viously published.[5] The melting points of none of the three were raised by attempted recrystallization.

Picramide of 1-Amino-2-methyl-2-propanol (IV).—Four and two-tenths grams (0.014 mole) of 2,2-dimethylethylenimmonium picrate was refluxed for one hour in 15 ml. of acetonitrile. Most of the acetonitrile was then removed by passing dry air over the reaction mixture. Ethyl acetate (3 ml.) was added and the mixture was cooled in ice. The yellow picramide of 1-amino-2-methyl-2-propanol was removed by filtration and washed once with 2 ml. of ice-cold ethyl acetate; yield 1.65 g. (40%), m.p. 156–158°. Sublimation at 140° (0.4 mm.) gave an analytical sample, m.p. 160.6–161.6°.

The structure of the picramide was established by an independent synthesis. Equivalent amounts of picryl chloride and 1-amino-2-methyl-2-propanol were allowed to react in absolute ethanol. This picramide had a m.p. 158–160° and a mixed m.p. with the preparation just described was not depressed.

Anal. Calcd. for $C_{10}H_{12}N_4O_7$: C, 40.01; H, 4.03; N, 18.65. Found: C, 40.16; H, 4.22; N, 18.33.

β-Aminoether Picrates (V). A. β-Methoxybutylammonium Picrate.—The following preparation is a representative procedure used in making the aliphatic aminoether picrates described in Table I.

B. β-Phenoxyisobutylammonium Picrate.—2,2-Dimethylethylenimmonium picrate (21 g., 0.07 mole) was kept at 80° with 20 g. of phenol (0.21 mole) for 2 hours and then was allowed to stand overnight. The reaction mixture was filtered without cooling to remove 2.27 g. (13%) of ammonium picrate.

Ethanol (40 ml. of 95%) was added to the filtrate and upon cooling 8 g. of a brown, crystalline precipitate was obtained. Two successive additions of 20 ml. of 50% ethanol gave a total yield of 13.9 g. of crude material, m.p. 150–165°. The crude product was extracted with 95% ethanol to give 5.65 g. (20%) of β-phenoxyisobutylammonium picrate, m.p. 195–200°. Repeated recrystallization from absolute ethanol gave an analytical sample, m.p. 200.0–200.5°. Analytical data appear in Table I.

The residue from the ethanol extraction was determined to be picramide in a mixed m.p. with an authentic sample, m.p. 188–190°; yield 8.0 g. (50%).

β-Phenoxy-*t*-butylammonium Picrate.—One-half gram (0.003 mole) of β-phenoxy-*t*-butylamine[3] in 5 ml. of toluene was added dropwise to 0.70 g. (0.003 mole) of picric acid dissolved in 10 ml. of toluene. The picrate (1.1 g., 91%) was washed with carbon tetrachloride and dried, m.p. 189–190°. Recrystallization from absolute ethanol gave an analytical sample, m.p. 194.0–195.0°

A mixture of this sample with that of β-phenoxyisobutylammonium picrate gave a lowered m.p. 175–190°. Since the structure of β-phenoxy-*t*-butylammonium picrate has been established[3] it is suggested that the picrate of m.p. 200.0–200.5° is the isomeric β-phenoxyisobutylammonium picrate. Therefore, 2,2-dimethylethylenimmonium picrate must have opened at the tertiary carbon with phenol as it does with alcohols.

Anal. Calcd. for $C_{16}H_{18}N_4O_8$: C, 48.73; H, 4.60; N, 14.21. Found: C, 48.76; H, 4.60; N, 14.15.

β-Aminoethers. β-Methoxybutylamine.—The amino ethers compiled in Table II were prepared by a method similar to the following procedure for β-methoxybutylamine.

The picrate of β-methoxybutylamine, m.p. 145–148° (33.2 g., 0.1 mole) was dissolved in 100 ml. of water, 150 ml. of concentrated hydrochloric acid was added, and the mixture was allowed to stand for 3 hours with occasional stirring. Picric acid was removed by filtration of the cold mixture and last traces were removed by extraction with 20-ml. portions of toluene until a last portion of toluene remained colorless. The water solution was evaporated nearly to dryness at room temperature and the aminoether hydrochloride was finally dried in a vacuum desiccator; yield 13 g. (93%). The amino ether hydrochloride was covered with 10 ml. of absolute methanol and treated with 6 g. (0.11 mole) of sodium methoxide. The reaction mixture was warmed one-half hour on the steam-bath, cooled, and filtered. Distillation removed the methanol and after a small forerun at 110–118°, the main fraction of β-methoxybutylamine was collected at 118–121°; yield 6.8 g. (67%).

