

m.p. 179–180°, also did not depress the m.p.'s of the corresponding derivatives of III obtained as above.

**Reaction of *m*-Dinitrobenzene with Thiophenol and Thiophenoxide Ion.**—The reaction was carried out as was done with 8-nitroquinoline. From 2 g. of *m*-dinitrobenzene 1.05 g. of fluffy white needles separated when the reaction mixture was poured into 250 ml. of water containing 2 g. of sodium hydroxide. Recrystallization from alcohol or benzene gave *m,m'*-dinitroazoxybenzene, m.p. 147.9–148.5°; reported m.p. 143°. <sup>23</sup>

*Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>N<sub>4</sub>O<sub>5</sub>: C, 50.0; H, 2.8. Found: C, 50.0; H, 2.9.

From the alkaline mother liquor, 3.3 g. of diphenyl disulfide was obtained.

**Reaction of 8-Quinolylhydroxylamine and Thiophenol-Thiophenoxide Ion.**—A solution of 0.6 g. of 8-quinolylhydroxylamine<sup>24</sup> in 6 ml. of anhydrous methanol was added to 10 ml. of methanol containing 0.13 g. of sodium, and 3 g. of thiophenol was heated under reflux for 1.5 hours and poured into 50 ml. of water and ice containing 0.8 g. of so-

dium hydroxide. The gummy precipitate dissolved almost completely in hexane. The hexane solution yielded a mixture of 0.9 g. of white needles and a yellow oil which was again taken up in hexane and treated with hydrogen chloride. The precipitated red hydrochloride (0.39 g.) was filtered. Evaporation of the hexane gave 0.6 g. of diphenyl disulfide. The hydrochloride was shaken with dilute ammonia and ether. Evaporation of the dried ether extract left 0.26 g. of a yellow gum which gave a small amount of II, m.p. 86–89° after crystallization from hexane. The mixture m.p.'s of this with II and of the acetyl derivatives were not depressed.

**5-Piperidino-8-nitroquinoline.**—5-Bromo-8-nitroquinoline (1 g.) was heated for four hours in 10 ml. of piperidine. The heavy yellow gum which separated when the mixture was poured into water slowly crystallized; yield 1 g. After recrystallization from alcohol, yellow prisms, m.p. 131.2–132.3°, were obtained. The product obtained by Bradley and Robinson<sup>4</sup> from 8-nitroquinoline and piperidine in the presence of sodamide is reported as melting at 131.5–132.5°.

*Anal.* Calcd. for C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 65.4; H, 5.9; N, 16.3. Found: C, 65.4; H, 5.6; N, 16.0.

NEW YORK 27, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY]

## The Single-Stage Conversion of 1-(3',4',5'-Trimethoxyphenyl)-6,7-methylenedioxy-3,4-dihydroisoquinoline to 2-(3',4',5'-Trimethoxybenzoyl)-4,5-methylenedioxy-1,2

BY WALTER J. GENSLE AND CARLOS M. SAMOUR

RECEIVED NOVEMBER 12, 1951

Evidence is presented for the reaction path in the formation of 2-(3',4',5'-trimethoxybenzoyl)-4,5-methylenedioxy-1,2-styrene by treatment of 1-(3',4',5'-trimethoxyphenyl)-6,7-methylenedioxy-3,4-dihydroisoquinoline with methyl sulfate and alkali.

We have recently described a method of converting 1-(3',4',5'-trimethoxyphenyl)-6,7-methylenedioxy-3,4-dihydroisoquinoline (I) directly to 2-(3',4',5'-trimethoxybenzoyl)-4,5-methylenedioxy-1,2-styrene (VII) by treating the dihydroisoquinoline with methyl sulfate and alkali.<sup>3</sup> This transformation had suggested itself originally on considering a sequence of separate reactions dealing with hydrastinine and related compounds.<sup>4</sup> In terms of the present compounds, the sequence is given in formulations I to VII. Now evidence is adduced for this as the path actually followed in the one-stage process. The mode of attack consisted in the preparation of intermediates and test of their behavior with methyl sulfate and with alkali.

That alkali alone was ineffective in the conversion of the dihydroisoquinoline (I) to the vinyl ketone (VII) was shown by the resistance of the former compound to the action of hot sodium hydroxide solution. The dihydroisoquinoline was recovered unchanged after long boiling with 20% aqueous alkali.

