The compound containing the syringyl radical was characterized as follows: melting point, 141–142.5°. *Analysis* of the *p*-nitrobenzoate. Calcd. for $C_{20}H_{21}NO_8$: C, 59.5; H, 5.3; N, 3.47; OCH_3, 23.1. Found: C, 59.5; H, 5.28; N, 3.5; alkoxyl as OCH_3, 23.0.

Presence of the carbonyl group was confirmed by preparing the 2,4-dinitrophenylhydrazone of the ester. Calcd. for $C_{26}H_{25}N_5O_{11}$: N, 12.0. Found: N, 11.9.

These two products undoubtedly are to be regarded as important constituents of the building unit of the lignin molecule.

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY
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MONTREAL, P. Q., CANADA   RECEIVED OCTOBER 3, 1938

The Dimerization of 3-Phenylindene

BY C. S. MARVEL AND H. A. PACEVITZ

Blum-Bergmann has reported[1,2] a dimer of 3-phenylindene (m. p. 207–209°) as a by-product in a reaction in which 3-phenylindene was treated with lithium. No exact method of producing or isolating the dimer was described. We have tried to obtain the same compound for comparison with an isomeric hydrocarbon melting at 210–211°.[3] Various combinations of conditions have been used but none yielded the dimer reported. A different dimer melting at 157° has, however, been obtained.

Dimer of 3-Phenylindene.—A mixture of 30 cc. of 47% hydrogen iodide solution and 2 g. of 3-phenylindene was shaken for sixteen hours. A dark brown solid separated out. This was separated and dissolved in about 400 cc. of low-boiling petroleum ether (b. p. 40–60°). The ether solution was concentrated to about 100 cc., at which point some crystals separated. The product was twice recrystallized from petroleum ether. The yield was 1.9 g. of a product melting at 156–157°.

Anal. Calcd. for $C_{30}H_{24}$: C, 93.6; H, 6.4; mol. wt., 384. Found: C, 93.55, 93.48; H, 6.36, 6.45; mol. wt. (Rast), 357, 359.

In a similar manner 2 g. of 3-phenylindene and 25 cc. of fuming stannic chloride gave 1.7 g. of dimer melting at 156–157°.

Heating 3-phenylindene with equal parts of sirupy phosphoric acid and water, with glacial acetic acid, with concentrated sulfuric acid or a mixture of sulfuric acid and hydrochloric acid did not cause it to dimerize.

(1) Blum-Bergmann, *Ann.*, **484**, 26 (1930).
(2) Through the kindness of Dr. E. Bergmann we have obtained a sample of the dimer of 3-phenylindene melting at 210–211°. This product proved to be a different hydrocarbon from the hydrocarbon of the same composition and melting point reported by Farley and Marvel,[3] since a mixture of the two melted at 185–190°.
(3) Farley and Marvel, THIS JOURNAL, **58**, 32 (1936).

Treating a benzene solution of 3-phenylindene with metallic lithium in an atmosphere of nitrogen for several days did not produce a dimer.

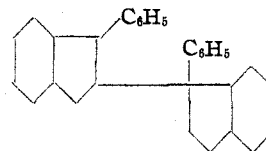Heating the dimer to 350° caused some charring but no 3-phenylindene was found in the distillate.

CHEMICAL LABORATORY OF THE
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS   RECEIVED JULY 15, 1938

The Dimerization of 3-Phenylindene

BY E. BERGMANN

The preceding Note by Marvel and Pacevitz has been made accessible to me through the courtesy of the Editor. The dimeric 3-phenylindene had only occasionally been obtained and its structure therefore had not been elucidated. Although the mechanism by which indene is dimerized[1] would lead only to one dimer of 3-phenyl-

indene, there may be other ways, too, of dimerization. An experiment has shown that the two substances, m. p. 210–211° and 156–157°, respectively, are not allyl isomeric forms, as they are not interconvertible by means of sodium ethylate solution.

(1) E. Bergmann and Taubadel, *Ber.*, **65**, 463 (1932).

THE DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE   RECEIVED AUGUST 30, 1938

β,β',β''-Trichlorotriethylamine

BY J. PHILIP MASON AND DALE J. GASCH

In the course of some other work, we had occasion to make trichlorotriethylamine and its hydrochloride. By a slight modification of the procedure used by Ward,[1] we were able to increase the yield of the hydrochloride from 70 to 92%.

