

slowly; the first material to be eluted consisted of red-orange crystals, m.p. 217–221°. Recrystallization twice from methyl ethyl ketone afforded brick-red needles, m.p. 218–220° (lit.,¹⁴ m.p. of 5,11-dichlorotetracene, 220°). When the reaction was repeated in refluxing chlorobenzene, an inseparable mixture of chlorinated products was obtained.

Anal. Calcd. for $C_{13}H_{10}Cl_2$: Cl, 23.87. Found: Cl, 24.04.

Action of cupric chloride on perylene. A mixture of 1.26 g. (0.005 mole) of perylene and 1.35 g. (0.01 mole) of cupric chloride was heated in 25 ml. of nitrobenzene at 100° for 3 days. A black precipitate which formed during the course of the reaction was removed by filtration. It disappeared on hydrolysis, yielding a yellow-orange organic product and, presumably, copper salts. A small portion of the product, dissolved in the solvent, had an infrared spectrum essentially the same as that obtained from the black precipitate and so the two were combined. No purification could be achieved by recrystallization from cyclohexane, benzene, acetone, or

(14) C. Marschalk and C. Stumm, *Bull. Soc. Chem. France*, **15**, 418 (1948).

ethyl alcohol. When purification with Norit was attempted, the product could not be desorbed even by boiling chlorobenzene and the reaction had to be repeated. The melting range was generally about 215–245°. If the material was chromatographed on alumina with cyclohexane, it moved very slowly, but finally yellow-orange crystals could be obtained in which the melting range was about the same as before. Infrared absorption maxima occurred at 10.20, 11.37, 12.15, 12.47, 12.75, 13.15, and 14.53 μ . Later fractions contained perylene contamination as well. There was obtained 1.29 g. of the yellow-orange material. A portion of the latter was recrystallized from cyclohexane, m.p. 218–245°.

Anal. Calcd. for $C_{22}H_{10}Cl_2$: C, 74.78; H, 3.14; Cl, 22.08. Found: C, 74.84; H, 3.26; Cl, 22.21.

If dichloroperylene had been formed, then 1 mole of cupric chloride introduced 1 mole of chlorine instead of 0.5 mole as experienced previously. On this basis, the yield of dichloroperylene was 80%. Oxidation by sulfuric acid yielded no distinct product.

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[CONTRIBUTION FROM THE OHIO STATE UNIVERSITY RESEARCH FOUNDATION]

Conversion of Trichloromethyl Groups into Dichloromethyl Groups¹

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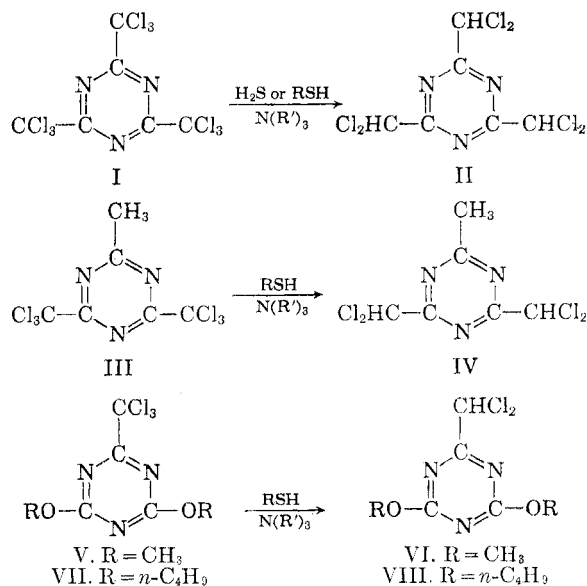
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Trichloromethyl-*s*-triazines and derivatives of trichloroacetic acid can be converted into the corresponding dichloromethyl compounds by means of mercaptans in the presence of tertiary amines; mercaptals are formed as by-products.

In connection with a study on the reactivity of trichloromethyl groups attached to the *s*-triazine nucleus we had found that the reaction of trichloromethyl-*s*-triazines with alcohols in the presence of certain tertiary amines led, depending on the reaction conditions, to the stepwise replacement of trichloromethyl groups by alkoxy groups.³ Furthermore, we reported that the reaction of 2,4,6-tris(trichloromethyl)-*s*-triazine (I) with water and certain tertiary amines resulted in the formation of tertiary amine salts of 2-hydroxy-4,6-bis(trichloromethyl)-*s*-triazine.³

It was of interest to know whether the reaction of trichloromethyl-*s*-triazines with mercaptans instead of alcohols would proceed in the presence of tertiary amines correspondingly and result in the formation of alkylthio-*s*-triazines. It also appeared desirable to determine whether the reaction of I with hydrogen sulfide instead of water would lead in the presence of tertiary amines, in an analogous fashion, to the formation of tertiary amine salts of 2-mercapto-4,6-bis(trichloromethyl)-*s*-triazine.