The analysis for nitrogen on the aminoether prepared in this way resulted in a high value, evidently due to the presence of some ammonia in the sample. The aminoether was therefore converted to the hydrochloride in ether solution with dry hydrogen chloride. The hydrochloride was recrystallized from acetone to remove ammonium chloride but was so hygroscopic the melting point could not be determined. The solid hydrochloride was allowed to stand on solid potassium hydroxide which had been covered with anhydrous ether. After adding a trace of water and allowing to stand a week, the ether solution of the amino ether was fractionated to give pure β-methoxybutylamine, b.p. 118–121°, of constant refractive index. Physical constants and analyses appear in Table II.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

A New Aldehyde Synthesis and its Use in the Characterization of Organic Halides

BY HENRY M. FALES[1]

RECEIVED MARCH 18, 1955

Aliphatic and aromatic Grignard reagents have been found to add to the double bond of the methiodide of 6-methyl-3-*p*-tolyl-3,4-dihydroquinazoline (II), itself formed by the reaction between *p*-toluidine, formaldehyde and formic acid. The resulting substituted tetrahydroquinazolines were hydrolyzed and the aldehydes of one more carbon atom converted directly to their 2,4-dinitrophenylhydrazone derivatives. A route to labeled aldehydes from labeled formaldehyde is suggested.

The conversion of a Grignard reagent to an aldehyde or aldehyde acetal with one more carbon atom has been accomplished by a great variety of reagents. The methods generally involve addition of a Grignard reagent to a C=X linkage (X = O,S,N) or the displacement of an alkoxide group from an orthoformate. Smith and Nichols,[2] after reviewing the field, conclude that N-ethoxymethyleneaniline and ethyl orthoformate are the most satisfactory reagents. The main disadvantage of ethyl orthoformate is the frequent necessity for the application of heat over long periods to cause the reaction to proceed at a reasonable rate while N-ethoxymethyleneaniline is costly and troublesome to prepare.

A new procedure, illustrated by the following reaction sequence I to V[3] accomplishes the same end without the above complications and further supplies the aldehyde as an easily hydrolyzed derivative III which may be converted directly to the corresponding 2,4-dinitrophenylhydrazone (IV). In spite of its apparent complexity the dihydroquina-

(1) Laboratory of Chemistry of Natural Products, National Heart Institute, National Institutes of Health, Department of Health, Education and Welfare, Bethesda 14, Maryland.

(2) L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 489 (1941).

(3) This reaction sequence was evolved during a study of methods for the synthesis of di- and tetrahydroquinazolines in connection with U. S. Army Ordnance Project #DA-30-069-ORD-884.