The quaternary dihydroisoquinolinium metho-

sulfate (II methosulfate) was prepared by allowing the dihydroisoquinoline (I) to react with methyl sulfate in inert solvent; the iodide of II was formed using methyl iodide. The corresponding chloride was obtained by reaction of the carbinolamine (III) with hydrochloric acid. Treatment of the quaternary dihydroisoquinolinium salts (II) with aqueous alkali produced the carbinolamine (III) in a virtually instantaneous reaction; but the latter compound remained unchanged even after long exposure to alkali. On the other hand, when the carbinolamine (III) was warmed with alkali and methyl sulfate, the vinyl ketone (VII) was produced in 84% yield.

No attempt was made to isolate the two forms III and IV of the carbinolamine. Judging from the absence of any carbonyl peak in the infrared absorption curve of the solid (as a mull with mineral oil) structure III is preferred to IV for the crystalline material.<sup>5</sup>

In experiments directed to the preparation of the dimethylamino ketone (V) it was found that the action of methyl sulfate in toluene on the carbinolamine produced the quaternary methosulfate of compound VI as the only isolated material. Methyl iodide in chloroform solution transformed the carbinolamine into a mixture from which the iodides of quaternary salts II and VI could be isolated; but

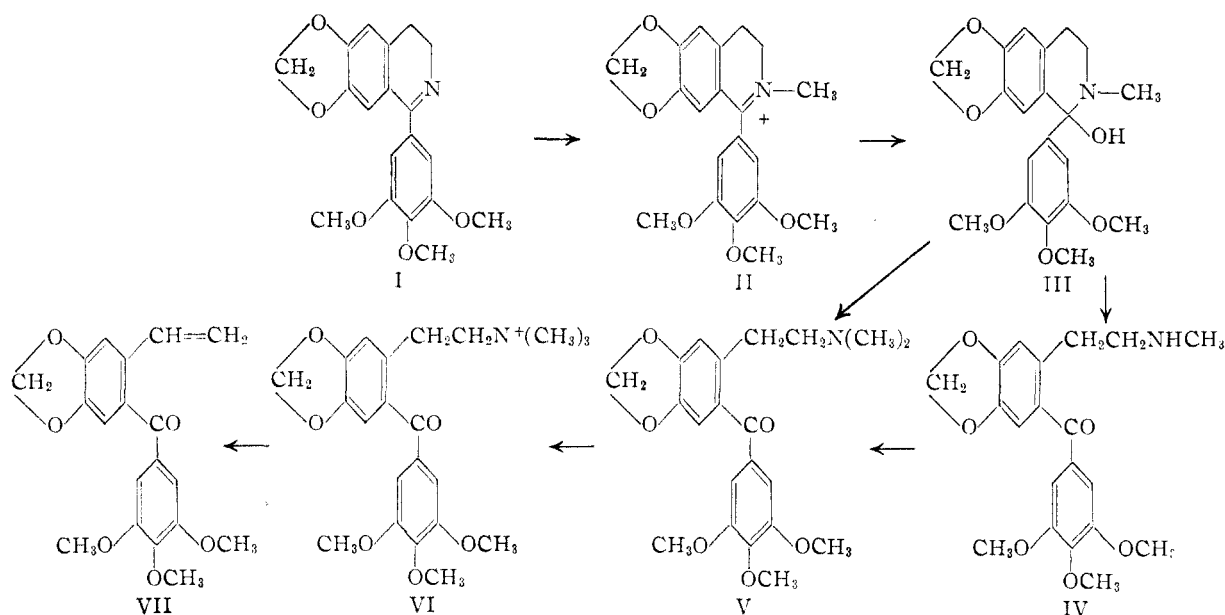
(1) This work was supported by American Cancer Society Grant-in-Aid No. CBC-6 as recommended by the Committee on Growth of the National Research Council.

(2) A summary of the material in this paper was presented in Boston, Mass., on April 3, 1951, before the Division of Organic Chemistry of the American Chemical Society.

(3) W. J. Gensler and C. M. Samour, *THIS JOURNAL*, **72**, 3318 (1950); **73**, 5555 (1951).

(4) (a) H. Becker, *et al.*, *Ann.*, **395**, 299, 321 (1913); M. Freund, *Ber.*, **22**, 2329 (1889); (b) W. Roser, *Ann.*, **249**, 156 (1888); M. Freund and F. Becker, *Ber.*, **36**, 1521 (1903); H. Decker and P. Becker, *Ann.*, **395**, 328 (1913); (c) W. H. Perkin, Jr., *J. Chem. Soc.*, **109**, 815 (1916).