It was surprisingly found that 2,4,6-tris(trichloromethyl)-*s*-triazine (I) reacted with either



ethanethiol or 1-butanethiol in the presence of triethylamine to give 2,4,6-tris(dichloromethyl)-*s*-triazine (II). This result indicated that the reaction of compound I with mercaptans in the presence of triethylamine took an entirely different course as compared with the reaction of compound I with alcohols; instead of being replaced by alkylthio groups, the trichloromethyl groups were converted into dichloromethyl groups.

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(2) Olin Mathieson Chemical Corporation, Organics Division, New Haven, Conn.

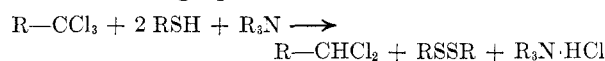
(3) E. Kober, *J. Org. Chem.*, **25**, 1728 (1960).

The general usefulness of this conversion for the *s*-triazine series was ascertained when other trichloromethyl substituted *s*-triazines were subjected to this type of reaction; the corresponding dichloromethyl-*s*-triazines were obtained in each case. Thus, 2-methyl-4,6-bis(trichloromethyl)-*s*-triazine (III) was converted into 2-methyl-4,6-bis(dichloromethyl)-*s*-triazine (IV), 2,4-bismethoxy-6-trichloromethyl-*s*-triazine (V) gave 2,4-bismethoxy-6-dichloromethyl-*s*-triazine (VI), and 2,4-bis-*n*-butoxy-6-trichloromethyl-*s*-triazine (VII) afforded 2,4-bis-*n*-butoxy-6-dichloromethyl-*s*-triazine (VIII).

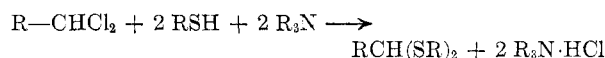
The reaction of compound I with hydrogen sulfide in the presence of triethylamine again did not occur as one might have expected from the corresponding reaction of compound I with water and triethylamine. Instead, the principal product proved to be II, indicating that the reaction with hydrogen sulfide proceeded in the same manner as with mercaptans.

Extending our studies, we found that derivatives of trichloroacetic acid also undergo this type of reaction. This was shown by the conversion of trichloroacetamide and ethyl trichloroacetate into the corresponding dichloro derivatives, dichloroacetamide (IX) and ethyl dichloroacetate (X).

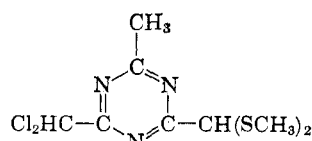
In all cases, including those studies in the *s*-triazine series, the reaction proceeded according to the following equation:



If an excess of the tertiary amine was used, part of the dichloromethyl compound reacted further with excess mercaptan to give the corresponding mercaptal:



Thus, the methylmercaptal of the 2-methyl-4-dichloromethyl-*s*-triazine-(6) carboxaldehyde (XI) was obtained as a by-product from the reaction of 2-methyl-4,6-bis(trichloromethyl)-*s*-triazine (III) with methanethiol and triethylamine. In addition, 1,1-bis(methylthio)acetamide (XII) and ethyl 1,1-bis(methylthio)acetate (XIII) were isolated along with the desired derivatives of dichloroacetic acid when trichloroacetamide and ethyl trichloroacetate, respectively, reacted with methanethiol in the presence of triethylamine.⁴



XI



(4) Sulfur-containing compounds were also formed in the other experiments reported here; however, no efforts were made to identify these products.

The conversion of trichloromethyl into dichloromethyl groups by means of mercaptans and tertiary amines represents a novel method which, in general, is more widely applicable than procedures reported previously for this transformation. Its limitations are indicated by the observation that—in contrast to trichloromethyl substituted *s*-triazines and derivatives of trichloroacetic acid—the trichloromethyl group was not affected when 2,2,2-trichloroethanol, 1,1,1-trichloro-2-methyl-2-propanol, chloral hydrate, 1,1,1-trichloroethane, or benzotrithiolide were treated with mercaptans and triethylamine. Apparently, only compounds having the trichloromethyl group attached to a rather strong electronegative moiety are being converted to the corresponding dichloromethyl compound. However, if the electronegative moiety is too strong an electron-withdrawing group such as the trichloromethyl group, the reaction will not stop after one chlorine atom has been exchanged by hydrogen. Thus, hexachloroethane reacted to give a mixture of partially chlorinated ethanes and ethenes, indicating that pentachloroethane was probably formed as an intermediate but underwent further reaction under the conditions employed.

