

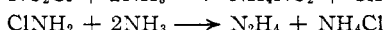
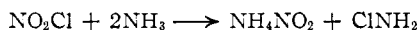


TABLE I  
 REACTION OF NO<sub>2</sub>Cl WITH SOME LEWIS ACIDS

Reactant	Conditions	Results	Products
SnCl <sub>4</sub>	Excess NO <sub>2</sub> Cl, -75°	No reaction	
SnBr <sub>4</sub>	Excess NO <sub>2</sub> Cl, -75°	Vigorous reaction, Br <sub>2</sub> evolved	(NO) <sub>2</sub> SnCl <sub>6</sub> <sup>a</sup> + oxychlorides of tin + N <sub>2</sub> O <sub>4</sub>
SnI <sub>4</sub>	Excess NO <sub>2</sub> Cl, -75°	Vigorous reaction, I <sub>2</sub> evolved	
BF <sub>3</sub>	Excess NO <sub>2</sub> Cl, -75°	No reaction	(N <sub>2</sub> O <sub>4</sub> impurity in NO <sub>2</sub> Cl forms some N <sub>2</sub> O <sub>4</sub> ·2BF <sub>3</sub> —a white crystalline solid)
PCl <sub>3</sub>	Excess PCl <sub>3</sub> ; NO <sub>2</sub> Cl distilled in at -75°	Exothermic reaction	PCl <sub>5</sub> , POCl <sub>3</sub> , NOCl, N <sub>2</sub> O <sub>4</sub>
SO <sub>3</sub>	Liq. SO <sub>3</sub> added to excess NO <sub>2</sub> Cl at -75°	Violent reaction, voluminous white precipitate	NO <sub>2</sub> Cl·2SO <sub>3</sub> <sup>b</sup> —presumably NO <sub>2</sub> (ClS <sub>2</sub> O <sub>6</sub> ) nitronium chlorodisulfate
SiCl <sub>4</sub>	Excess NO <sub>2</sub> Cl; -75°	No reaction	Residue contained no Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , or NO <sub>2</sub> <sup>-</sup>
WO <sub>2</sub>	NO <sub>2</sub> Cl refluxed over WO <sub>2</sub> for 12 hours	No reaction	Residue contained no Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , or NO <sub>2</sub> <sup>-</sup>
MoO <sub>3</sub>	NO <sub>2</sub> Cl refluxed over MoO <sub>3</sub> for 12 hours	No reaction	Residue contained no Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , or NO <sub>2</sub> <sup>-</sup>
I <sub>2</sub> O <sub>5</sub>	NO <sub>2</sub> Cl refluxed over I <sub>2</sub> O <sub>5</sub> for 12 hours	No reaction	Residue contained no Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , or NO <sub>2</sub> <sup>-</sup>
SO <sub>2</sub>	Equal volumes of liquid SO <sub>2</sub> and NO <sub>2</sub> Cl refluxed for 36 hours	Miscible. No apparent reaction	No residue

<sup>a</sup> Bright, yellow, solid sublimes above 150°. *Anal.* Calcd.: Cl, 54.31; Sn, 30.37. Found: Cl, 50.88; Sn, 33.68. Product thus is impure, but agrees with properties reported for (NO)<sub>2</sub>SnCl<sub>6</sub> by H. Reinbolt and R. Wasserfuhr, *Ber.*, **60B**, 732 (1927). <sup>b</sup> *Anal.* Calcd. for NO<sub>2</sub>(ClS<sub>2</sub>O<sub>6</sub>): Cl, 14.67; S, 26.54; N, 5.79. Found: Cl, 12.90; S, 26.65; N, 5.48. Product was so susceptible to hydrolysis that some chlorine was lost as HCl during analysis. Melted at about 120° and crystallized as long sharp needles. Exceedingly hygroscopic. Fumes even in the presence of phosphoric anhydride.

zinc monohydrochloride and ammonium chloride were obtained. Yields of hydrazine monohydrochloride amounting to 15% of theoretical based on the nitryl chloride used were obtained. As already shown in a previous publication<sup>4</sup> the yields can be increased. We were, however, interested here in the primary reaction of the nitryl chloride. The above results are in agreement with those obtained by Schmiesser and with the equations



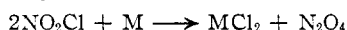
Qualitative results obtained for the liquid phase reaction likewise fit this picture.

