

the isomers, which have boiling points in close proximity. Finally, preparation of the 1,3 sulfites by an independent route from 2-chlorotrimethylene sulfite proves beyond doubt that a rearrangement as postulated above, does take place.

A significant and almost identical difference in the refractive indices for each isomeric pair (0.011 and 0.010) tends to corroborate the formation of these isomeric substances along the lines formulated.

#### EXPERIMENTAL

*3-Chloropropylene sulfite* was prepared by the method of De la Mare *et al.*<sup>1</sup> Fractional distillation of the reaction mixture gave 3-chloropropylene sulfite (9.7 g.; 67.3%) b.p. 210°/760 mm.,  $n_D^{25}$  1.4807.

*Anal.* Calcd. for  $C_3H_5ClO_3S$ : C, 23.0; H, 3.20; Cl, 22.70; S, 20.50. Found: C, 23.5; H, 3.67; Cl, 19.69; S, 22.47.

*2-Chloropropane-1,3-diol* was prepared by the method of Glattfeld *et al.*<sup>4</sup> The product obtained (60 g.) had b.p. 96–98°/3 mm.,  $n_D^{25}$  1.4817.

*2-Chlorotrimethylene sulfite* was prepared by the method of De la Mare *et al.*<sup>1</sup> Distillation of the reaction mixture under reduced pressure gave, in the temperature range, 70–90°/15 mm. a mixture of *cis*- and *trans*-2-chlorotrimethylene sulfite which was used for reactions with phenol and *o*-cresol without further treatment.

*Anal.* Calcd. for  $C_3H_5ClO_3S$ : C, 23.0; H, 3.20; Cl, 22.7; S, 20.5. Found: C, 23.0; H, 3.1; Cl, 22.5; S, 20.3.

*Reaction of phenol with 3-chloropropylene sulfite.* To absolute ethanol (25 cc.) were added gradually 1.15 g. ( $1/20$  g. atom) of sodium in thin slices so that the mixture boiled steadily; heating was then continued on steam bath and pure redistilled phenol (4.7 g.  $1/20$  mole) added. This was followed by redistilled 3-chloropropylene sulfite (7.9 g.;  $1/20$  mole). After one hour of heating, the mixture was filtered hot and precipitate washed with 3 portions of absolute ethanol. The filtrate and washings were distilled under reduced pressure and the residue under further reduced pressure to yield the following substances:

(a) 2-Phenoxy-1,3-propylene sulfite (II) (7.1 g.; 65.7%) white oil, b.p. 77–81°/8 mm.,  $n_D^{25}$  1.5130. Infrared spectrum (in chloroform)  $\nu_{max}$ : 1470(s), 1250(m) (=C—O— grouping), 1189(s) (S=O stretch. vibration), 1071 (m), 1000 (m), 885 (m), 828 (w), 960 (m) (S—O stretch. vibration), 810 (m), 688 (s)  $cm^{-1}$  (s, strong; m, medium; w, weak).

(b) 1-Phenoxy-2,3-propylene sulfite (I) (0.9 g.; 8.3%) white oil, b.p. 85–91°/8 mm.,  $n_D^{25}$  1.5020. Infrared spectrum (in chloroform)  $\nu_{max}$ : 1471 (s), 1253 (m) (=C—O— grouping), 1221 (s) (S=O stretch. vibration), 1105 (w), 1080 (w), 1072 (w), 1025 (w), 950 (s) (S—O stretch. vibr.) 885 (w), 841 (m), 810 (m), 688 (s)  $cm^{-1}$ .

The two fractions gave almost identical analyses.

*Anal.* Calcd. for  $C_9H_{10}O_4S$ : C, 50.45; H, 4.7; S, 14.97. Found for II: C, 50.1; H, 4.4; S, 14.7. Found for I: C, 50.1; H, 4.5; S, 14.6.