Two moles (238 g.) of thionyl chloride dissolved in 150 ml. of benzene was added to 0.5 mole (92.7 g.) of triethanolamine hydrochloride in a 1-liter round-bottomed flask equipped with a reflux condenser and a gas absorption trap. The mixture was heated to 55° and kept at that temperature for three hours. The benzene and excess thionyl chloride were distilled under diminished pressure at 50°. In order to decompose the last portion of thionyl chloride, about 50 ml. of ethyl alcohol was added. The mixture was warmed for

(1) Ward, THIS JOURNAL, **57**, 914 (1935).

ten to fifteen minutes and then the alcohol was distilled. This step was found desirable because otherwise charring occurred when acetone was added to recrystallize the product. The residue was recrystallized from boiling acetone; yield, 106.3 g. (88%). By concentrating the acetone filtrate, a second crop of crystals (4.5 g.) was obtained, bringing the total yield up to 92%. McCombie and Purdie[2] made trichlorotriethyl-amine hydrochloride directly from triethanolamine and thionyl chloride, using chloroform as a solvent, and obtained a yield of 73.8%.

The free trichlorotriethylamine, obtained in the usual way from the hydrochloride, had a b. p. of 143–144° at 15 mm., which is 6° higher than that reported by McCombie and Purdie[2] at the same pressure.

Anal. Calcd. for $C_6H_{12}Cl_3N$: Cl, 52.1; mol. wt., 204.5. Found: Cl, 51.6, 51.8; mol. wt. (benzene), 205.9.

The amine was almost colorless when freshly distilled, but turned to a light brown color on standing for sixty hours. The color darkened on longer standing. Crystals, which were not identified, appeared in the liquid after standing for a month. Ether solutions of the amine darkened more slowly and no crystals were observed. Instead, a small amount of dark brown material was deposited from an ether solution which had been kept for two months. No attempt was made to identify this material.

(2) McCombie and Purdie, *J. Chem. Soc.,* 1217 (1935).

CHEMISTRY LABORATORY
BOSTON UNIVERSITY
BOSTON, MASS.   RECEIVED SEPTEMBER 3, 1938

The Catalytic Reaction between Sodium Nitrite and Dichlorodiethylenediamine Cobaltic Chloride

BY J. P. MCREYNOLDS AND JOHN C. BAILAR, JR.

In the course of stereochemical studies on the complex inorganic compounds, it was observed that racemic dichlorodiethylenediamine cobaltic chloride reacts almost instantaneously with sodium nitrite according to the equation $[Coen_2Cl_2]^+ + 2NaNO_2 \longrightarrow [Coen_2(NO_2)_2]^+ + 2NaCl$[1] but that the material which has been resolved into its optical antipodes reacts very slowly. This resolution is carried out through the α-bromocamphor-π-sulfonate, which is reconverted to the chloride by means of hydrochloric acid in alcohol and

(1) The symbol "en" represents ethylenediamine.

ether. The active product is then washed with alcohol and ether.[2] It was found that washing the racemic material with alcohol and ether caused it to lose its reactivity toward sodium nitrite. The washings contained cobaltous ion. That cobaltous ion catalyzes the reaction in question was demonstrated easily.[3]

Werner has noted[4] briefly that traces of acids catalyze this reaction but no other example of such catalytic substitution has been reported for compounds of this type. A study was therefore made to determine the mechanism of the reaction. Two compounds which seemed possible intermediates are sodium cobaltinitrite, $Na_3Co(NO_2)_6$, and sodium cobaltonitrite, $Na_2Co(NO_2)_4$. Sodium cobaltinitrite was found to have no catalytic effect in this reaction. On the other hand, the cobalto-nitrite ion could be precipitated (as the potassium salt) from mixtures which had been catalyzed artificially by addition of cobaltous ion. This seems to point to the intermediate formation of sodium cobaltonitrite.

The mechanism postulated for this catalysis must explain the very rapid replacement of chloro by nitro groups and the apparent absence of oxygen to cobalt linkages at any step in the reaction. This latter requirement is evidenced by the fact that at no time is there any indication of a red coloration such as is found in nitrito cobalt compounds. The isolated intermediate and the almost instantaneously formed product both have the yellow color characteristic of the nitrogen to cobalt bond. Further, nitrite complexes of trivalent cobalt have been prepared and characterized. They are stable in solution for a considerable period, changing to nitro complexes quite slowly.

The explanation offered here involves a shift of the electrons upon the nitrogen to allow it to form a coördinate bond to both trivalent and bivalent cobalt. This is a very unstable arrangement and is broken up immediately, leaving the nitrogen attached to the trivalent cobalt. This latter step seems quite logical since the trivalent cobalt complexes are very much more stable than those of bivalent cobalt. It must be assumed that

(2) Bailar and Auten, THIS JOURNAL, **56**, 774 (1934).

(3) The traces of cobaltous ion present in the racemic material evidently are produced during the conversion of the *trans* form of the complex to the *cis* form by evaporation of the solution and subsequent heating of the residue in the oven. A dry sample of optically active material unreactive to sodium nitrite became reactive after several hours of such heating. It lost a large part of its optical activity during the heating.

(4) Werner, *Ber.,* **34**, 1734 (1901).