(5) This is not necessarily the case for solutions of the carbinolamine. A preliminary study of the infrared absorption in solvents such as chloroform, dihydrofuran and dioxane indicates that the relative amount of the carbinolamine (III) and of the monomethylamino ketone (IV)—the latter form being detected by an absorption peak at 6.0μ—depends on the nature of the solvent.



the hydroiodide of the dimethylamino ketone (V) was not detected.<sup>6</sup> Treatment with hydriodic acid transformed the methosulfate of the trimethylamino ketone (VI) to the corresponding iodide.

Because there is no reaction path leading to the quaternary trimethylamino ketone (VI) which does not proceed by way of the dimethylamino ketone (V), we must accept the latter compound as intermediate. This dimethylamino compound (V) could form by the monomethylation of the monomethylamino ketone (IV), as indicated in the formulation. An alternate path would proceed by direct methylation of the carbinolamine (III) followed by loss of proton from the hydroxyl group of

able than methylation of the monomethylamino ketone (IV). Salts of the dihydroisoquinolinium compound (II) are produced in the methylation of the carbinolamine (III) in an inert solvent and in the absence of alkali. However, where there is excess alkali, as in the single-stage I to VII conversion, the dihydroisoquinolinium compound (II) would not be formed.

The last in the sequence of reactions, a standard Hofmann elimination, was shown to be possible by the smooth conversion of the quaternary trimethylamino ketone salts (VI) with alkali to the vinyl ketone (VII).

It was considered desirable to eliminate the possibility that compound V, by loss of dimethylamine, was the immediate precursor of the vinyl ketone (VII).<sup>8</sup> Because compound V could not be obtained and tested, an indirect demonstration was resorted to. It was shown first that *only* trimethylamine was evolved in the single-stage conversion of I to VII. Then, in order to eliminate the chance that dimethylamine was formed from compound V but was methylated by methyl sulfate to trimethylamine before leaving the reaction mixture, an experiment was carried out in which dimethylamine hydrochloride was added to methyl sulfate and excess alkali, and the emergent gases collected. In this way, it was found that, under conditions obtaining in the single-stage I to VII conversion in which only trimethylamine was formed, at least 40% of the dimethylamine emerged unchanged. Thus we conclude that the V-to-VII reaction could account for only a minor amount of product VII, if indeed for any at all.

Taken together, these results support the reaction path I-VII for the single-stage transformation of

the resulting quaternary tetrahydroisoquinolinium compound (VIII) and ring opening. Actually, if the conclusions reached as the result of ultraviolet absorption studies on hydrastinine and cotarnine<sup>7</sup> are applicable to the present series, the existence of the monomethylamino ketone (IV) in strongly alkaline solution is unlikely, and consequently, in the single-stage conversion, direct methylation of the carbinolamine (III) is to be considered more prob-

(6) It is interesting to note that the related carbinolamine, hydrastinine, on treatment with methyl iodide leads not to the dimethylamino hydroiodide but to a mixture of hydrastinine iodide and 2-(dimethylaminoethyl)-piperonal methiodide (ref. 4a). Analogous behavior is reported for cotarnine (ref. 4b). However, Perkin (ref. 4c) did succeed in isolating the three possible products from the reaction of methyl iodide and 1-hydroxy-2-methyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline.

(7) J. J. Dobbie, A. Lauder and C. K. Tinkler, *J. Chem. Soc.*, **83**, 598 (1903); **85**, 121 (1904); J. J. Dobbie and C. K. Tinkler, *ibid.*, **85**, 1005 (1904). See also B. Skinner, *ibid.*, 823 (1950).

(8) This reaction, or for that matter the formation of product VII by loss of methylamine from the monomethylamino ketone (IV) (if this material were present at all in strong alkali), *a priori*, could not be disregarded. Removal of a proton from the carbon atom  $\beta$  to the nitrogen and next to the ring should be facilitated by resonance distribution of the negative charge to the carbonyl oxygen. Appropriate electronic shifts, etc., would result in the release of dimethylamine and the formation of the vinyl group. The process would be entirely analogous to a base-catalyzed  $\beta$ -elimination reaction.

the dihydroisoquinoline to the vinyl ketone. The limits to the general applicability of this process will be determined by further work.

