portions. The reaction mixture was refluxed for three hours and then kept overnight at room temperature. After treatment with cold dilute hydrochloric acid, the ethereal solution was dried and evaporated. The reaction products were worked up as follows: The oily residue, obtained in the case of IIIa, was washed several times with light petroleum (*ca.* 50 ml.); the resultant solid powder was crystallized from petroleum ether to give benzenesulfonamide (0.34 g.).

Evaporation of the light petroleum washings gave an oil which, on treatment with benzoyl chloride in the presence of aqueous sodium hydroxide and crystallization from ethyl alcohol, yielded 0.22 g. of phenylthiobenzoate; identification by m.p. and mixed m.p.

Anal. Calcd. for $C_{13}H_{10}OS$: C, 72.9; H, 4.7; S, 14.9. Found: C, 72.8; H, 4.5; S, 14.5.

The solid residues, which were obtained in the case of IVb and Vb after the washing with light petroleum, were crystallized to yield carbazole (0.42 g.) and benzanilide (0.38 g.), respectively. The light petroleum washings, on evaporation, gave benzyl alcohol which was identified as the α-naphthylurethan (m.p. and mixed m.p.[37]).

(b) **1,8-Naphthosultone I and Derivatives (Ib-d).**—One gram each of I, Ib′, Ic and Id was treated with lithium aluminum hydride as described above and the reaction mixture refluxed for two hours. After treatment with cold aqueous ammonium chloride solution the ethereal benzene solution was dried and evaporated.

The oily residue from I was washed with light petroleum (b.p. below 40°, *ca.* 40 ml.). On slow evaporation of the washings pale yellow crystals (0.1 g.) separated, which were recrystallized from light petroleum (b.p. below 40°) as 1-hydroxy-8-thionaphthol.

The residue from the light petroleum washings (b.p. below 40°) was crystallized from benzene–light petroleum (b.p. 50–60°), as yellow crystals of Xa, yield 0.45 g.

The solid residue, in the case of Ib, Ic and Id, was crystallized from benzene–light petroleum (b.p. 50–60°) to yield pale yellow crystals which proved in every case to be Xb; the yields were 65, 72 and 78%, respectively.

Action of Benzoyl Chloride on Xa and Xb.—Benzoyl chloride (2 ml.) was added to a solution of 0.4 g. of Xa in 20 ml. of aqueous sodium hydroxide (8%) and the mixture shaken for about 30 minutes. The resulting solid was filtered, washed thoroughly with water, dried and crystallized from benzene to give colorless crystals of the dibenzoyl derivative Xc, in an almost quantitative yield. The dibenzoyl derivative of Xb (Xd) was similarly prepared in almost quantitative yield.

(c) **N-Phenylsulfonylnaphthosultam (XI).**—XI[15] (1 g.) was treated with lithium aluminum hydride as described above. The solid residue was crystallized from benzene as colorless crystals of Xe, yield 0.52 g. The analytical values for 1-hydroxy-8-thionaphthol and Xa-e are given in Table II.

Action of Phenyllithium on: (a) **Phenanthraquinone Monoxime (XIII).**—A solution of 1 g. of XIII[38] in 40 ml. of dry benzene was treated with phenyllithium. The ether-benzene solution of the organic matter was dried and evaporated. The solid residue, upon crystallization from benzene, gave colorless crystals (m.p. 162°, yield 71%) which were identified as XIV by m.p. and mixed m.p.[21] and color reaction with sulfuric acid.

(b) **α-Benzil Monoxime (XV).**—XV treated as above yielded colorless crystals (m.p. 153–154°) which were proved to be XVI by m.p. and mixed m.p. with an authentic specimen.[22] The yield is almost quantitative.

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[37] A. I. Vogel, "A Text-book of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 776.

