

dinitrophenylhydrazone, and refuted the contention of Campbell³ that the second modification is merely a product contaminated with the dinitrophenylhydrazone of another carbonyl compound. On the basis of the evidence then available the relationship between these two crystal modifications was assumed to be one of polymorphism. However, a new melting point study using a Kofler and Hilbck micro heating stage⁴ has been completed and the results indicate dynamic isomerism rather than polymorphism as the true relationship. This explanation was proposed by Allen and Richmond⁵ on the basis of some work by Bredereck⁶ with substituted furfural derivatives, and is in accord with the new experimental results.

Experimental

The new melting point observations were made using a Kofler and Hilbck micro heating stage⁷ mounted on the object stage of a chemical microscope equipped with a 10X Reichert heat resisting objective. By this means thermal changes in individual crystals could be followed and the temperatures read by means of a calibrated thermocouple. Melting points by this method were found accurate to $\pm 2^\circ$ and precise to $\pm 0.5^\circ$. The samples of acetaldehyde 2,4-dinitrophenylhydrazone employed were prepared during the two earlier investigations.

Acetaldehyde 2,4-dinitrophenylhydrazone I (previously called the "stable form") recrystallized five times from 95% ethanol¹ was found to melt sharply without transition at 168–170° in agreement with 168.5° obtained previously by the more precise macro method. Above 115° in the initial heating a slight sublimate of orange lozenge-shaped crystals appeared and was recognized as the II modification (previously designated as "metastable"). These crystals melted at 156–157°. A few of these crystals in contact with modification I began melting at slightly lower temperature. The resulting liquid noticeably eroded plates of the I form below their regular melting temperature. In another experiment the sublimate was the I form (plates) and melted at the higher temperature (168–170°). On slowly cooling the liquid phase after complete fusion, the II form often reappeared first, usually at 130–140°; on reheating, this form was in equilibrium with the liquid at 148°, a slight change of temperature being sufficient to induce either growth or solution. In cases where the I form reappears first, the fusion or solution process begins at 150–155° and complete solution occurs between 155 and 160°. The above behavior is typical of a system in which the two compounds are, strictly speaking, different chemical entities but mutually convertible one into the other.

(3) Campbell, *Analyst*, **61**, 391 (1936).

(4) Kofler and Hilbck, *Mikrochemie*, **9**, 38 (1931).

(5) Allen and Richmond, *J. Org. Chem.*, **2**, 222 (1937).

(6) Bredereck, *Ber.*, **65**, 1833 (1932).

(7) This instrument manufactured by the optical firm of C. Reichert, Vienna, was obtained from Pfaltz and Bauer, Inc., Empire State Building, New York City.

A sample of derivative recrystallized once from benzene² had an initial melting point of 148–151°. Crystals (mainly the II modification) reappeared at 131° and were completely fused (or dissolved) at 149.5°. After several repetitions the fusion temperature was lowered to 142°.

The above observations indicate that acetaldehyde 2,4-dinitrophenylhydrazone exists in two chemically different forms (dynamic isomers), the ordinary form (I) melting sharply near 169° and a form (II) obtained by sublimation melting at 157°. Crystallization of the melt produces a mixture (probably an equilibrium mixture) melting near 148°. The derivative recrystallized from benzene although optically identical with the I modification melts near 149° as does the "equilibrium mixture," hence must contain traces of a catalyst (possibly sulfuric acid) capable of inducing a rapid isomerization. This accounts for the low melting points sometimes observed.² In the writer's earlier experiments¹ slow isomerization was mistaken for a more fundamental thermal breakdown and hence not given the attention it deserved.

AMMONIA DEPARTMENT

E. I. DU PONT DE NEMOURS & Co., INC.

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Structure of Lignin

By M. J. HUNTER, A. B. CRAMER AND HAROLD HIBBERT

In a recent note¹ the isolation of an aromatic ketone, $C_{13}H_{18}O_4$, from spruce wood by organic solvent extraction was reported and the additional presence of derivatives containing the syringyl group from hard woods noted.

Using maple wood and similar organic solvent extraction, there is obtained a mixture of two ketones, having in the pure state the empirical formulas $C_{12}H_{16}O_4$ and $C_{13}H_{18}O_5$, respectively, which can be readily separated by conversion into their *p*-nitrobenzoates.

One of these corresponds to the ester from the ketone previously reported, while the new crystalline *p*-nitrobenzoate is derived from the second ketone, the latter being related to the former by possessing an additional methoxyl group. They are apparently present in approximately equal amounts.

The theoretical conclusion drawn previously that hard woods differ from soft in having present in the building unit not only the guaiacyl but also the syringyl radical has thus been substantiated.

(1) *THIS JOURNAL*, **60**, 2274 (1938).

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; alkoxy 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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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 $C_{20}H_{24}$: 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.

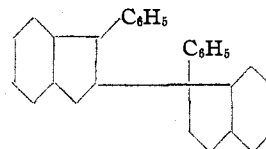
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The Dimerization of 3-Phenylindene

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 dimerized¹ 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).