### Experimental<sup>9</sup>

**Stability of 1-(3',4',5'-Trimethoxyphenyl)-6,7-methylenedioxy-3,4-dihydroisoquinoline (I) in the Presence of Alkali.**—Acidification of the mixture obtained on boiling 2.0 g. of the dihydroisoquinoline (I)<sup>8</sup> in 20% sodium hydroxide solution overnight gave rise to a clear solution. Addition of sodium hydroxide solution, filtration of the alkaline mixture, and crystallization of the solids from benzene-petroleum ether solvent furnished 1.9 g. of starting material, m.p. 160.1–160.6°.

**1-(3',4',5'-Trimethoxyphenyl)-2-methyl-6,7-methylenedioxy-3,4-dihydroisoquinolinium Methosulfate (II Methosulfate).**—A solution of 3.41 g. (0.01 mole) of the dihydroisoquinoline (I) and 1.6 g. (0.0127 mole) of methyl sulfate in 30 ml. of xylene was heated on the steam-bath for one hour. The cooled mixture was filtered, the solids were washed with ether, and were dried *in vacuo*. The yellow solid (4.4 g.), m.p. 191.6–192.8° on crystallization from absolute alcohol, afforded 3.74 g. (80%) of pure II methosulfate, m.p. 193.8–194.3°.

*Anal.* Calcd. for  $C_{21}H_{25}O_5NS$ : C, 54.0; H, 5.4; N, 3.0. Found: C, 53.9; H, 5.4; N, 3.0.

**1-(3',4',5'-Trimethoxyphenyl)-2-methyl-6,7-methylenedioxy-3,4-dihydroisoquinolinium Iodide (II Iodide).**—A solution of 5.41 g. (0.016 mole) of the dihydroisoquinoline (I) and 4.1 g. (0.03 mole) of methyl iodide in 150 ml. of benzene was allowed to stand at room temperature for 4 days. The precipitate was removed by filtration, washed on the funnel with benzene, and dried *in vacuo*. The yellow crystalline methiodide weighed 7.7 g. (99.6%) and, when the melting point was taken by inserting the sample in a bath preheated to 200°, showed m.p. 233.3–233.8° dec. Otherwise the melting point was observed to be 228–229° dec. (reported<sup>10</sup> m.p. 222–223° dec.). This material, admixed with the corresponding material (m.p. 233–233.8° dec.) obtained on treating the carbinolamine (III) with methyl iodide (see below), melted at 229.6–230.6° dec.

**1-(3',4',5'-Trimethoxyphenyl)-6,7-methylenedioxy-3,4-dihydroisoquinolinium Chloride (II Chloride) from the Carbinolamine (III).**—To a suspension of 1.5 g. (0.0044 mole) of the dihydroisoquinoline (I) in 30 ml. of water was added 1.0 g. (0.0079 mole) of methyl sulfate, and the mixture heated and stirred until a clear yellow solution resulted. Sodium hydroxide solution was added until an alkaline reaction was obtained and the mixture was then cooled in the ice-bath for one hour. Precipitated carbinolamine (III) was collected, washed several times with cold water, and dried *in vacuo*.

To the carbinolamine dissolved in acetone was added 1 ml. of concentrated hydrochloric acid, and the acid solution held at –4° overnight. The precipitated product was collected, washed with cold acetone, and dried *in vacuo*. The dihydroisoquinolinium chloride (II chloride), obtained in the form of yellow crystals (1.6 g., 93%), m.p. 228.4–229.1° dec., was analytically pure.

*Anal.* Calcd. for  $C_{20}H_{22}O_5NCl$ : C, 61.3; H, 5.7. Found: C, 61.1; H, 5.8.

**Direct Conversion of 1-(3',4',5'-Trimethoxyphenyl)-2-methyl-6,7-methylenedioxy-3,4-dihydroisoquinolinium Methosulfate (II Methosulfate) to 2-(3',4',5'-Trimethoxybenzoyl)-4,5-methylenedioxy-styrene (VII).**—A mixture of 4.7 g. (0.01 mole) of the isoquinolinium (II) methosulfate, 5.0 g. (0.04 mole) of methyl sulfate, 15 ml. of water, 10 ml. of alcohol and 10 g. of potassium hydroxide in 20 ml. of water was boiled for two hours. After addition of 1 g. more of methyl sulfate, heating was continued for another half hour. The reaction mixture was then diluted with 100 ml. of water, cooled, and filtered, and the solids washed several times on the funnel with cold water. Crystallization of the solids (3.4 g. after drying *in vacuo*) from aqueous methanol afforded 2.9 g. (85%) of compound VII, m.p. 139.2–139.8° (reported<sup>8</sup> m.p. 139.2–139.8°).