[38] H. Goldschmit, *Ber.*, **16**, 2176 (1883).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY]

Studies in Mixed Ester Condensations. III

BY E. EARL ROYALS AND DEREK G. TURPIN

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A comparative study has been made of the use of sodium methoxide, sodium hydride, diethylaminomagnesium bromide and diisopropylaminomagnesium bromide as condensing agents for acylation of aliphatic esters with methyl benzoate and methyl 2-furoate. Diisopropylaminomagnesium bromide proved an excellent condensing agent for this purpose. Ethyl benzoylacetate, methyl α-benzoylpropionate, methyl α-benzoyl-*n*-butyrate and methyl 2-furoylpropionate have been prepared in yields of 44–51%, by appropriate mixed ester condensations using diisopropylaminomagnesum bromide as condensing agent and an equimolar ratio of acylating and acetylated ester; self-condensation of the aliphatic ester is virtually absent, obviating the necessity for an excess of this reagent. Sodium hydride has afforded good yields of mixed condensation products, but offers certain experimental difficulties in this use.

It has been shown previously[1] that various aliphatic esters may be acylated successfully by means of methyl benzoate, methyl furoate, methyl isobutyrate and methyl isovalerate using sodium methoxide as condensing agent and forcing conditions. Since considerable self-condensation of the aliphatic ester occurs under these experimenal conditions, it is necessary to use an excess of this reactant for maximum conversion of the acylating ester to the mixed condensation product. Relatively few mixed ester condensations have been reported using basic condensing agents stronger than alkoxides. Ethyl formate, ethyl oxalate and ethyl benzoate have been condensed with ethyl isobutyrate by means of triphenylmethylsodium to afford the mixed condensation products in 16, 61 and 20% yields, respectively.[2] Ethyl nicotinate and certain phenyl esters have been used to acylate ethyl phenylacetate and several isopropyl and *t*-butyl esters in good yields with sodium amide as condensing agent.[3] Several successful mixed ester condensations have been effected using sodium hydride as condensing agent[4]; methyl and ethyl *n*-butyrate, ethyl laurate and ethyl isovalerate were the only aliphatic esters acylated in this work. Although diisopropylaminomagnesium bromide has been shown[5] to be an excellent reagent for the self-condensation of esters, no mixed ester condensations using this reagent have been reported.

We have investigated the use of several strong bases as catalysts for the acylations of aliphatic esters with methyl benzoate and methyl 2-furoate. Procedures have been developed whereby aliphatic esters may be acylated by means of these two acyl-

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[1] E. E. Royals, THIS JOURNAL, **70**, 489 (1948); E. E. Royals, J. C. Hoppe, A. D. Jordan and A. G. Robinson, *ibid.*, **73**, 5857 (1951).

[2] B. E. Hudson and C. R. Hauser, *ibid.*, **63**, 3156 (1941), W. B. Renfrow and C. R. Hauser, *ibid.*, **60**, 463 (1938).

[3] J. C. Shivers, M. L. Dillon and C. R. Hauser, *ibid.*, **69**, 119 (1947).

[4] F. W. Swamer and C. R. Hauser, *ibid.*, **72**, 1352 (1950).

[5] F. C. Frostick and C. R. Hauser, *ibid.*, **71**, 1350 (1949).