#### Reaction of Nitryl Chloride with A Series of Lewis Acids.

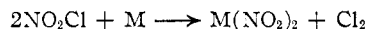
—A series of qualitative or semi-quantitative experiments were carried out in which the behavior of nitryl chloride toward various Lewis acids most of which might be expected to coordinate negative chlorine was observed. The results of these experiments are summarized in Table I.

These results indicate that, with the exception of sulfur trioxide, there is no reaction with these Lewis acids except where oxidation-reduction processes occur.

**Reaction of Nitryl Chloride with Metals.**—In order to determine whether NO<sub>2</sub> or Cl can be readily displaced from nitryl chloride by metals in such reactions as



or

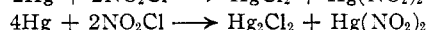
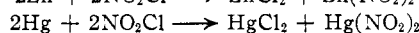
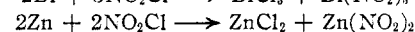
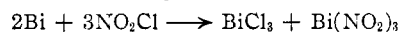


a series of tests with a variety of metals was carried out. Samples of chemically pure zinc, mercury, bismuth, copper, magnesium, iron, aluminum and tin were added to 10-ml. portions of nitryl chloride and kept at -30° in sealed tubes for six hours. At the end of this time only mercury showed any evidence of having reacted. The samples were then cooled to -75° at which temperature they were held for an additional 36 hours. At the end of this time the nitryl chloride was allowed to boil off. The metal specimens and their containers were thoroughly washed and the wash liquid tested for metal cation, nitrate ion, nitrite ion and chloride ion.

With copper, magnesium, iron, aluminum and tin there was no indication of reaction with nitryl chloride.

With mercury, bismuth and zinc, however, the aqueous wash liquid gave strong tests for metal cations, nitrite and chloride. In the reaction with mercury a thin film of gray solid formed on the mercury surface stopping the reaction. The reaction could be started again by shaking the mercury so as to expose a fresh metal surface. The reactions with zinc and bismuth were much less apparent and proceeded very slowly under the conditions of the experiment. The reactions of zinc, bismuth and mercury with nitryl chloride yield a mixture of the metal nitrites and chlorides and in the

case of mercury, of mercurous and mercuric salts. The reactions which occur are probably



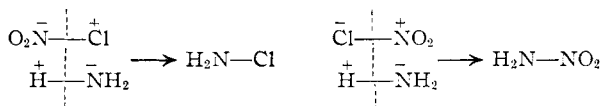
#### Discussion

The results reported above indicate that the nitrogen to chlorine bond in nitryl chloride is not so polarized as to act as a source of negative chlorine except toward exceedingly strong electron acceptors such as sulfur trioxide. This is supported strongly by the facts that the reaction with ammonia yields chloramine and ammonium nitrite rather than nitramide and ammonium chloride, and that nitryl chloride does not react with tin tetrachloride or with boron trifluoride. The reactions with tin tetrabromide, tin tetraiodide and phosphorus trichloride indicate that nitryl chloride can act as an oxidizing agent either by losing oxygen and forming nitrosyl chloride or by losing chlorine and forming dinitrogen tetroxide. This is in accord with the structure O<sub>2</sub>N-Cl.

Schmiesser<sup>2</sup> has stated that the formation of chloramine and of hypochlorite by the reactions of nitryl chloride with liquid ammonia and aqueous sodium hydroxide, respectively, indicates that nitryl chloride is in reality nitrosyl hypochlorite with the structure



Such an assumption is clearly unnecessary for the ammonolysis of nitryl chloride may yield either nitramide or chloramine depending upon the polarity of the N-Cl bond, as represented



The chlorine in nitrosyl chloride is clearly negative in polarity. The addition of a second oxygen atom to the nitrogen atom in nitryl chloride has either

greatly reduced this negative polarity or actually changed it to positive.