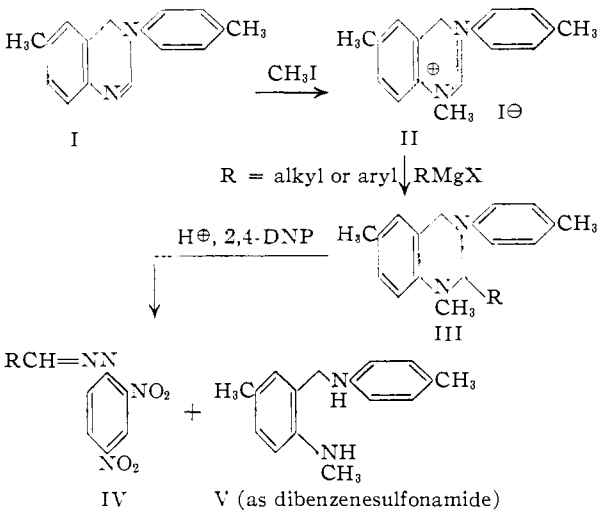
TABLE I

EXAMPLES OF THE SYNTHESIS

Grignard reagent	Product (isolated as 2,4-dinitrophenylhydrazone)	Yield, %	M.p., °C.	Ref.
CH_3MgI	CH_3CHO	78	147	*c*
n-C_4H_9MgBr	n-C_4H_9CHO	87	106	*d*
$C_6H_5CH_2MgCl$	$C_6H_5CH_2CHO$	74	120–121	*e*
n-$C_{12}H_{25}MgBr$	n-$C_{12}H_{25}CHO$	73	107–108	See Exptl. part
$C_2H_5(CH_3)CHMgBr$	$C_2H_5(CH_3)CHCHO$	34	128	*f*
$(CH_3)_2CHMgBr$	$(CH_3)_2CHCHO$	45	183 (lit. 187°)	*g*
C_6H_5MgBr	C_6H_5CHO	95	237	*h*
p-$CH_3OC_6H_4MgBr$	p-$CH_3OC_6H_4CHO$	80	253	*i*
2,5-Dimethoxyphenylmagnesium bromide	2,5-Dimethoxybenzaldehyde	34	198	*j*
2,5-Dimethoxyphenyllithium + magnesium iodide	2,5-Dimethoxybenzaldehyde	23	198	*j*
2,5-Dimethoxyphenyllithium	HCHO	94	165–166	*h*
C_6H_5Li	C_6H_5CHO	29	237	*h*
o-$CH_3OC_6H_4MgBr$	o-$CH_3OC_6H_4CHO$	*a*	249	*k*
Cyclopentylmagnesium bromide	Cyclopentanal	*a*	158	*l*
2,6-Dimethylphenylmagnesium iodide	2,6-Dimethylbenzaldehyde	*a*	252	*m*
4-Biphenylmagnesium iodide	Biphenyl-4-carboxaldehyde	*a*	242–243	*n*
2,4-Dimethylphenylmagnesium iodide	2,4-Dimethylbenzaldehyde	*a*	228–229	*m*
p-ClC_6H_4MgBr	p-ClC_6H_4CHO	63[b]	266–268	*o*
β-Bromonaphthalene	β-Naphthaldehyde	62[b]	270	*p*

[a] No effort was made to determine yields in these examples which were run according to the test-tube procedure. [b] These yields were based on aryl halide instead of Grignard reagent. The aldehydes were isolated in the free state before conversion to 2,4-dinitrophenylhydrazones. [c] W. M. D. Bryant, THIS JOURNAL, **58**, 2335 (1936). [d] H. J. Backer and N. H. Haack, *Rec. trav. chim.*, **57**, 225 (1938). [e] R. T. Gilsdorf and F. F. Nord, THIS JOURNAL, **72**, 4327 (1950). [f] V. I. Lyubomilov and A. P. Terent'ev, *J. Gen. Chem.*, **21**, 1479 (1951). [g] W. M. D. Bryant, THIS JOURNAL, **54**, 3758 (1932). [h] John D. Roberts and Charlotte Green, *ibid.*, **68**, 214 (1946). [i] Michele Ragno, *Gazz. chim. ital.*, **75**, 175 (1945). [j] R. A. Barnes and I. Nicholson, private comm. [k] E. K. Harvill and R. M. Herbst, *J. Org. Chem.*, **9**, 21 (1944). [l] R. E. Dunbar and H. Adkins, THIS JOURNAL, **56**, 442 (1934). [m] W. Th. Nauta, M. J. E. Ernsting and A. C. Faber, *Rec. trav. chim.*, **60**, 915 (1941). [n] D. H. Hey, *J. Chem. Soc.*, 2476 (1931). [o] O. L. Brady and S. G. Jarrett, *ibid.*, 1021 (1950). [p] G. B. Pickering and J. C. Smith, *Rec. trav. chim.*, **69**, 535 (1950).

zoline (I) is prepared in a one-step process by the interaction of *p*-toluidine, formaldehyde and formic acid.[4] The methiodide (II) forms quantitatively when the amine is shaken or refluxed with methyl iodide in benzene. Although it appears quite insoluble in ether, this methiodide reacts smoothly with primary aliphatic and aromatic Grignard reagents in this solvent to produce the tetrahydroquinazolines (III) in high yield. In favorable cases, the tetrahydroquinazolines may be isolated as crystalline compounds.



