twenty-four hours the rotation, calculated as the expected dialdehyde, was $+120.8°$; this value was unchanged at the end of forty hours. At that time titration of a 10-cc. portion for excess periodate revealed that 2.01 equivalents of oxidant had been consumed. Titration of another 10-cc. portion with 0.1 N sodium hydroxide, and methyl red as indicator, showed the presence of 0.97 equivalent of acid, presumably formic acid.

Oxidation of α-Methyl-D-altroside with Periodic Acid.—To 3.112 g. of pure α-methylaltroside in 50 cc. of water was added 150 cc. of 0.2355 molal aqueous periodic acid (2.2 equivalents). After three days the solution was diluted exactly to 250 cc. The rotation, calculated as the dialdehyde, was $+117.7°$. Titration of an aliquot portion for excess periodic acid showed that 2.08 equivalents had been consumed. The lowered rotation, and the extra oxidizing agent consumed, indicate a slow continuing oxidation probably due to cleavage of the aldehyde because of the acidity of the solution. The remainder of the solution was neutralized with strontium hydroxide, the dialdehyde isolated, oxidized with bromine water and strontium carbonate as described by Jackson and Hudson,[16] and the strontium salt isolated in 60% yield. This salt was recrystallized, dried to constant weight at room temperature *in vacuo* over calcium chloride, and identified as strontium D′-methoxy-D-hydroxymethyldiglycolate dihydrate. *Anal.* Calcd. for $C_6H_8O_7Sr{\cdot}2H_2O$: Sr, 27.75; H_2O, 11.41. Found: Sr, 27.61, 27.61; H_2O (dried at 138° *in vacuo*), 11.24. The rotation of the strontium salt, calculated as anhydrous (c, 0.6), was $-53.1°$, and the rotation of the dibasic acid (c, 1.4) liberated from the salt with an equivalent amount of hydrochloric acid was $+26.0°$. These values are in agreement with those reported by Jackson and Hudson.[16]

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Summary

1. D-Altrosan$<1,5>\beta<1,6>$ has been converted to the following new crystalline substances: 2,3,4-triacetyl-D-altrosan; α-pentaacetyl-D-altrose; α-acetochloro-D-altrose; β-2,3,4,6-tetraacetyl-D-altrose; tetraacetyl-β-methyl-D-altroside; tetraacetyl-α-methyl-D-altroside; α-methyl-D-altroside.

2. α-Methyl-D-altroside, of $[\alpha]^{20}\text{D}$ $+125.8°$ in water, has been proved by periodic acid oxidation methods to possess the α-configuration and a pyranoside ring.

3. The series of reactions developed by G. J. Robertson and his collaborators for the transformation of α-methyl-D-glucoside to α-methyl-D-altroside has been modified to facilitate the preparation of crystalline α-methyl-D-altroside.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Blocking Effects in Condensation Reactions*

BY JOSEPH B. NIEDERL AND JOHN S. MCCOY

In the course of studies on condensations of aldehydes with phenols, only the alkylidene-di-phenol type of condensation involving one mole of the aldehyde with two moles of the phenol has been exhaustively studied.[1] A one to one ratio condensation has been described by J. B. Niederl and co-workers.[2] Aliphatic aldehydes and monohydroxy phenols in such condensations yielded polymers which upon pyrolysis gave the respective saturated alkylated phenols. With resorcinol a one to one ratio condensation was observed, the condensation products being tetramers.[3]

The purpose of the investigation presented in this paper was to determine what molar ratios between aldehydes and phenols are possible when only one ring position is available for reaction. Thus particular emphasis was placed on the condensation of equi- and multimolar quantities of the aldehyde. In the ensuing studies representative aldehydes of the three fundamental types, *i. e.*, saturated and unsaturated aliphatic and aromatic aldehydes were chosen. As properly blocked phenols, the 2,4- and 2,6-dimethylphenols were selected. The aldehydes subjected to condensation were acetaldehyde, crotonaldehyde and benzaldehyde.

It was found that, regardless of the mole ratio, only alkylidene-di-phenol type[1] of crystalline condensation products were obtained with blocked

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* Abstracted from the thesis submitted by John S. McCoy to the faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of doctor of philosophy.

(1) Schmedlin and Lang, *Ber.*, **43**, 2806 (1910); Claus and Trainer, *ibid.*, **19**, 3009 (1886); Moehlan and Kock, *ibid.*, **11**, 283 (1878); L. Claus, *Ann.*, **237**, 261 (1887); Th. Zincke, *ibid.*, **363**, 255 (1908).