(9) All melting points are corrected. Analyses by Carol K. Fitz, 115 Lexington Ave., Needham Heights 94, Mass.

(10) W. Reeve and W. M. Eareckson, III, *THIS JOURNAL*, **73**, 5195 (1950).

**The Carbinolamine (III) from 1-(3',4',5'-Trimethoxyphenyl)-2-methyl-6,7-methylenedioxy-3,4-dihydroisoquinolinium Methosulfate (II Methosulfate).**—To a cold solution of 4.6 g. (0.0097 mole) of the methosulfate of II in 100 ml. of water was added 10 ml. of a 10% sodium hydroxide solution. The colorless crystalline carbinolamine, which formed immediately, was collected, washed with water and dried *in vacuo*. The dry product weighed 3.55 g. (98%) and, when inserted in a bath a few degrees below the melting point, showed m.p. 146–147° dec. If the sample was heated in the bath from room temperature the melting point was lower. A sample crystallized from ethyl acetate melted at 147–148° (dec.) in a preheated bath, and otherwise at 137–137.8° (reported<sup>10</sup> 146–147°).

*Anal.* Calcd. for  $C_{20}H_{23}O_5N$ : C, 64.3; H, 6.2. Found: C, 64.2; H, 6.2.

From 4.83 g. (0.01 mole) of the methiodide (II iodide), by following essentially the same procedure, there could be obtained 3.6 g. (96.2%) of crystalline carbinolamine (III), m.p. 146.2–147.4° dec. (preheated bath).

**Stability of the Carbinolamine (III) to Alkali.**—A mixture of 0.20 g. of the carbinolamine (III) and 10 ml. of 20% sodium hydroxide solution was heated on the steam-bath for 2 hours. The cooled mixture was filtered, and the solids washed with cold water and dried *in vacuo*. The recovered carbinolamine (0.18 g.) melted at 146–147° dec. (preheated bath).

**Reaction of the Carbinolamine (III) with Methyl Sulfate.**—A solution of 0.50 g. (0.00134 mole) of the carbinolamine (III) and 0.50 ml. of methyl sulfate (0.053 mole) in 100 ml. of dry toluene was warmed on the steam-bath for 30 minutes. The clear solvent was decanted from the cooled mixture, and the oily residue was dissolved in 25 ml. of acetone and cooled. The resulting yellow crystals, after collection and drying *in vacuo*, weighed 0.60 g. and melted at 193–197° dec. Presumably this material was a mixture of the isoquinolinium (II) methosulfate and the quaternary trimethylamino ketone (VI) methosulfate. Recrystallization from acetone afforded 0.35 g. of analytically pure VI methosulfate, m.p. 230.7–231.3° dec.

*Anal.* Calcd. for  $C_{23}H_{31}O_5NS$ : C, 53.8; H, 6.1. Found: C, 53.6; H, 6.0.

**Reaction of the Carbinolamine (III) with Methyl Iodide.**—To a solution of 1.5 g. (0.0040 mole) of the carbinolamine (III) in 50 ml. of chloroform was added 2 ml. of methyl iodide, and the solution was allowed to stand at room temperature for 24 hours. The yellow solid obtained on evaporating the solution to dryness was digested with benzene, collected on the funnel, washed with benzene, and dried *in vacuo*. This material (2.2 g.) was then boiled with acetone and the mixture filtered hot. The insoluble yellow crystals were rinsed with acetone and dried *in vacuo*. Crystallization from a mixture of chloroform and acetone afforded 1.1 g. of yellow 1-(3',4',5'-trimethoxyphenyl)-2-methyl-6,7-methylenedioxy-3,4-dihydroisoquinolinium iodide (II iodide), m.p. 233–233.8° dec.

*Anal.* Calcd. for  $C_{20}H_{22}O_5NI$ : C, 49.7; H, 4.6. Found: C, 49.5; H, 4.6.