*Reaction of o-cresol with 3-chloropropylene sulfite.* Same procedure as for phenol, but 5.5 g. ( $1/20$  mole) of *o*-cresol. The following isomers were obtained:

(a) 2-*o*-Cresoxy-1,3-propylene sulfite (IIa) (7.3 g.; 63.4) white oil, b.p. 99–101°/30 mm.,  $n_D^{25}$  1.5199. Infrared spectrum (in chloroform)  $\nu_{max}$ : 1465 (m), 1385 (w), 1330 (m), 1300 (m), 1250 (s) (=C—O— grouping), 1192 (s) (S=O stretch. vibration), 1169 (s), 1104 (s), 1040 (m), 960 (m) (S—O stretch. vibr.), 844 (s).

(b) 1-*o*-Cresoxy-2,3-propylene sulfite (Ia), (1.1 g.; 9.6) white oil, b.p. 106–107°/30 mm.,  $n_D^{25}$  1.5099. Infrared spec-

trum (in chloroform)  $\nu_{max}$ : 1385 (w), 1300 (m), 1250 (s) (=C—O— grouping), 1220 (s), (S=O stretch. vibr.), 1168 (s), 1104 (s), 1040 (m), 950 (s) (S—O stretch. vibr.) 844 (s).

Calcd. for  $C_{10}H_{12}O_4S$ : C, 52.61; H, 5.3; S, 14.04. Found for IIa: C, 52.5; H, 5.1; S, 13.8. Found for Ia: C, 52.58; H, 5.1; S, 13.85.

*Reaction of phenol with 2-chlorotrimethylene sulfite.* The procedure was the same as was used for phenol with 3-chloropropylene sulfite. Distillation under reduced pressure yielded 2-phenoxy-1,3-propylene sulfite (II) (8.2 g.; 75.9) white oil of b.p. 81–82°/9 mm.,  $n_D^{25}$  1.5131.

*Reaction of o-cresol with 2-chlorotrimethylene sulfite.* Same procedure as for *o*-cresol with 3-chloropropylene sulfite. Distillation under reduced pressure yielded 2-*o*-cresoxy-1,3-propylene sulfite (IIa) (8.7 g.; 75.6) white oil of b.p. 101–102°/30 mm.,  $n_D^{25}$  1.5197.

Examination of both compounds (II and IIa) as synthesized by independent route from 2-chlorotrimethylene sulfite, in the infrared spectrum showed identical contours of the absorption bands particularly in the 1180–1250  $cm^{-1}$  region.

The infrared absorption spectra were obtained by means of a Perkin-Elmer Model 12c, double beam spectrophotometer, fitted with a sodium chloride prism.

*Acknowledgment.* I am indebted to Professor H. Heiman for making laboratory space available to me at the Department for Industrial Chemistry of the Israel Institute of Technology, Haifa, and to the Chemistry Department for the infrared spectra. I am grateful to Dr. S. Fruman of this department for helpful discussion.

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### Reaction of 2,4-Dinitrophenylhydrazine with Aralkyl Alcohols

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The reaction of 2,4-dinitrophenylhydrazine (D-NP) with aldehydes and ketones is generally accepted as being a specific test for the presence of the carbonyl function in organic molecules.<sup>1–3</sup> It is also stated<sup>1</sup> that interfering materials are mainly those that oxidize the hydrazine to form tars, and substances that hydrolyze in the conditions of the reaction to give an aldehyde or a ketone, which may then react with the reagents.

According to Braude<sup>4</sup> further interference may be caused by alcohols containing ethylenic or aromatic substituents conjugated with the carbinol

(1) S. Siggia, *Quantitative Organic Analysis via Functional Groups*, 2nd ed., John Wiley & Sons, New York, 1954, p. 31.

(2) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., John Wiley & Sons, New York, 1956, p. 97.

(3) K. G. Stone, *Determination of Organic Compounds*, McGraw-Hill Book Co., New York, 1956, p. 73.

(4) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 1762 (1951).

