml of morpholine for 15 min; upon heating the solution turned in the sequence of yellow, yellowish green, yellow, and finally red. After being cooled, the whole was poured in 30 ml of ice-water and stirred thoroughly. The solid product was collected, washed with water and ether, and dried: yield 0.4 g. Recrystallization from ethanol gave colorless plates (*ca.* 0.2 g), mp 175–176°.

*Anal.* Found: C, 41.14; H, 6.29; N, 19.02; S, 22.19.

The compound was not investigated further.

**2-Ethyldihydro-2,5,6-trimethyl-4H-3,1-thiazine-4-thione (X).**—A mixture of methyl ethyl ketone (50 g, 0.69 mol), carbon disulfide (53 g, 0.63 mol), and 145 ml of aqueous ammonia (28%) was reacted as mentioned already below 0°. When the crude product was recrystallized from methanol, *ca.* 12 g of yellow plates (X) was obtained: mp 145–146°; Grote test, yellow ochre; color reaction toward cupric ion, deep red; uv max (99% EtOH) 334 mμ (log ε 3.65), 406 (ε 3.35); ir (KBr) 3165 (s), 1548 (s), 1516 (vs), 1452 cm$^{-1}$ (m); ir (CHCl$_3$) 3396 (s), 1525 (s), 1455 cm$^{-1}$ (m).

*Anal.* Calcd for $C_9H_{15}NS_2$: C, 53.72; H, 7.51; N, 6.96; S, 31.81; mol wt (vapor pressure osmometer), 201.22. Found: C, 53.87; H, 7.44; N, 6.82; S, 31.88; mol wt, 200 (in acetone).

In this case, XI (mentioned below) could not be isolated, and XII (also mentioned below) was isolated in poor yield (0.5 g).

**4-Ethyl-3,4-dihydro-4,5,6-trimethyl-2(1H)-pyrimidinethione (XI).**—The proceding reaction was carried out at 25–30° for *ca.* 70 hr and then kept overnight. The reaction mixture was concentrated, and the yellow pasty mass which separated from the solution was collected and washed with water and ether. The crude product, which weighed *ca.* 16 g, was washed with methanol and recrystallized from ethanol to give *ca.* 12 g of colorless short prisms (XI): mp 246–247°; Grote test, light yellowish green tinged with ochre; uv max (99% EtOH) 265 mμ (log ε 4.08); ir (KBr) 3210 (s), 1702 (m), 1575 cm$^{-1}$ (s).

*Anal.* Calcd for $C_9H_{16}N_2S$: C, 58.67; H, 8.75; N, 15.21; S, 17.37; mol wt (vapor pressure osmometer), 184.23. Found: C, 58.64; H, 8.48; N, 15.14; S, 17.33; mol wt, 189 (in chloroform).

An additional amount (*ca.* 0.5 g) of X was isolated by concentrating the above methanol washings.

**4,5-Dimethyl-1,2-dithiole-3-thione (XII).**—To a mixture of methyl ethyl ketone (50 g, 0.69 mol), carbon disulfide (53 g, 0.63 mol), and 300 ml of aqueous ammonia (28%) was gently passed hydrogen sulfide for *ca.* 8 hr with stirring at 25–33° and then kept overnight. When the reaction mixture was concentrated, an yellow-orange pasty mass was obtained, washed with water, and dried; yield *ca.* 2 g. The crude product was shaken with carbon tetrachloride and filtered. The filtrate was concentrated to give *ca.* 1 g of yellow needles (XII): mp 96°; Grote test, dark green; uv max (99% EtOH) 225 mμ (log ε 4.00), 243 (sh) (3.77), 275 (3.81), 310 (3.73), 409 (4.01).

*Anal.* Calcd for $C_5H_6S_3$: C, 37.05; H, 3.73; S, 59.22; mol wt (vapor pressure osmometer), 162.10. Found: C, 37.05; H, 3.78; S, 59.27; mol wt, 161.2 (in chloroform).

The above crude product from which XII was removed was recrystallized from methanol to give *ca.* 1 g of X.

**Registry No.**—I, 16504-29-3; II, 16504-30-6; III, 16504-31-7; IV, 16504-32-8; V, 5778-17-6; VI, 16504-34-0; X, 16504-35-1; XI, 16504-36-2; XII, 3354-39-0; carbon disulfide, 75-15-0; ammonia, 7664-41-7; acetone, 67-64-1; methyl ethyl ketone, 78-93-3.

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# The Rearrangement of Methoxylated Phenylanthranils

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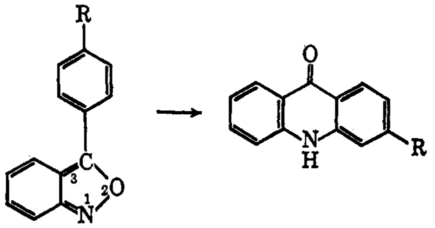
Methoxylated phenylanthranils rearrange under pyrolytic conditions to acridones in which the nitrogen is *para* instead of *meta* to the methoxyl function. In the presence of nitrous acid, these methoxylated anthranils yield substituted azoxybenzoic acids instead of the anticipated acridones. This new rearrangement and reaction of methoxylated phenylanthranils may be explained by the activating effect of the methoxyl function on the position *para* to it. A nitrene has been proposed as the intermediate in the rearrangement. The application of these new reactions to the synthesis of compounds related to the anticancer alkaloid, acronycine, is reported.

Acridones are often synthesized by the rearrangement of phenylanthranil and *para*-substituted phenylanthranils[1-6] catalyzed by nitrous acid or heat. The yields are generally high and the *para* relationship of the substituent R of the phenyl ring to the carbon 3 of the anthranil ring system has been shown to remain after the rearrangement.[5] The lack of information concerning the rearrangement of alkoxyphenylanthranils and the need for methoxyacridones prompted us to investigate this rearrangement. These methoxyacridones were necessary as starting materials for our work



R = alkyl or halogen

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