I II III IV V (as dibenzenesulfonamide)

The complete sequence from the methiodide can be carried out on a test-tube scale in a few minutes with no special precautions. In fact, the dihydroquinazoline methiodide may be added along with the halide and ether to the magnesium. It does not hinder Grignard formation and even assists the reaction in those cases where the Grignard reagent normally precipitates as an oil. The method would appear to have utility in the qualitative identification of aliphatic and aromatic halides as 2,4-dinitrophenylhydrazones of the corresponding aldehydes.

Results of several experiments are given in Table I. The yields were obtained from only one small-scale run in each case and are presumably not the maximum obtainable. In the final two cases shown the aldehydes were isolated in the free state by hydrolysis of the tetrahydroquinazolines and steam distillation or extraction.

When the organomagnesium reagents were replaced by their lithium analogs a marked lowering of yield was observed. Thus the increased coördination tendency of magnesium compared with lithium appears to have an important effect on the reaction,[5] and suggests a mechanism which involves primary coördination of the metallic atom with a nitrogen atom of the methiodide. A similar mechanism has been suggested by Swain for addition of Grignard reagents to nitriles.[6]

In the case of hydroquinone dimethyl ether the lithium aryl appeared to reduce the dihydroquinazo-

(4) E. C. Wagner, *J. Org. Chem.*, **2**, 157 (1937).

(5) Replacement of magnesium reagents by lithium analogs is also known to cause an increase in the ratios of 1,2- to 1,4-addition in the reaction with α,β-unsaturated systems and the same explanation has been offered. See H. Gilman and R. H. Kirby, THIS JOURNAL, **63**, 2046 (1941).

(6) C. G. Swain, *ibid.*, **69**, 2306 (1947).

line salt to the unsubstituted tetrahydroquinazoline (III, R = H), since upon hydrolysis a 94% yield of formaldehyde 2,4-dinitrophenylhydrazone was obtained. The magnesium reagent of hydroquinone dimethyl ether, when formed directly by magnesium on the halide or indirectly by the addition of magnesium iodide to the previously formed lithium compound, underwent normal reaction to yield the aryl aldehyde derivative.

The reagent employed in this synthesis might well be replaced by simpler straight-chain tetra-alkyl formamidinium salts, although there appear to be no examples in the literature of the addition of Grignard reagents to such salts. Recently Elderfield and Meyer[7] have noted a similar addition of phenyllithium to a free 1,2-dialkylbenzimidazole and have hydrolyzed the product to a low yield of the corresponding ketone. On the other hand the free dihydroquinazoline (I) did not successfully undergo reaction with either methylmagnesium iodide or methyllithium. Salt formation *via* the methiodide probably assists these reactions by increasing the polarity of the bond being attacked. It is suggested that benzimidazole methiodides and organomagnesium compounds would afford improved yields in this reaction.

Manganese dioxide prepared according to Attenburrow[8] has been found to oxidize 6-methyl-3-*p*-tolyl-1,2,3,4-tetrahydroquinazoline to the dihydroquinazoline (I) in high yield. Since the tetrahydroquinazoline is itself prepared in a nearly quantitative yield by the action of formaldehyde (or presumably C^{14}-formaldehyde) on N-(2-amino-5-methylbenzyl)-*p*-toluidine,[9] the sequence constitutes a convenient method for the synthesis of radioactive aldehydes labeled at the aldehyde carbon atom.

Experimental[10]

6-Methyl-3-*p*-tolyl-3,4-dihydroquinazoline (I).—The following is a slight modification of the procedure described by Wagner.[4] *p*-Toluidine (428 g.) was stirred in an open beaker with 37% formalin (325 ml.) until a heavy solid precipitated. A solution of 88% formic acid (394 ml.) was added rapidly and the red mixture heated just below its boiling point for 2 hours. The hot reaction product was made strongly alkaline with sodium hydroxide and the mixture of methylated *p*-toluidines volatilized with steam. The residue in the flask was cooled and washed by decantation with several portions of water and air-dried. The resulting yellow gum was stirred with cold ether and filtered. The precipitate was recrystallized once from methanol or ethanol, m.p. 158–160° (lit. 163°[4]), yield 109 g.

The methiodide (II) was formed easily by shaking the dihydroquinazoline with an excess of methyl iodide in benzene solution in a pressure bottle until no more precipitate formed. The white salt which precipitated was suitable for use in the synthesis without further purification but it was easily recrystallized from alcohol or a large volume of hot water, m.p. 272–274°.