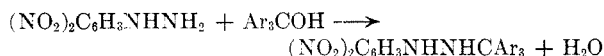
(4) J. W. E. Glattfeld, G. Leavell, G. E. Spieth, and D. Hutton, *J. Am. Chem. Soc.*, 53, 3169 (1931).

TABLE I  
 1-(2,4-DINITROPHENYL)-2-ARALKYLHYDRAZINES, RNHNHC<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)<sub>2</sub>

R-	M.P., °C.	Crystal- lized from	Appear- ance	Reflux Time	Yield, %	Formula	Analysis			
							Carbon		Hydrogen	
							Calcd.	Found	Calcd.	Found
Trityl-	193-194	CCl <sub>4</sub>	Yellow needles	2 hr.	53	C <sub>25</sub> H <sub>20</sub> O <sub>4</sub> N <sub>4</sub>	68.2	68.0	4.6	4.8
Phenyldi( <i>p</i> -tolyl)- methyl-	160	CHCl <sub>3</sub>	Yellow prisms	10 min.	49	C <sub>27</sub> H <sub>24</sub> O <sub>4</sub> N <sub>4</sub>	69.2	69.2	5.1	5.5
Diphenyl( <i>p</i> -tolyl)- methyl-	181	CCl <sub>4</sub>	Orange needles	10 min.	47	C <sub>26</sub> H <sub>22</sub> O <sub>4</sub> N <sub>4</sub>	68.8	68.9	4.85	4.85
9-Phenyl-9-fluo- renyl-	233-234	CHCl <sub>3</sub>	Yellow prisms	2 hr.	59	C <sub>25</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> <sup>a</sup>	68.5	69.1	4.1	4.1
1,1-Diphenylethyl-	241	CCl <sub>4</sub> + petrol ether	Bright red needles	2 hr.	16	C <sub>20</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> <sup>b</sup>	63.5	63.4	4.8	4.2

<sup>a</sup> Calcd.: N, 12.8. Found: N, 12.6%. <sup>b</sup> Calcd.: N, 14.8. Found: N, 14.4%.

group. These may be oxidized by the DNP to an aldehyde or ketone, giving poor (4-25%) yields of the corresponding 2,4-dinitrophenylhydrazones. In the course of another investigation, we found that triarylcarbinols give precipitates with DNP, in fair yields in most cases. The product of the reaction is the corresponding 1-(2,4-dinitrophenyl)-2-aralkylhydrazine (see Table I).



As in a similar reaction between trityl alcohol and phenylhydrazine Baeyer<sup>5</sup> obtained as the final product (after prolonged standing) an azo compound, PhN=NCPH<sub>3</sub>, it was thought necessary to prove the constitution of our products.

Therefore, we examined the spectra of the reactants and the products both in the infrared and in the ultraviolet regions. In the infrared absorption spectra of all the products peaks appear at 3400-3500 cm.<sup>-1</sup>, which can be attributed to the NH-group.<sup>6</sup>

As hydroxyl groups absorb almost in the same region<sup>7</sup> much care was taken in drying these samples before determining their infrared spectra. The presence of the NH-absorption is in itself already a strong indication of the structure of our products. Moreover, practically no absorption was observed at 927 cm.<sup>-1</sup> which is claimed to be characteristic for C—N=N—C— groups.<sup>8</sup> Additional confirmation could be gathered from the ultraviolet spectra (see Table II). Comparison of the absorption maxima of the starting materials and the products show that the *position* of the characteristic bands of DNP and of the carbinols remains unchanged in the product. The absorption maxima of DNP at about 2600 and 3500 Å. are considerably exalted in the reaction products, but the absence of any shift

in these characteristic wave lengths again confirms the proposed structure: in azo derivatives, one would expect to observe considerable shifts in the wave lengths of the maxima, as compared to DNP.