TABLE I

ACYLATIONS OF ALIPHATIC ESTERS WITH METHYL BENZOATE AND METHYL 2-FUROATE

Acetylating ester (A)	Acylated ester (B)	Catalyst (C)	Mole ratio, A/B/C	Solvent	Reaction time, hr.	Yield of mixed cond. prod., %
Methyl benzoate	Methyl propionate	CH_3ONa	1:1:1	None[a]	6	15
Methyl benzoate	*t*-Butyl propionate	CH_3ONa	1:1:1	None	6	29
Methyl furoate	Methyl propionate	CH_3ONa	1:1:1	None	5	28
Methyl benzoate	Methyl propionate	NaH	1:1:2	Benzene	6	56
Methyl benzoate	*t*-Butyl propionate	NaH	1:1:2	Benzene	6.5	33
Methyl benzoate	*t*-Butyl propionate	NaH	2:3:4	Benzene	22	47
Methyl furoate	Methyl propionate	NaH	1:1:2	Benzene	6	42
Methyl benzoate	Methyl propionate	Sodium	1:4:2	None	48	34
Methyl benzoate	Methyl propionate	$(C_2H_5)_2NMgBr$	1:1:2	Ether	0.5	16[b]
Methyl benzoate	Ethyl acetate	$(C_3H_7)_2NMgBr$[c]	1:1:2	Ether	2.5	49
Methyl benzoate	Methyl propionate	$(C_3H_7)_2NMgBr$[c]	1:1:2	Ether	2.5	51
Methyl furoate	Methyl propionate	$(C_3H_7)_2NMgBr$[c]	1:1:2	Ether	1.5	47
Methyl benzoate	Methyl *n*-butyrate	$(C_3H_7)_2NMgBr$[c]	1:1:2	Ether	1.5	57[b]
Methyl benzoate	Methyl *n*-butyrate	$(C_3H_7)_2NMgBr$[c]	1:1:2	Ether	2.0	44[d]

[a] Use of benzene or ether as solvent led to no reaction and recovery of unchanged esters. [b] The product was a mixture of the β-ketoester and amide; the yield given was obtained by subtracting the amount of amide present as indicated by nitrogen analysis. [c] Diisopropylaminomagnesium bromide. [d] In this condensation, the condensing agent was added to the mixture of esters.

ating esters without the use of forcing conditions or an excess of the aliphatic ester and with practically no self-condensation of the aliphatic ester. Our results are given in Table I.

The results using sodium methoxide as condensing agent are principally for comparison with those using the stronger bases. Mixed condensations between methyl benzoate and aliphatic esters using an equimolar ratio of the two esters and non-forcing conditions give quite low yields of mixed condensation products, *e.g.*, 15% of methyl α-benzoyl propionate. It is interesting that the use of inert solvents such as ether or benzene under non-forcing conditions results in complete failure of reaction, presumably because of the diminished solubility of sodium methoxide in these media. Benzoylation of *t*-butyl propionate gave considerably better results, a yield of 29% of *t*-butyl α-benzoylpropionate being obtained under the same conditions which gave only 15% of methyl α-benzoylpropionate from benzoylation of methyl propionate. The improvement probably results from lowered self-condensation of the hindered carbonyl of the *t*-butyl ester. Use of a more reactive acylating ester also leads to better yields of mixed condensation products; *e.g.*, 27.5% of methyl α-2-furoylpropionate was obtained from the mixed condensation of methyl 2-furoate and methyl propionate under non-forcing conditions with an equimolar ratio of the two esters.

The use of sodium hydride as condensing agent in the condensation of methyl benzoate with methyl propionate gave very considerable improvement over the results obtained using sodium methoxide; a 56% yield of methyl α-benzoylpropionate was obtained under non-forcing conditions using an equimolar ratio of reactants. Very little self-condensation of methyl propionate occurred. Benzoylation of *t*-butyl propionate using sodium hydride as catalyst gave a lower yield of mixed condensation product than was obtained under similar conditions from benzoylation of methyl propionate. The lowered yield undoubtedly was due to mechanical difficulty in the condensations using *t*-butyl esters. The reaction mixtures invariably became quite thick, sometimes completely solid, with the result that considerable unreacted sodium hydride remained. This led to incomplete reaction and to vigorous, difficultly controllable decomposition of the unused sodium hydride during hydrolysis of the reaction mixtures. The use of a larger ratio of *t*-butyl propionate to methyl benzoate and a longer reaction period led to some improvement. Results were still, however, inferior to those from the benzoylation of methyl propionate. The mixed condensation of methyl furoate with methyl propionate using sodium hydride as catalyst gave methyl α-2-furoylpropionate in 42% yield as compared to a 28% yield from the same condensation using sodium methoxide as catalyst.