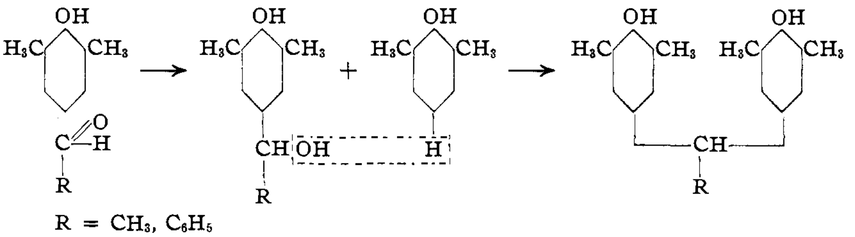
(2) J. B. Niederl and co-workers, THIS JOURNAL, **59**, 1113 (1937).

(3) J. B. Niederl and H. Vogel, *ibid.*, **62**, 2512 (1940).

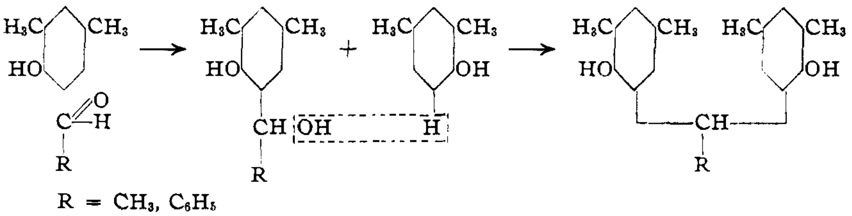
phenols. In addition to this it was found that in the case of unsaturated aldehydes the catalyst partook in the reaction, giving rise to side chain halogen substituted alkylidene-di-phenols.

Benzaldehyde with 2,6-dimethylphenol gave 4,4′-dihydroxy-3,3′,5,5′-tetramethyltritane (Reaction "A") and with 2,4-dimethylphenol gave 2,2′-dihydroxy-3,3′,5,5′-tetramethyltritane (Reaction "B"). Acetaldehyde reacted in a similar manner, yielding with 2,6-dimethylphenol, 1,1-bis-(4-hydroxy-3,5-dimethylphenyl)-ethane (Reaction "A") and with 2,4-dimethylphenol, 1,1-bis-(2-hydroxy-3,5-dimethylphenyl)-ethane (Reaction "B"). Crotonaldehyde, in the presence of hydrochloric acid, condensed with 2,6-dimethylphenol to give 1,1-bis-(4-hydroxy-3,5-dimethylphenyl)-3-chlorobutane and condensed with 2,4-dimethylphenol to give 1,1-bis-(2-hydroxy-3,5-dimethylphenyl)-3-chlorobutane (Reaction "C"). As suitably crystalline derivatives, the acetates of the above condensation products were prepared.

REACTION A



REACTION B



REACTION C

$$HOC_6H_3(CH_3)_2 + CH_3CH{=}CHCHO \longrightarrow HOC_6H_2(CH_3)_2CHOHCH{=}CHCH_3 + HOC_6H_3(CH_3)_2 \longrightarrow$$

$$[HOC_6H_2(CH_3)_2]_2CHCH{=}CHCH_3 \xrightarrow{HCl} [HOC_6H_2(CH_3)_2]_2CHCH_2CHClCH_3$$

Experimental

Condensation of Dimethylphenol with Acetaldehyde and with Benzaldehyde. Ratio 1:1.—One quarter of a mole of the dimethylphenol and aldehyde and 50 cc. of glacial acetic acid were placed in a 500-cc. three-necked round-bottom flask equipped with a gas inlet tube leading to the bottom of the flask. The solution was cooled in an ice-bath and a vigorous stream of dry hydrogen chloride was passed in for one hour. On standing overnight a semi-solid mass was obtained. This was filtered onto a Büchner funnel and washed with a small amount of glacial acetic acid. The condensation product was extracted in a Soxhlet extractor with petroleum ether and then recrystallized from ethyl alcohol.

Ratio 1:2.—Two one-hundredths of a mole of the dimethylphenol, 0.10 mole of the aldehyde and 10 cc. of glacial acetic acid were placed in an eight-inch test-tube

TABLE I

Compound	Ratio	Formula	M. p., °C. (uncor.)	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
4,4′-Dihydroxy-3.3′,5,5′-tetramethyltritane	1:1	$C_{23}H_{24}O_2$	131	83.13	82.84	7.23	7.20
	1:2	$C_{23}H_{24}O_2$	129	83.13	82.96	7.23	7.53
Acetate		$C_{27}H_{28}O_4$	148	77.88	78.01	6.75	6.67
2,2′-Dihydroxy-3,3′,5,5′ - tetramethyltritane	1:1	$C_{23}H_{24}O_2$	163	83.13	83.26	7.23	7.35
	1:2	$C_{23}H_{24}O_2$	163	83.13	82.86	7.23	7.50
Acetate		$C_{27}H_{28}O_4$	155	77.88	77.43	6.75	7.01
1,1-Bis-(4-hydroxy-3,5-dimethylphenyl)-ethane	1:1	$C_{18}H_{22}O_2$	143	80.00	80.17	8.15	7.86
	1:2	$C_{18}H_{22}O_2$	142	80.00	79.52	8.15	7.86
Acetate		$C_{22}H_{26}O_4$	111	74.58	75.05	7.34	7.24
1,1-Bis-(2-hydroxy-3,5-dimethylphenyl)-ethane	1:1	$C_{18}H_{22}O_2$	133	80.00	80.63	8.15	7.46
	1:2	$C_{18}H_{22}O_2$	130	80.00	79.70	8.15	8.65
1,1-Bis-(4-hydroxy-3,5-dimethylphenyl)-3-chlorobutane	1:1 or 1:2	$C_{20}H_{25}O_2Cl^a$	199	72.29	72.19	7.53	7.60
Acetate		$C_{24}H_{29}O_4Cl^b$	108	69.23	69.17	6.25	6.35
1,1-Bis-(2-hydroxy-3,5-dimethylphenyl)-3-chlorobutane	1:1 or 1:2	$C_{20}H_{25}O_2Cl$	152	72.29	72.46	7.53	7.52