EXPERIMENTAL⁵

2,4-Bismethoxy-6-trichloromethyl-s-triazine (V). (a) An amount of 39 g. of 2,4-dichloro-6-trichloromethyl-*s*-triazine⁶ was dissolved, with stirring, in a solution of 6.7 g. of sodium in 150 ml. of methanol and kept at 0° for 6 hr. The sodium chloride formed was removed by filtration. After removal of the methanol from the filtrate by vacuum distillation at room temperature, an oily residue was obtained from which, upon addition of ether, a solid precipitated. The solid was filtered and the ether removed from the filtrate. The resulting oily residue was fractionated to give 18.5 g. of 2,4-bismethoxy-6-trichloromethyl-*s*-triazine (V), b.p. 100–103° (0.6 mm.), n_D^{20} 1.5228.

Anal. Calcd. for $\text{C}_6\text{H}_6\text{N}_3\text{Cl}_3\text{O}_2$: C, 27.88; H, 2.34; N, 16.26; Cl, 41.15. Found: C, 27.89; H, 2.39; N, 16.14; Cl, 41.41.

When the same reaction was carried out with triethylamine instead of sodium as hydrogen scavenger, a mixture of products was obtained which could not be separated by fractional distillation.

(b) 2,4-Bismethoxy-6-trichloromethyl-*s*-triazine (V) was also obtained by employing the method recently described for the preparation of other 2,4-bisalkoxy-6-trichloromethyl-*s*-triazines.³

An amount of 56 g. of 2,4,6-tris(trichloromethyl)-*s*-triazine (I) reacted with methanol (200 ml.) in the presence of triethylamine (48 g.) at room temperature. The desired compound V was isolated from the reaction mixture by vacuum distillation; b.p. 99–105° (0.6 mm.); n_D^{33} 1.5222; yield: 24.0 g.

Procedures for the conversion of trichloromethyl into dichloromethyl groups. (a) One mole equivalent of a trichloromethyl substituted *s*-triazine (I, III, V, or VII) or of a derivative of trichloroacetic acid is added, with stirring,

(5) Melting points were determined with the Fisher-Johns apparatus; analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(6) E. Kober and Ch. Grundmann, *J. Am. Chem. Soc.*, **81**, 3769 (1959).

TABLE I
 DICHLOROMETHYL COMPOUNDS

Com- pound	Hydrogen Source	Yield, %	M.P.	B.P. (mm.)	n_D^{20}	t	Empirical Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
II	C_6H_9SH	77.3	68 ^a				$C_6H_4N_3Cl_6$	21.82	21.79	0.91	0.92	12.74	12.88	64.56	64.47
II	C_2H_5SH	64.7	66.5-68 ^a												
II	H_2S	23.8	65-67 ^a												
IV	CH_3SH	90.5	88-90	128-142 (0.2)	1.5197	26	$C_6H_8N_3Cl_4$	27.62	27.69	1.91	1.97	16.11	16.28	54.35	54.04
VI	CH_3SH	66.9		90-93 (0.06) ^c	1.4968	26.5	$C_{12}H_{19}N_3Cl_2O_2$	46.76	47.19	6.22	6.43	13.64	13.64	23.01	22.72
VIII	CH_3SH	53.2		153.5-157 (1.4)											
IX	CH_3SH	87.1	95-96.5 ^b	70.5-73.5 (30) ^d	1.4397	26	$C_4H_6Cl_2O_2$	30.61	30.91	3.85	3.99			45.17	43.89
X	CH_3SH	26.5													

^a Lit.⁷ m.p. 68°. ^b Lit.⁸ m.p. 98°. ^c Lit.⁹ b.p. 86-88° (0.045 mm.); n_D^{20} 1.5200. ^d Lit.¹⁰ b.p. 156° (738 mm.); n_D^{20} 1.4386.

 TABLE II
 MERCAPTALS

Com- pound	Yield, %	B.P. (mm.) or M.P.	n_D^{20}	t	Empirical Formula	Carbon, %		Hydrogen, %		Nitrogen, %		Sulfur, %		Chlorine, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
XI	4.5	120-122 (0.07)	1.5869	20	$C_8H_{11}N_3S_3Cl_2$	33.82	34.11	3.90	4.18	14.79	15.28	22.56	22.58	24.95	24.33
XII	11.7	146-147			$C_4H_9NS_2O$	31.79	31.96	6.01	6.09	9.27	9.37	42.34	41.99		
XIII	41.6	98-102 (8)	1.5069	27	$C_6H_{13}S_2O_2$	39.97	39.86	6.71	6.72			35.57	35.72		

to a mixture of a mercaptan (5–20 mole equivalents) and triethylamine (1.5–5 mole equivalents) at -20° (if methanethiol is employed) or at 0° (if ethanethiol or 1-butanethiol are used). The reaction mixture is allowed to warm to room temperature upon stirring. The precipitated triethylamine hydrochloride is filtered off and washed with ether or petroleum ether (b.p. $30-40^{\circ}$). The wash solvent, excess triethylamine, and the dialkyl disulfide formed are removed from the filtrate by distillation. If the reaction product is volatile, the residue is fractionated *in vacuo* to give the desired dichloromethyl substituted compound (II, IV, VI, VIII, or X) and a higher boiling, sulfur-containing material (XI and XIII were thus obtained in pure form and identified as mercaptals). If the reaction product is a solid, the residue is recrystallized from suitable solvents to isolate the dichloromethyl compound (II) was isolated in one experiment by recrystallization of the residue from ligroin; compound IX was purified by dissolving the residue in ether and reprecipitation with ligroin, the mercaptal XII was

contained in the triethylamine hydrochloride filter cake and was separated and purified by crystallization from water).