Anal. Calcd. for $C_{17}H_{19}N_2I$: C, 53.98; H, 5.06. Found: C, 53.70; H, 4.99.

Procedure for Grignard Reactions (a).—In several of the examples listed above no attempt was made to ascertain yields. One to three drops of the halide was crushed with several magnesium turnings in a test-tube containing anhydrous ether. A wad of cotton in the top of the test-tube served to protect the contents against moisture. After the reaction had subsided, dihydroquinazoline methiodide (II) was added in spatulafulls until no more remained undissolved after 15 min. Alcohol (5 ml.) and dilute sulfuric acid (2 ml.) were added and the mixture was rapidly filtered. Addition of 2,4-dinitrophenylhydrazine reagent[11] precipitated the derivative which was filtered and recrystallized from an appropriate solvent. When the Grignard reagent precipitated as an oil, improved results were obtained by adding the dihydroquinazoline salt along with the halide to the magnesium in ether. The magnesium was then crushed with a large stirring rod to initiate and propagate the reaction. This technique also improved the yields of aldehyde from especially reactive halides such as benzyl and allyl chlorides and was never found to inhibit Grignard formation.

(b).—To determine yields, the halide (0.5–1.0 g.) was combined with a slight excess over the calculated amount of magnesium or lithium in anhydrous ether (4 ml.) and stirred rapidly under nitrogen. After the reaction had subsided ether was added to bring the total volume to 15 ml. No effort was made to obtain maximum yield of Grignard reagent since a 5-ml. aliquot was subsequently withdrawn and titrated using methyl orange as an indicator in order to determine the true concentration of organometallic reagent. The calculated quantity of dihydroquinazoline methiodide (II) was added in small portions. In favorable cases the methiodide slowly but completely dissolved. Heavy gums formed with the secondary halides, but they dissolved very slowly upon continued stirring. In these cases, thorough mixing with a Hershberg-type stirrer was essential. When the solution appeared homogeneous the excess ether was evaporated in a current of nitrogen. Alcohol (5 ml.) was next added followed by a 10% molar excess of 2,4-dinitrophenylhydrazine reagent.[11] The precipitated derivative was collected on a tared glass filter, washed with 5% sulfuric acid, water, 50% ethanol in that order and finally dried. The 2,4-dinitrophenylhydrazones were identified by m.p. and mixture m.p. Cyclopentanal, *sec*-valeraldehyde, 2,6-dimethylbenzaldehyde, 2,4-dimethylbenzaldehyde and biphenyl-4-carboxaldehyde were identified by m.p. alone.

Tridecanal 2,4-dinitrophenylhydrazone was prepared as described above and recrystallized from cyclohexane, m.p. 108–109°.

Anal. Calcd. for $C_{19}H_{30}N_4O_4$: C, 60.29; H, 7.99. Found: C, 60.41; H, 7.98.

(c) ***p*-Chlorobenzaldehyde.**—*p*-Chlorobromobenzene (1.9 g.) was combined with magnesium turnings (0.31 g.) in dry ether. After the initial reaction had subsided, the methiodide (II, 3.8 g.) was added and then allowed to stir 2 hours. Hydrochloric acid (3 ml., 10%) was next added and the mixture subjected to steam distillation. The *p*-chlorobenzaldehyde (0.89 g., 63%) which distilled over melted at 45–47° and did not depress authentic material. It formed a 2,4-dinitrophenylhydrazone, m.p. 266–268°.[12] **β-Naphthaldehyde** was isolated in 62% yield by allowing the Grignard reaction product from β-bromonaphthalene (2.55 g.), magnesium (0.30 g.) and II (3.8 g.) to stir ½ hour in the presence of an excess of formalin solution[13] and acetic acid. The ether layer was removed and evaporated leaving an oil which slowly crystallized (1.16 g., 62%) m.p. 55–60°. One recrystallization from water raised the m.p. to 58–60°. The aldehyde formed a 2,4-dinitrophenylhydrazone, m.p. 270°.[14]

1,6-Dimethyl-2-phenyl-3-*p*-tolyl-1,2,3,4-tetrahydroquinazoline.—The reaction between II and phenylmagnesium bromide was performed as described above but the Grignard complex was hydrolyzed with aqueous alcoholic ammonium chloride to avoid extensive hydrolysis. After evaporation of the residual ether, the alcoholic mixture was warmed and filtered. The product crystallized on cooling; recrystallized from petroleum ether, m.p. 105°.