The use of metallic sodium as catalyst for ester condensations is attractive because of the irreversibility of such condensations.

$$2RCH_2CO_2R + 2Na \longrightarrow [RCH_2COC(R){-}CO_2R]^-Na^+ + NaOR + H_2$$

This condensing agent, however, causes the acyloin condensation[6] of aliphatic esters. Our attempt to effect the mixed condensation of methyl benzoate with methyl propionate using an equimolar ratio of the esters and 1 g. atom of sodium per mole of ester as condensing agent gave none of the desired mixed condensation product; at least some acyloin condensation of the methyl propionate occurred under these conditions as evidenced by the bright yellow color and other physical properties of the isolated products.[7] The reaction was quite vigorous and difficult to control. Use of an excess of methyl propionate as solvent for this condensation and a longer reaction time permitting quite slow addition of powdered sodium and better control of the reaction led to the formation of methyl α-benzoylpropionate in 34% yield, quite poor in comparison with that obtainable[1] using sodium methoxide as catalyst and forcing conditions. Attempted condensation of

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(6) See McElvain in Adams, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1948, Chap. 4.

(7) Unreacted methyl benzoate has a boiling point quite near that of propionoin, so that a sharp separation of products was not achieved.

methyl benzoate with *t*-butyl propionate using metallic sodium as catalyst gave none of the mixed condensation product; this reaction was exceedingly vigorous and difficult to control. In addition to recovered esters, small amounts of *t*-butyl alcohol, acyloin condensation products, and much resinous material were isolated from this reaction mixture.

One attempt was made to utilize diethylaminomagnesium bromide as catalyst for the condensation of methyl benzoate with methyl propionate. Although some methyl α-benzoylpropionate was formed (about 16%), this product was contaminated with much larger amounts of a nitrogen compound, probably N,N-diethylbenzamide resulting from reaction of the diethylaminomagnesium bromide at the carbonyl function of methyl benzoate. This result is consistent with those of Hauser and Walker[8] who utilized diethylaminomagnesium bromide as catalyst for the self-condensation of esters. In contrast to this poor result, diisopropylaminomagnesium bromide proved to be an excellent condensing agent for mixed condensations of methyl benzoate and methyl 2-furoate with aliphatic esters. These condensations were effected by adding an equimolar mixture of the acylating and aliphatic esters to an ether solution of diisopropylaminomagnesium bromide. The condensations proceeded rapidly and smoothly at the reflux temperature of ether to produce the mixed condensation products in good yield and with *virtually no self-condensation of the aliphatic ester.* Ethyl α-benzoylacetate, methyl α-benzoylpropionate and methyl α-2-furoylpropionate were produced by this procedure in yields of 49, 51, and 47%, respectively. These yields of mixed condensation products obtained by a simple, non-forcing procedure and using an equimolar mixture of the esters compare quite favorably with those obtained earlier[1] by a slower forced condensation requiring the use of an excess of the aliphatic ester. The virtual absence of self-condensation of the aliphatic esters may be explained on the assumption that the strong base, diisopropylaminomagnesium bromide, rapidly and completely converts the aliphatic ester to its anion. There remains then in the reaction mixture only the aromatic ester for condensation with the aliphatic ester anion. The correctness of this explanation is indicated by the fact that when the condensing agent was added in small portions to the mixture of esters, the yields of the mixed condensation products were diminished and some self-condensation of the aliphatic esters occurred. Under these conditions, the aliphatic ester anion is formed in the presence of excess of both esters permitting the result of both mixed and self-condensation. This inverse method of bringing together the reactants was necessary in the case of the condensation of methyl benzoate with methyl *n*-butyrate, since there was considerable formation of N,N-diisopropylbenzamide which could not be separated by distillation from methyl α-benzoyl-*n*-butyrate when the condensation was effected in the presence of excess of the condensing agent. Even under these conditions, however, the mixed condensation product was obtained in 44% yield.