(b) Hydrogen sulfide was passed into a solution of 33 g. of 2,4,6-tris(trichloromethyl)-s-triazine (I) and 35.1 g. of triethylamine in 200 ml. of ether at 0° for 7 hr. The reaction mixture was allowed to stand for 12 hr. at room temperature. Then, 250 ml. of ether were added to the reaction mixture, the salts and sulfur formed were removed by filtration, and the ether distilled from the filtrate. The resulting dark residue was recrystallized from 25 ml. of ligroin. Upon cooling to -20° , crystals and an oily product separated from the ligroin. The crystals were collected and freed from adhering oil by pressing on a clay plate. Thus, 5.96 g. of 2,4,6-tris(dichloromethyl)-s-triazine (II) was isolated.

Compounds prepared according to these procedures are listed in Tables I and II. Dichloromethyl compounds for which an analysis is not recorded were identified either by a mixed melting point or by comparing the boiling point and refractive index with an authentic sample.

(7) Ch. Grundmann, G. Weisse, and S. Seide, *Ann.*, **577**, 77 (1952).

(8) A. Pinner and F. Fuchs, *Ber.*, **10**, 1066 (1877).

(9) Ch. Grundmann and E. Kober, *J. Am. Chem. Soc.*, **79**, 944 (1957).

(10) J. W. Brühl, *Ann.*, **203**, 22 (1880).

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Reduction of Phthalimides with Sodium Borohydride

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Reduction of phthalimide derivatives with sodium borohydride in methanol results in the formation of 3-hydroxyphthalimidines (II), or a mixture of II and *o*-hydroxymethylbenzamides III depending on the amount of reducing agent present. The mechanism of this reduction is proposed.

Although it has been known that the imido group does not undergo reduction by sodium borohydride,¹ we have found that *N*-(6-oxo-5,6,7,8-tetrahydro-1-naphthyl)phthalimide is reduced by sodium borohydride in methanol to *o*-hydroxymethyl-*N*-(6-hydroxy-5,6,7,8-tetrahydro-1-naphthyl)benzamide. It would be of interest to establish this novel reduction of the phthalimide since sodium borohydride has prominent selectivities toward various groups on reduction and, thus, this reduction may be expected to serve as a useful preparative method. The present paper describes the reduction of the phthalimide derivatives (Ia-i) shown in Fig. 1 with sodium borohydride.

The reduction was carried out by adding a methanolic solution of sodium borohydride to a suspension of the phthalimide in methanol at $25-30^{\circ}$, followed by stirring at this temperature for seven to ten hours. When two molecular equivalents of sodium borohydride was employed, the product was the 3-hydroxyphthalimidine (II) or a mixture of II and the *o*-hydroxymethylbenzamide (III). Thus, phthalimide (Ia) and *N*-methyl-

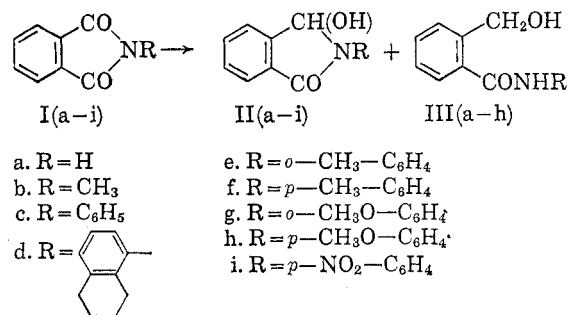


Figure 1

phthalimide (Ib) were converted to 3-hydroxyphthalimidine (IIa) and 3-hydroxy-2-methylphthalimidine (IIb) in yields of 66% and 56%, respectively. Similarly, *N*-(*p*-nitrophenyl)phthalimide (Ii) was converted to 3-hydroxy-2-(*p*-nitrophenyl)phthalimidine (IIIi) in 81% yield. Compounds IIa and IIb were prepared previously by reduction with zinc in sodium hydroxide solution² or with magnesium and ammonium chloride in methanol,³

(2) A. Reissert, *Ber.*, **46**, 1484 (1913).

(3) A. Dunet and A. Willemart, *Bull. soc. chim. France*, 1081 (1948).

(1) N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience, New York, 1956, p. 629.