(7) R. C. Elderfield and V. B. Meyer, THIS JOURNAL, **76**, 1891 (1954).

(8) J. Attenburrow, *et al.*, *J. Chem. Soc.*, 1094 (1952).

(9) A. Eisner and F. C. Wagner, THIS JOURNAL, **56**, 1938 (1934).

(10) All melting points were observed on a Kofler microscope equipped with polarizer and are corrected. Microanalyses were performed by J. Alicino, Metuchen, N. J., and Dr. W. C. Alford and Staff, National Institute of Arthritis and Metabolic Diseases, Bethesda, Maryland, and Clark Microanalytical Laboratories, Urbana, Illinois.

(11) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(12) See Table I, footnote *o*.

(13) Formalin was included in an effort to effect metathesis with the β-naphthaldehyde.

(14) See Table I, footnote *p*.

Anal. Calcd. for $C_{28}H_{24}N_2$: C, 84.10; H, 7.37. Found: C, 84.10; H, 7.10.

N-(3-Methyl-6-methylaminobenzyl)-*p*-toluidine Dibenzenesulfonamide (IV).—Acetone was added to the filtrates from two of the above syntheses (R = C_6H_5, CH_3) to precipitate excess 2,4-dinitrophenylhydrazine reagent. The filtrate was made strongly basic with sodium hydroxide (20%) and excess benzenesulfonyl chloride added. The precipitate which formed after several hours of shaking was collected and recrystallized from ethanol, m.p. 159–161°.

Anal. Calcd. for $C_{22}H_{28}N_2S_2O_4$: C, 64.59; H, 5.42. Found: C, 64.73; H, 5.32.

Manganese Dioxide Oxidation of 6-Methyl-3-*p*-tolyl-1,2,-3,4-tetrahydroquinazoline.—The tetrahydroquinazoline was prepared according to Eisner and Wagner[9] from formaldehyde and N-(2-amino-5-methylbenzyl)-*p*-toluidine. The product even when pure exhibited a variable m.p. from 141–151° possibly due to polymorphism. After one recrystallization from ethanol, the tetrahydroquinazoline (0.700 g.) was stirred with specially prepared manganese dioxide (1.5 g.)[8] in benzene–ether (1:1, 20 ml.) for 4 hours. The solvents were removed from the product with a current of dry nitrogen and the product was recrystallized from ligroin, m.p. 158° (0.558 g., 81%) alone or when mixed with authentic II.

BETHESDA, MD.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Reactions with Halogen Substituted Xanthones. II[1]

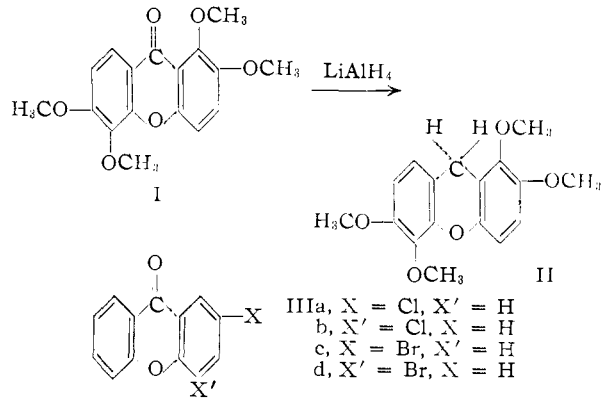
BY AHMED MUSTAFA, WAFIA ASKER AND MOHAMED EZZ EL-DIN SOBHY

RECEIVED APRIL 12, 1955

Reduction of halogen-substituted xanthones (IIIa-d) with lithium aluminum hydride and with metallic sodium and alcohol led to the formation of xanthene with loss of the halogen. The reduction of xanthone to xanthene with lithium aluminum hydride is discussed. Xanthones IVa-b and the thiaxanthone IVc with halogen in position I condense with aromatic thiols in the presence of potassium hydroxide, to yield the corresponding arylmercapto derivatives Va-c which are oxidized readily to the corresponding sulfone derivatives VIa-c. Whereas IIIa undergoes photochemical addition reaction with xanthene in sunlight to give the carbinol VIIb, IIIb effects the photochemical dehydrogenation of xanthene to 9,9′-bixanthene. 9-Phenyl-2-chloroxanthene (VIIIb) undergoes photochemical oxidation in sunlight in the presence of oxygen, yielding 9-phenyl-2-chloroxanthyl peroxide (IXb).