Experimental[9]

Materials.—The esters used were either purchased from Matheson, Coleman and Bell, Inc., East Rutherford, N. J., or were prepared by direct esterification or by interaction of an acid chloride with an alcohol in pyridine solution. The esters were dried over sodium sulfate or calcium chloride, then over drierite, fractionally distilled and stored over drierite in glass-stoppered bottles until use. The sodium methoxide was a commercial product purchased from Matheson, Coleman and Bell. The sodium hydride also was a commercial product and generously supplied to us by E. I. du Pont de Nemours and Company, Electrochemicals Department, Wilmington, Delaware.

Condensations Using Sodium Methoxide.—These condensations were carried out as previously described.[1]

Condensations Using Sodium Hydride.—A mixture of 68 g. (0.5 mole) of methyl benzoate, 24 g. (1 mole) of sodium hydride and 150 ml. of dry benzene was maintained at reflux while 44 g. (0.5 mole) of methyl propionate was introduced during a period of 4 hours. Several round stones were placed in the reaction vessel to aid in pulverizing the sodium hydride. Heating was continued for 2 hours after all of the methyl propionate had been added. The reaction mixture was cooled in an ice-bath, and 15 ml. of methyl alcohol was added with stirring to destroy any unused sodium hydride. After stirring for 10 minutes, sufficient ether was added to obtain a fluid system. The ether slurry was thoroughly cooled in an ice-bath and poured into an ice-cold solution of 125 ml. of glacial acetic acid in an equal volume of water. When all solid material had disappeared, the system was twice extracted with 100-ml. portions of ether. The ether extracts were combined, washed once with water, then with sodium bicarbonate solution until acid-free and again with water. The ether extract was dried over sodium sulfate and then overnight over Drierite. After removal of the drying agent and ether, the residue was distilled through a 24-inch, total reflux, partial takeoff column packed with glass helices to give 54 g. (56%) of methyl α-benzoylpropionate, b.p. 119–120° (1 mm.), n^{25}D 1.5200. The product was characterized through its physical properties and conversion to 4-methyl-3-phenylisoxazalone, m.p. 121–122°.

A similar condensation was run using *t*-butyl propionate rather than methyl propionate. This reaction mixture became exceedingly thick during the condensation, and much unreacted sodium hydride remained. A 33% yield of *t*-butyl α-benzoylpropionate was obtained, b.p. 122-126° (5 mm.), n^{21}D 1.5128. The product was characterized by conversion to 4-methylphenylisoxazalone, m.p. 121–122°. Extending the reaction period for this condensation to 24 hours increased the yield of *t*-butyl α-benzoylpropionate to 47%.

Condensation of methyl 2-furoate with methyl propionate by the procedure described above led to the formation of methyl α-2-furoylpropionate in 42% yield; b.p. 120–122° (2 mm.), n^{25}D 1.4993. The product was characterized by conversion to α-2-furoylpropionamide, m.p. 182–183.5°; reported[10] m.p. 183°.

Condensations Using Sodium.—A mixture of 176 g. (2 moles) of methyl propionate, 68 g. (0.5 mole) of methyl benzoate and 5.4 g. (0.1 mole) of sodium methoxide was maintained at 60–70° with stirring while 23 g. (1 mole) of powdered sodium was introduced during 12 hours. Stirring and heating were continued for an additional 36 hours. Methyl alcohol (20 ml.) was added to dissolve residual sodium, and the reaction mixture was worked up as described in the preceding section. Fractional distillation of the product gave 41 g. of material boiling in the range 54–62° (2 mm.), colored deeply yellow, and probably consisting of unchanged methyl benzoate, propionoin and 3,4-diketohexanedione, as well as 33 g. (34%) of methyl α-benzoylpropionate, b.p. 117–124° (1 mm.), n^{25}D 1.5189. The product was characterized by conversion to 4-methyl-3-phenylisoxazalone, m.p. 120.5–121.5°.