The acetone extract was concentrated, cooled first to room temperature, and then held at –10° overnight. The colorless crystals were collected, washed with cold acetone, and dried *in vacuo*. Recrystallization of this material (0.82 g., m.p. 221.2–222.2° dec.) from acetone yielded the quaternary trimethylamino ketone iodide (VI iodide) in the form of needles, m.p. 223.5–224.3° dec.

*Anal.* Calcd. for  $C_{22}H_{28}O_6NI$ : C, 49.9; H, 5.3. Found: C, 50.1; H, 5.5.

**Conversion of the Quaternary Methosulfate of Compound VI to the Corresponding Iodide.**—The relatively water-soluble methosulfate of VI was converted to the insoluble iodide by cooling a solution of 0.10 g. of the methosulfate (m.p. 230.7–231.3° dec.) in 5 ml. of water containing a few drops of concentrated hydriodic acid. The colorless needles of the iodide after collection, washing with water, and drying *in vacuo*, weighed 0.08 g. and melted at 221.2–222.2° dec.

**Conversion of the Quaternary Trimethylamino Ketone (VI) Salts to 2-(3',4',5'-Trimethoxybenzoyl)-4,5-methylenedioxy-styrene (VII).**—No precipitate appeared on adding 2 ml. of 40% sodium hydroxide solution to 0.30 g. of the methosulfate of VI dissolved in 20 ml. of water. However, after allowing the solution to stand for 3 days, a precipitate

did form. The reaction was completed by heating the mixture for one hour. Acidification with dilute hydrochloric acid, and filtration afforded the desired product (VII) which, after washing with water and drying *in vacuo*, weighed 0.18 g. (90%) and melted at 139–139.8°.

In essentially the same way, the iodide of VI could be converted in high yield to the styrene derivative (VII), m.p. 139.8–140.3°.

**The Volatile Amine Derived from the Direct Conversion of the Dihydroisoquinoline (I) to Vinyl Ketone (VII).**—The gases evolved on heating a mixture of 3.50 g. (0.0102 mole) of 1-(3',4',5'-trimethoxyphenyl)-6,7-methylenedioxy-3,4-dihydroisoquinoline (I), 8 ml. of methyl sulfate, 50 ml. of 40% sodium hydroxide solution, and 50 ml. of water for six hours were passed into dilute hydrochloric acid. Removal of all solvent from the acid solution left 0.85 g. (89%) of residual white solid, m.p. 265–266.7° dec. Shaking a portion of this solid with benzoyl chloride and cold aqueous alkali furnished no trace of an N-benzoyl derivative. One crystallization of the solid from absolute alcohol yielded trimethylamine hydrochloride, m.p. 272–273° dec.<sup>11</sup>

(11) Melting points of 271–272° and 271–275° dec. have been observed [E. Winterstein and A. Guyer, *Z. physiol. Chem.*, **128**, 175 (1923); M. Delépine, *Ann. chim. phys.*, [7] **8**, 439 (1896)] although trimethylamine hydrochloride has been reported to melt as high as 280–282° [G. S. Hiers and R. Adams, *Ber.*, **59**, 162 (1926)]. The

The 2-(3',4',5'-trimethoxyphenyl)-4,5-methylenedioxy styrene (VII) isolated from this reaction weighed 3.5 g. (100%), and melted at 139–139.8°. After crystallization from benzene-petroleum ether, the material weighed 3.4 g. and showed m.p. 139.4–139.9°.

**Reaction of Dimethylamine and Methyl Sulfate under Conditions Similar to those Employed in the Direct Conversion of I to VII.**—A solution of 0.82 g. (0.01 mole) of dimethylamine hydrochloride (m.p. 172.4–173.4°) in 40 ml. of water was added slowly over a period of 4 hours under the surface of a stirred and heated mixture of 85 ml. of 20% sodium hydroxide solution and 7 ml. of methyl sulfate. The evolved gases were passed into dilute hydrochloric acid. After the addition, stirring and heating were continued for another two hours. Evaporation of the hydrochloric acid solution left 0.62 g. of solid amine hydrochloride, m.p. 142–164°. Treatment of 0.26 g. of this salt with benzenesulfonyl chloride in the usual manner afforded 0.30 g. (54%) of N-benzenesulfonyldimethylamine. The melting point of the derivative alone or admixed with an authentic sample (m.p. 45.5–46.5°) was 45.5–46.5°.

melting point of dimethylamine hydrochloride is 171° [M. Delépine, above] while that of methylamine hydrochloride is 232–233.5° [M. Sommelet, *Compt. rend.*, **178**, 217 (1924)].