(a) Reactions with Lithium Aluminum Hydride.—Recently, Shah, Kulkarni and Joshi[2] have shown that when desussatin methyl ether (I), a naturally occurring xanthone, is boiled with excess of lithium aluminum hydride in ether for about 12 hours to give the xanthene derivative II, xanthone is reduced by this reagent to xanthydrol.[3] Mustafa and Hilmy[1] previously have reported that reduction of xanthones, *e.g.*, xanthone, 1,2-benzo- and 3,4-benzoxanthones, with the same reagent proceeds a step further to give the corresponding xanthenes[4] in an almost quantitative yield when the reaction was carried out in boiling ether–benzene solution.

We now have investigated the action of excess lithium aluminum hydride on halogen substituted xanthones, namely, 2-chloro- (IIIa), 4-chloro- (IIIb), 2-bromo- (IIIc) and 4-bromoxanthone (IIId) in boiling ether–benzene solution and have obtained xanthene in each case with the loss of halogen.[5] Similar results are obtained when IIIa-d are treated with metallic sodium and alcohol under the same experimental conditions by which xanthone is reduced to xanthene.[6,7]



On the other hand, the reduction of 1-chloro-4-methylxanthone with lithium aluminum hydride under the same conditions, led, without loss of halogen, to the formation of a colorless product believed to be 1-chloro-4-methylxanthydrol. The formation of the hydrol and not the methylene derivative may be attributed to the precipitation phenomenon.[2,4]

(b) Reactions with Aromatic Thiols.—In conjunction with a study of pharmacological action of sulfur-containing compounds against bilharziasis,[8] the action of the thiolate anion on halogen substituted xanthones IVa-b and 1-chloro-4-methylthiaxanthone (IVc) now has been investigated. The lability of the halogen in halogenated xanthones was demonstrated by effecting a replacement reac-

(1) For part I *cf.* A. Mustafa and Mustafa K. Hilmy, *J. Chem. Soc.*, 1343 (1952).

(2) R. C. Shah, A. B. Kulkarni and C. G. Joshi, *J. Sci. Ind. Res.*, **13B**, 186 (1954).

(3) *Cf.* R. Mirza and R. Robinson, *Nature*, **166**, 929, 997 (1950).

(4) Generally, carbonyl compounds are reduced to carbinols by lithium aluminum hydride. Scattered observations of further reduction of the carbinol to the methylene derivative have been reported. B. Witkop (THIS JOURNAL, **72**, 614 (1950)) observed hydrogenolysis of spiro-(cyclopentane-1,2′-dihydroindoxyl) to spiro-(cyclopentane-1,2′-dihydroindole). L. H. Conover and D. S. Tarbell (*ibid.*, **72**, 3586 (1950)) have shown that 4,4′-dimethoxybenzophenone and N,N-dialkyl-*p*-aminobenzophenone gave a considerable amount of 4,4′-dimethoxydiphenylmethane and of N,N-dialkyl-*p*-aminodiphenylmethane, respectively, on reduction with lithium aluminum hydride.

(5) *Cf.* the reduction of 2,7-dibromoxanthone (A. Lespagnol and B. Bertrand, *Bull. soc. chim.*, **10**, 50 (1943)) and of 2,7-diiodoxanthone (B. Bertrand and A. Lespagnol, *ibid.*, **15**, 428 (1948)) with aluminum isopropoxide to give the propyl ether of the xanthydrol derivative without the loss of halogen.

(6) J. Heller and St. v. Kostanecki, *Ber.*, **41**, 1325 (1908).

(7) This part was carried out with Mohamed Ezz El-Din Sobhy.

(8) A. Mustafa, A. H. E. Harhash and M. Kamel, THIS JOURNAL, **77**, 3860 (1955).