 TABLE II  
 ULTRAVIOLET ABSORPTION SPECTRA OF CARBINOLS AND THEIR 2,4-DINITROPHENYLHYDRAZIDES IN DIOXANE

Compound	Conc., mole/l.	λ <sub>max</sub>	ε <sub>max</sub>
2,4-Dinitrophenyl- hydrazine <sup>a</sup>	7.5 × 10 <sup>-5</sup>	2610	7200
Triphenylcarbinol	1.78 × 10 <sup>-4</sup>	3490	11800
		2400	1450
1-Triphenylmethyl-2- (2,4-dinitrophenyl)- hydrazine	4.05 × 10 <sup>-5</sup>	2530	1800
		2600	1900
Phenyldi( <i>p</i> -tolyl)- carbinol	2.95 × 10 <sup>-4</sup>	2410	9560
		2600	9360
1-Phenyldi( <i>p</i> -tolyl)- methyl-2-(2,4-dinitro- phenylhydrazine	3.9 × 10 <sup>-5</sup>	3490	15820
		2400	1645
9-Phenyl-9-fluorenyl	4.79 × 10 <sup>-4</sup>	2640	1320
		2740	1110
1-(9-Phenyl-9-fluorenyl)- 2-(2,4-dinitrophenyl- hydrazine	3.73 × 10 <sup>-5</sup>	2600	11150
		3500	17950
9-Phenyl-9-fluorenyl	4.79 × 10 <sup>-4</sup>	2420	1675
		2720	1160
1-(9-Phenyl-9-fluorenyl)- 2-(2,4-dinitrophenyl- hydrazine	3.73 × 10 <sup>-5</sup>	2800	1200
		3110	574
1-(9-Phenyl-9-fluorenyl)- 2-(2,4-dinitrophenyl- hydrazine	3.73 × 10 <sup>-5</sup>	2420	23150
		2600	24700
		3100	10000
		3470	21300

<sup>a</sup> A. K. Macbeth and I. R. Price, *J. Chem. Soc.*, 1565 (1935).

The same product was obtained in dry ether as the solvent, in a very high yield, with DNP from trityl chloride as from trityl alcohol.

It seems to us reasonable to assume that the reaction is an acid-catalyzed nucleophilic attack by the DNP on the methyl carbon atom of the carbinols. The much higher yield obtained with trityl chloride in ether may be explained by the more polar character of the C—Cl bond (as compared to the C—OH bond), which would make the carbon atom more susceptible to a nucleophilic attack.

(5) A. Baeyer and V. Villiger, *Ber.*, **35**, 3017 (1902).

(6) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen & Co., London, 1954, pp. 212-19.

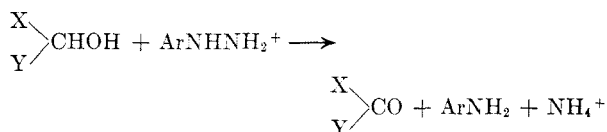
(7) See ref. 6, p. 84 ff.

(8) K. S. Tetlow, *Research*, **3**, 187 (1950).

Experiments were made with different amounts of acid as the catalyst, so as to ascertain the influence of the acid concentration on the yields of the product. It was found that mixtures of 5 g. of trityl alcohol and 5 g. of DNP in 200 ml. of ethanol refluxed for 2 hr. gave about the same yields irrespective of the amount of the added aqueous concentrated hydrochloric acid, which was varied between 10 and 100 ml. On the other hand, an attempt to carry out the reaction in concentrated sulfuric acid as the solvent, proved unsuccessful. Here, probably, the DNP is converted into an unreactive salt, which is incapable of attack even though the trityl carbonium ion is present in a high concentration in concentrated sulfuric acid.<sup>9</sup>

The reaction gave no results with *p*-nitrotritylcarbinol and with tri(*p*-nitrophenyl)carbinol. It seems that only carbinols in which the heterolysis of the C—OH bond is strongly promoted can react in the manner described, whereas in nitro-substituted aralkyl alcohols, the electron attracting substituents hinder the heterolysis. Neither does any reaction take place with less reactive alcohols, *e.g.*, benzyl alcohol.<sup>4</sup>