BOSTON, MASSACHUSETTS

[COMMUNICATION FROM THE DEPARTAMENTO DE QUÍMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO, BRASIL]

## Interchange Reactions of Mercaptals and Mercaptols with Thiols<sup>1,2</sup>

BY M. MOURA CAMPOS AND H. HAUPTMANN

RECEIVED OCTOBER 3, 1951

The action of four thiols (ethanethiol, thiophenol, benzylmercaptan and propanedithiol-1,3) upon benzaldehyde mercaptals is studied. Interchange reactions are observed, which are analogous to those between alcohols and acetals. The cyclic mercaptals are obtained in highest yields and do not react with monovalent mercaptals. Steroid mercaptols and thioenol-ethers are able to undergo the same reactions.

Some years ago it was reported that mercaptols and alcohols undergo interchange reactions in the presence of catalysts of the "Friedel-Crafts type" such as hydrochloric acid, zinc chloride or *p*-toluenesulfonic acid.<sup>3</sup> The reaction is of practical value for the preparation of ketals.<sup>4</sup> No indication could be found about reactions of mercaptals or mercaptols with thiols.<sup>5</sup> In order to find out whether such interchange reactions take place we allowed several benzaldehydemercaptals to react with thiols in the presence of hydrochloric acid and other similar catalysts. The results gathered in Table I show that interchange reactions of mercaptals with thiols:  $\text{H}_2\text{C}_6\text{C}(\text{SR})_2 + 2\text{R}'\text{SH} \longrightarrow \text{H}_2\text{C}_6\text{C}(\text{SR}')_2 + 2\text{RSH}$  do indeed exist. Thus benzaldehyde diethylmercaptal (I) reacted with thiophenol, benzylmercaptan and propanedithiol-1,3 and the mercaptals of these thiols (II, III, IV) could be isolated from the reaction mixtures. Benzaldehyde diphenylmercaptal (II) in an analogous manner interchanged with

benzylmercaptan and propanedithiol-1,3, whereas from benzaldehyde dibenzylmercaptal (III) the trimethylene mercaptal (IV) could be obtained by reaction with propanedithiol-1,3. Besides benzaldehyde diphenylmercaptal (II) the mixed ethyl phenylmercaptal (V) was formed in the reaction of benzaldehyde diethylmercaptal (I) with thiophenol as could be proved by isolation of its disulfone of m.p. 178–181.5 after oxidation with hydrogen peroxide.<sup>6</sup>

When benzaldehyde trimethylenemercaptal (IV) was allowed to react with either benzylmercaptan or thiophenol or ethanethiol it could be recovered in high yield and no other mercaptal could be isolated from the reaction mixture. The same is true for the reaction of benzaldehyde dibenzylmercaptal (III) with ethanethiol. However, when thiophenol was allowed to react with benzaldehyde dibenzylmercaptal (III) only about a third of this substance could be recovered and from the oily residue the disulfone of benzaldehyde benzylphenylmercaptal (VI) was isolated after oxidation with hydrogen peroxide. In the reaction between benzaldehyde diphenylmercaptal (II) and ethanethiol the presence of the mixed benzaldehyde ethylphenylmercaptal (V) was demonstrated by the isolation of its disulfone after oxidation with hydrogen peroxide.

The reactions were carried out with catalysts of

(1) Presented to the XIIth International Chemical Congress, New York City, September, 1951.

(2) Extracted from a thesis submitted by M. Moura Campos to the Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo in partial fulfillment of the requirements for the degree of Doutor em Ciências.

(3) W. E. Mochel, C. L. Agre and W. E. Hanford, *THIS JOURNAL*, **70**, 2268 (1948).

(4) W. E. Hanford and W. E. Mochel, U. S. Patent 2,229,651 (1941); W. E. Mochel, U. S. Patent 2,229,665 (1941).

(5) Mochel and co-workers state in a footnote that thiol esters give interchange reactions with thiols, but less readily than with alcohols.

(6) Th. Posner, *Ber.*, **36**, 300 (1903). The m.p. indicated by Posner is 155–156°. From the analysis there can, however, be no doubt that we had the benzaldehyde ethylphenyldisulfone in hand.