A similar condensation using *t*-butyl propionate instead

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(8) C. R. Hauser and H. G. Walker, Jr., THIS JOURNAL, **69**, 295 (1947).

(9) All melting points reported were determined in capillary tubes and are uncorrected.

(10) A. Mironexcu and G. Ionaid, *Bul. Soc. Chem. Roumania*, **17**, 107 (1935).

of methyl propionate gave no *t*-butyl α-benzoylpropionate. A small amount of *t*-butyl alcohol, unchanged *t*-butyl propionate, and fractions colored deeply yellow, probably consisting of propionin and the corresponding diketone, were isolated. A large tarry residue remained from the fractional distillation of this product.

Condensations Using Diethylaminomagnesium Bromide.—Methyl propionate (0.2 mole) was condensed with methyl benzoate (0.2 mole) in the presence of diethylaminomagnesium bromide according to the procedure described below for diisopropylaminomagnesium bromide condensations. The diethylaminomagnesium bromide solution was prepared as described by Hauser and Walker.[11] Fractional distillation gave, in addition to lower boiling fractions, 16.6 g. of material, b.p. 133–134° (5 mm.), n^{21}D 1.5216. This last fraction corresponds in b.p. to the expected methyl α-benzoylpropionate. Qualitative test, however, indicated the presence of nitrogen, and quantitative determination by the Kjeldahl procedure showed 5.7% nitrogen. Assuming the nitrogen compound to be N,N-diethylbenzamide, this corresponds to the presence of 73.4% of this substance.

Condensations Using Diisopropylaminomagnesium Bromide.—The diisopropylaminomagnesium bromide for these condensations was prepared as described by Frostick and Hauser.[5] A mixture of 27.2 g. (0.2 mole) of methyl benzoate and 17.6 g. (0.2 mole) of ethyl acetate was added dropwise during 30 minutes to a solution of 0.4 mole of diisopropylaminomagnesium bromide in 250 ml. of ether. Stirring was continued for an additional 2 hours. The reaction mixture was poured onto a mixture of 300 g. of cracked ice and 25 ml. of concd. sulfuric acid. The ether layer was separated, and the aqueous layer twice extracted with 100-ml. portions of ether. The ether extracts were combined, washed with water, then with saturated sodium bicarbonate solution, and finally dried over sodium sulfate followed by Drierite. Removal of the drying agents and solvent followed by fractional distillation of the residue gave, after a very small amount of lower boiling material, 18.7 g. (49%) of ethyl benzoylacetate, b.p. 116–122° (2 mm.). This fraction did not give a test for nitrogen. It was characterized by conversion to ethyl α,α′-dibenzoylglutarate, m.p. 91°; reported[12] m.p. 92.5°.

A similar condensation of methyl benzoate (0.2 mole) with methyl propionate (0.2 mole) gave 19.6 g. (51%) of methyl α-benzoylpropionate, b.p. 132–136° (7–8 mm.), n^{21}D 1.5200. This material gave no test for nitrogen and was characterized by conversion to 4-methyl-3-phenylisoxazolone-5, m.p. 121–122°.

Condensation of methyl 2-furoate (0.2 mole) with methyl propionate (0.2 mole) by this same procedure gave 17 g. (47%) of methyl α-2-furoylpropionate, b.p. 114–116° (2 mm.), n^{25}D 1.5006. The product gave a negative nitrogen test and was characterized by conversion to α-furoylpropionamide, m.p. 182–183.5°; reported[10] m.p. 183°.