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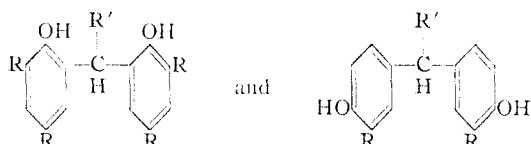
### Preparation of Substituted Bis-phenols

BY DAVID J. BEAVER AND PAUL J. STOFFEL

RECEIVED FEBRUARY 21, 1952

Since the original synthesis<sup>1</sup> of Baeyer, numerous papers on phenol-aldehyde condensations have appeared in the literature.<sup>2</sup> More recently, an increasing interest has been shown by various investigators of this type compound as intermediates for phenolic resins,<sup>3</sup> as antioxidants for wax,<sup>4</sup> as rubber chemicals,<sup>5</sup> as bacteriocides,<sup>6</sup> and as fungicides.<sup>7</sup>

The present work was directed toward the preparation of bis-phenols of the general formulas



in which R = alkyl, aryl or chlorine and R' = alkyl or aryl, for use as rubber antioxidants and bacteriostatic agents. A search of the literature revealed a surprisingly small number of bis-phenols other than derivatives of phenol and the cresols with formaldehyde<sup>3</sup> and chloral.<sup>6</sup>

This paper describes the preparation of 35 poly-

condensation products not reported previously. They are white crystalline compounds in all cases except 4,4'-(*p*-hydroxybenzylidene)-bis-(6-*t*-butyl-*m*-cresol), #9, which is lemon yellow.

The wide applicability and versatility of the described procedures can readily be seen from the following tables. The reaction time, as given, was the point at which resin formation was observed and the batch quenched with the designated precipitant. The reaction times are, therefore, not true measures of the reaction rates but they do definitely indicate the wide variations observed by changing the structure of the phenols and aldehydes. Since the formation of bis-phenol and resin is a competitive reaction, the low yields can be attributed to either insufficient reaction time for bis-phenol formation or, conversely, not quenching quickly enough to prevent the bis-phenols formed from condensing further to resinous products. The reported yields have no quantitative significance, since in most cases the figures given are the results of a single run.

The compounds described in Table I are 4,4'-alkylidene or arylidene bis-phenols since they do not form nitroso derivatives as does the unreacted 6-*t*-butyl-*m*-cresol. The specific preference for 4,4'-linkage in ortho-para competition is probably a result of partial steric hindrance,<sup>8</sup> although condensation in the ortho position does occur, if the para position is occupied. Examples are given in compounds 20, 28 and 34 in which 4,6-di-*t*-butyl-*m*-cresol is condensed in the one available ortho position with three different aldehydes.