A further limitation of this reaction is the fact described by Braude<sup>4</sup> that easily oxidizable alcohols yield derivatives of the corresponding aldehyde or ketone. According to Braude the alcohol is oxidized as follows:



Braude did not prove the presence of either the ammonium ions or of the 2,4-dinitroaniline in the reaction mixture. Several alternative mechanisms could be proposed for Braude's reaction, such as self-oxidation of diphenylcarbinol with formation of benzophenone and diphenylmethane, or primary formation of a hydrazine derivative with subsequent oxidation to the hydrazone, or again an oxidation of diphenylcarbinol by the nitro groups of the DNP. We repeated therefore part of Braude's work with diphenylcarbinol and searched for by-products, especially for 2,4-dinitroaniline and for diphenylmethane. None of these attempts was successful. Owing to the low yields and the reactivity of these by-products the negative results can be relied upon probably only in the case of diphenylmethane, for which a sensitive and specific color test<sup>10</sup> exists and was used. The absence of diphenylmethane from the mixture seems to support although does not yet prove, Braude's reaction scheme.

Some 1,1-diarylethylenes, especially 1,1-di(*p*-anisyl)- and 1,1-di(*p*-chlorophenyl)ethylene are

known to give stable carbonium ions in the presence of acids.<sup>11</sup> We thought, therefore, that products similar to those obtained from carbinols and DNP might also be obtained from the corresponding ethylenes and DNP, as *e.g.*, both 1,1-diphenylethanol and 1,1-diphenylethylene can give rise to the same carbonium ion in acid solutions. Several attempts were therefore made to react DNP with 1,1-diphenylethylene and also with 1,1-di(*p*-anisyl)- and 1,1-di(*p*-chlorophenyl)ethylene but all these attempts failed. Probably the acidity of ethanolic hydrochloric acid is not sufficiently great, and concentrated sulfuric acid cannot be used, as the DNP is deactivated in this solvent, owing to salt formation (see above).

#### EXPERIMENTAL

*Reaction of carbinols with DNP.* An excess (50–100%) of DNP was refluxed with the carbinol in a mixture of ethanol and concentrated HCl, until no more precipitate formed. The mixture was filtered while hot and the precipitate crystallized from chloroform or from carbon tetrachloride. (See Table I.)

*Attempted reaction of trityl alcohol with DNP in conc. sulfuric acid.* Five grams of trityl alcohol and 5 g. of DNP were dissolved in 200 ml. of concentrated sulfuric acid. The mixture was stirred at room temperature for 1 hr., poured on ice, and worked up as usual. Only the starting materials could be recovered.

*Attempted reaction of DNP with diarylethylenes.* Two grams of either 1,1-diphenyl-, 1,1-di(*p*-chlorophenyl)- or 1,1-di(*p*-anisyl)ethylene in 100 ml. of ethanol and 15 ml. of concentrated HCl was refluxed with 2.5 g. of DNP for 2 hr. Only resinous products (probably polymers of the ethylenes) and DNP could be recovered.

*Reaction of DNP with trityl chloride in ether.* Fourteen grams of tritylchloride and 20 g. of DNP were refluxed in 200 ml. of dry ether for 1 hr. Worked up as usual, the product was obtained in 88% yield and was proved to be identical to the product from the reaction of trityl alcohol with DNP.

*Spectra.* The infrared spectra of the substances were determined in KBr, on a Baird-Atomic Inc., I.R. Spectrophotometer. Ultraviolet spectra were determined on a Beckman Model DU spectrophotometer.

*Acknowledgment.* We are indebted to Mrs. H. Feilchenfeld and Mrs. L. Prince for the determinations of the infrared spectra.

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#### Preparation of Fluoroalkyl Iodides from Fluorinated Acid Chlorides

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Fluoroalkyl iodides can generally be prepared in excellent yield by the reaction of the anhydrous

(9) For references see: R. J. Gillespie and J. A. Leisten, *Quart. Reviews (London)*, VIII, 49 (1954).

(10) S. Hilpert and L. Wolf, *Ber.*, 46, 2217 (1913).