[a] Chlorine, calcd. 10.45, found, 10.98. [b] Chlorine, calcd. 8.41; found, 8.40.

and cooled in an ice-bath. A vigorous stream of dry hydrogen chloride gas was passed into the solution for a few minutes. A precipitate was obtained immediately. This was filtered off and recrystallized from ethyl alcohol.

Condensation of Dimethylphenol with Crotonaldehyde.—Twelve grams of the dimethylphenol (0.10 mole) and 3.5 or 7.0 g. of crotonaldehyde (0.05 or 0.10 mole) were dissolved in 100 cc. of glacial acetic acid. To this solution was added 20 cc. of concentrated hydrochloric acid. On standing for two days a crystalline precipitate was obtained. This was filtered off, washed with a small amount of glacial acetic acid and then recrystallized from benzene.

Acetates.—Two grams of the condensation product was dissolved in 50 cc. of acetic anhydride and refluxed for two hours. The solution was poured into water and allowed to stand for one day. The resulting crystalline derivatives were recrystallized from dilute ethyl alcohol solution.

Summary

1. Phenols with only one ring position available for reaction were condensed with equi- and multimolar quantities of saturated, unsaturated and aromatic aldehydes. Crystalline condensation products of the alkylidene-di-phenol type were obtained exclusively in all cases.

2. When aldehydes are condensed with properly blocked phenols having only one ring position available for reaction, no Bakelite types of condensation products are formed, indicating that the formation of such types of condensation products requires at least *two* available ring positions in the reacting phenol. In blocked phenols, the possibility for the formation of ether types of condensation products definitely exists, yet, since no such products were formed, it appears that in aldehyde–phenol condensation formation of oxygen–carbon linkages is not favored. The results obtained when multimolar quantities of the aldehyde were used, indicate that the resinous character of Bakelite is not due to ante- or posterior polymerization of the aldehyde, but is due to *multiple diphenylmethane* type of linkages.

3. In the case of the condensation systems involving an unsaturated aldehyde, the catalyst partook in the reaction, a fact never before observed in this type of condensation.

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The Preparation of Cyclopropene

BY MAURICE J. SCHLATTER

Cyclopropene was synthesized in 1922 by Demjanow and Dojarenko[1a] and our entire knowledge regarding this interesting compound is due to the researches[1] carried out by these Russian scientists. In order to make it available in amounts sufficient for an extended investigation of its physical and chemical properties, the conditions attending its formation were studied in some detail. The steps employed in the synthesis are outlined in the accompanying chart.

The yields indicated are conservative, reproducible values obtained on a preparative scale as the result of four to thirty runs at each step. The over-all yield based on these figures and choosing the path (bold-faced arrows) found to be most convenient is 3.3%. Taking into account the quaternary iodide recovered from the dimethylcyclopropylamine formed in the last step, this value becomes 4.7%.

From a detailed study of the decomposition of the quaternary base on platinized asbestos it was shown that the optimum temperature for cyclopropene formation is 320–330°. Dimethylcyclopropylamine and methylacetylene which had been reported[1a] previously were also obtained. A more detailed discussion of the thermal decomposition is given in the experimental part.

Pure cyclopropene was obtained by distilling the hydrocarbons through a Podbielniak column. It distilled at -36 to $-35°$ at 744 mm. and analyzed for C_3H_4. In confirmation of Demjanow and Dojarenko[1] it was found that the olefin reacts energetically with bromine and polymerizes readily. It could not be conveniently stored, even at $-78°$. The[1a] statement that cyclopropene can be regenerated from dibromocyclopropane by treatment with zinc and alcohol was not confirmed. This procedure gave a product consisting to a large extent of cyclopropane. The problem of the reconversion of the stable dibro-

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[1] (a) Demjanow and Dojarenko, *Ber.*, **56**, 2200 (1923); *Bull. acad. sci. Russ.*, [6] 297 (1922); (b) *Bull. acad. sci. U. R. S. S.*, [7] 653 (1929); [*C. A.*, **24**, 1848 (1930)].