Condensation of methyl benzoate (0.2 mole) with methyl *n*-butyrate (0.2 mole) by this procedure gave 28.9 g. of material of b.p. 126–130° (2 mm.) corresponding to the expected b.p. of methyl α-benzoyl-*n*-butyrate. Kjeldahl analysis, however, showed the presence of 1.24% nitrogen, indicating contamination of the mixed condensation product with N,N-diisopropylbenzamide. Very little material boiling in the expected range for the self-condensation product of methyl *n*-butyrate was isolated. Another condensation of methyl benzoate (0.2 mole) with methyl *n*-butyrate (0.2 mole) was effected by the technique of adding the ether solution of diisopropylaminomagnesium bromide to the mixture of esters. This condensation led to the formation of 18.2 g. (47%) of methyl α-benzoyl-*n*-butyrate, b.p. 125–132° (3–4 mm.). This material did not give a test for nitrogen. Under these conditions of effecting the condensation, 9.8 g. (56%) of methyl α-*n*-butyryl-*n*-butyrate was also formed by self-condensation of methyl *n*-butyrate.

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[11] C. R. Hauser and H. G. Walker, Jr., THIS JOURNAL, **69**, 295 (1947).

[12] F. R. Japp and A. C. Mitchie, *J. Chem. Soc.*, **79**, 1010 (1901).

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Action of Hydrochloric and Nitric Acids on Some Derivatives of Phenothiazine[1]

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The formation of 3-chloro-10-methylphenothiazine (IV) by reductive chlorination of 10-methylphenothiazine-5-oxide (I) has been confirmed by synthesis of IV. Under similar conditions 10-(3-diethylaminopropyl)-phenothiazine-5-oxide gave 3(?)-chloro-10-(3-diethylaminopropyl)-phenothiazine while 10-(3-diethylaminopropyl)-phenothiazine-N,5-dioxide gave a dichlorophenothiazine. 3,7-Dichloro-10-methylphenothiazine-5-oxide furnished a tetrachlorophenothiazine as well as 3,7-dichloro-10-methylphenothiazine. Nitration of 10-methylphenothiazine and of I under ordinary conditions gave 3-nitro-10-methylphenothiazine and not the expected sulfoxide. Mechanisms for these and allied reactions are proposed.

The product obtained by heating 10-methylphenothiazine-5-oxide (I) with hydrochloric acid was recognized by Page and Smiles[2] as a chloro-10-methylphenothiazine, but the position of the chlorine atom was not established. In a similar "reductive chlorination" of 3-nitrophenothiazine-5-oxide, the chlorine atom was assumed to have entered the 7-position, but no proof for the structure of the resulting compound was offered.[3] We have now synthesized 3-chloro-10-methylphenothiazine (IV) in order to establish the structure of the product from the reaction of 10-methylphenothiazine-5-oxide with hydrochloric acid. 4-Chlorodiphenylamine was fused with sulfur in the presence of iodine, and the 3-chlorophenothiazine from this reaction was methylated with sodamide and methyl iodide. The product was identical with that from the above reaction.

A mechanism for the first phase of the reductive chlorination has been suggested by Page and Smiles.[2] It was based on the observation that 10-methylphenazothionium chloride can be isolated from the reaction of 10-methylphenothiazine-5-oxide (I) with hydrochloric acid,[4] and the same conditions initiate the reduction of this sulfoxide. Indeed, the *o*-quinonoid phenazothionium salts[5] are believed to be the materials undergoing a rearrangement underlying the reaction, and the protonation of the sulfoxide I with formation of the sulfonium base II should therefore be the first in this sequence of steps. It now appears that in the strongly acid medium required for the rearrangement the diacid

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[1] This study was carried out under Contract AF33 (038)-22947 between the University of Virginia and Wright Air Development Center, U. S. Air Force, Wright-Patterson Air Force Base, Dayton, Ohio.

[2] H. J. Page and S. Smiles, *J. Chem. Soc.*, **97**, 1112 (1910).

[3] F. Kehrmann and O. Nossekno, *Ber.*, **46**, 2809 (1913).

[4] E. de B. Barnett and S. Smiles, *J. Chem. Soc.*, **97**, 186 (1910).

[5] F. Kehrmann, *Ann.*, **322**, 1 (1902).