TABLE I  
BIS-PHENOLS FROM 6-*t*-BUTYL-*m*-CRESOL<sup>a</sup>

No.	Aldehyde	Precipitant <sup>b</sup>	Time, hr.	M.p., °C.	Yield, %	Recrystallizing solvent	Empirical formula	Carbon		Analyses, % Hydrogen		Chlorine	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
1	Formaldehyde	1	2	178.7-179.2	39.0	Heptane	C <sub>23</sub> H <sub>32</sub> O <sub>2</sub>	81.12	81.01	9.47	9.53		
2	Acetaldehyde	1	1/4	201.1-201.5	87.0	Heptane	C <sub>24</sub> H <sub>34</sub> O <sub>2</sub>	81.31	80.93	9.67	9.99		
3	Chloroacetaldehyde	1	1/4	228.5-229.5	45.9	Heptane	C <sub>24</sub> H <sub>33</sub> ClO <sub>2</sub>	74.09	73.93	8.55	8.58	9.12	8.95
4	Propionaldehyde	1	4	190.0-190.4	43.4	Heptane	C <sub>25</sub> H <sub>36</sub> O <sub>2</sub>	81.48	81.29	9.85	9.92		
5	Butyraldehyde	2	8	210.0-210.7	62.8	Heptane	C <sub>25</sub> H <sub>38</sub> O <sub>2</sub>	81.64	81.91	10.01	10.23		
6	Isobutyraldehyde	1	24	229.8-230.7	50.8	Heptane	C <sub>25</sub> H <sub>38</sub> O <sub>2</sub>	81.64	81.47	10.01	9.94		
7	Heptaldehyde	2	12	160.2-160.4	24.5	Heptane	C <sub>29</sub> H <sub>44</sub> O <sub>2</sub>	82.03	81.85	10.44	10.61		
8	Benzaldehyde	1	1/2	199.3-199.8	43.3	Heptane	C <sub>29</sub> H <sub>38</sub> O <sub>2</sub>	83.62	83.54	8.71	8.55		
9	<i>p</i> -Hydroxybenzaldehyde	3	1/2	262.4-263.1	35.2	Acetic acid	C <sub>29</sub> H <sub>36</sub> O <sub>3</sub>	80.53	80.33	8.39	8.10		
10	Salicylaldehyde	1	1/2	216.7-217.0	18.9	Toluene	C <sub>29</sub> H <sub>36</sub> O <sub>3</sub>	80.53	80.37	8.39	8.59		
11	2,4-Dichlorobenzaldehyde	1	4	209.9-210.4	59.6	Heptane	C <sub>29</sub> H <sub>34</sub> Cl <sub>2</sub> O <sub>2</sub>	71.73	71.91	7.06	6.96	14.61	14.65
12	5-Chlorosalicylaldehyde	1	6	214.2-215.9	29.2	Benzene	C <sub>29</sub> H <sub>33</sub> ClO <sub>3</sub>	74.58	74.86	7.55	7.49	7.59	7.58
13	<i>o</i> -Chlorobenzaldehyde	1	1/2	226.3-226.9	23.5	Toluene	C <sub>29</sub> H <sub>33</sub> ClO <sub>2</sub>	77.22	77.20	7.82	7.76	7.86	8.02
14	Veratraldehyde	1	1/2	231.2-231.9	52.5	Heptane	C <sub>31</sub> H <sub>40</sub> O <sub>4</sub>	78.12	78.17	8.46	8.60		
15	Pyruvic aldehyde	2	1/4	196.2-197.1	34.8	Benzene	C <sub>25</sub> H <sub>34</sub> O <sub>3</sub>	78.50	78.38	8.96	8.78		
16	Chloral	2	6	218.8-219.3	65.6	Toluene	C <sub>24</sub> H <sub>31</sub> Cl <sub>3</sub> O <sub>2</sub>	62.94	63.28	6.82	7.01	23.23	23.05
17	2-Methyl-2-pentenal	1	18	190.1-190.5	18.5	Heptane	C <sub>28</sub> H <sub>40</sub> O <sub>2</sub>	82.30	82.15	9.87	9.52		
18	2-Ethyl-2-hexenal	1	3	210.2-210.6	38.4	Heptane	C <sub>30</sub> H <sub>44</sub> O <sub>2</sub>	82.46	82.46	10.16	9.89		
19	2-Thiophenaldehyde	1	1/4	223.3-223.7	42.0	Heptane	C <sub>27</sub> H <sub>34</sub> O <sub>2</sub> S	76.75	76.68	8.11	8.41		

<sup>a</sup> The compounds in Table I were all prepared following Procedure A. <sup>b</sup> 1, Heptane; 2, benzene; 3, glacial acetic acid; 4, water. <sup>c</sup> Sulfur, %: calcd. 7.57; found 7.64.

alkylated and chlorinated phenol-aldehyde con-

- (1) A. Baeyer, *Ber.*, **5**, 280, 1096 (1872).
- (2) L. Kahl, *ibid.*, **31**, 143 (1898); A. Lunjac, *Chem. Centr.*, **75**, I, 1650 (1904); T. Zincke, *Ann.*, **363**, 255 (1908); M. Koebner, *Z. angew. Chem.*, **46**, 251 (1933).
- (3) L. H. Baekeland and H. L. Bender, *Ind. Eng. Chem.*, **17**, 225 (1925); N. T. L. Megson and A. A. Drummond, *J. Soc. Chem. Ind.*, **49**, 251 (1930).
- (4) H. Morawetz, *Ind. Eng. Chem.*, **41**, 1442 (1949).
- (5) A. S. Briggs and J. Haworth, British Patent 621,004 (1949).
- (6) W. C. Harden and E. E. Reid, *THIS JOURNAL*, **54**, 4325 (1932).
- (7) P. B. Marsh, M. I. Butler and B. S. Clark, *Ind. Eng. Chem.*, **41**, 2176 (1949).

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

The compounds described in this paper have been prepared by two procedures—modifications of the original Baeyer synthesis. In both cases, the choice of precipitant was determined by spot testing during the initial reaction period. One ml. of the reaction mix was added to 3 ml. of each of the four selected precipitants and when crystal formation was noted, the reaction mixture was quenched with the chosen precipitant as indicated in the tables.

- (8) G. H. Stillson, D. W. Sawyer and C. K. Hunt, *THIS JOURNAL*, **67**, 303 (1945); J. B. Niederl and V. Niederl, *ibid.*, **61**, 1785 (1939); E. D. Hughes, *Quart. Revs. (London)*, **2**, 107 (1948).

<sup>9</sup> All melting points are corrected.