and the undissolved substance filtered off. The product thus obtained proved to be unchanged triazole.

Calc. for $C_{15}H_{13}ON_3$: C, 71.71; H, 5.18; N, 16.73. Found: C, 71.79; H, 5.14; N, 16.89.

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[CONTRIBUTION FROM BOWNE HALL OF CHEMISTRY, SYRACUSE UNIVERSITY.]

DIPHENYL BUTADIENE.

BY J. M. JOHLIN.

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Dimethyl butadiene is most readily prepared by the dehydration of pinakon. Diphenyl butadiene should be similarly obtained by the dehydration of acetophenon-pinakon. The object of this paper is to define more definitely a compound, $C_{16}H_{14}$, melting at 49°, obtained by Thoerner[1] and Zinke when they dehydrated acetophenon-pinakon by heating it with acetic anhydride, and to describe several new methods by which acetophenon-pinakon can be obtained.

Acetophenon-pinakon has been prepared by the reduction of acetophenon with metallic sodium.[2] The process is a slow one and the yield small. Three new methods were tried. Acetophenon was reduced with magnesium ribbon, in the presence of mercuric chloride, according to the method used by Holleman to prepare pinakon from acetone. Small amounts of acetophenon-pinakon could be isolated from the product obtained by this process. Somewhat better yields were obtained by converting diacetyl into its diphenyl pinakon by means of magnesium methyl iodide by Grignard's reaction. It is very conveniently obtained by converting benzil into its dimethyl pinakon by means of magnesium phenyl bromide by Grignard's reaction.

Acetophenon-pinakon by dehydration yields a hydrocarbon, $C_{16}H_{14}$, and although the compound has not been defined beyond being a hydrocarbon of the above composition, it is undoubtedly diphenylbutadiene. Characteristic derivatives of this compound could not be formed. A bromine derivative by the addition of bromine cannot be prepared, a fact no doubt to be laid to the proximity of the phenyl group to the unsaturated carbon atom. Attempts to brominate acetophenon-pinakon likewise were without satisfactory results. The dehydration of the pinakon when carried out in a sealed glass tube by heating with acetic anhydride at 180° yields varying results. There is generally formed a brown liquid from which, after neutralization, the hydrocarbon can be obtained by steam distillation. In one instance a viscous somewhat elastic ribbon was formed in the glass tube. This material, insoluble in acetic anhy-

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[1] *Ber.*, 13, 641 (1880).

[2] Beilstein, "Organische Chemie."

dride, was likewise insoluble in many of the solvents in which diphenyl butadiene is soluble—such as ether, alcohol, acetone and petrol ether. It was quite soluble in benzene and chloroform. This substance could not be obtained a second time but is probably the condensation product of $C_{16}H_{14}$, comparable to gums obtained by the polymerization of the aliphatic hydrocarbons having the constitution $CH_2 = CX_1 — CX_2 = CH_2$.

In the preparation of acetophenon-pinakon from acetophenon, 95 g. of acetophenon were mixed in a round-bottomed flask of hard glass with 20 g. of magnesium ribbon and 20 g. of finely powdered mercuric chloride. The mixture was carefully heated over a free flame until it had attained a purple color. At this stage a violent reaction sets in, which, to prevent decomposition, is checked by immersing the flask in a vessel of water previously heated to the boiling point. The end of the reaction is noted by the cessation of steam bubbles forming on the surface of the flask. The reaction product is stirred up with water and the resulting gray mud acidified with dilute sulfuric acid and extracted with ether. The ether extract is dried over fused sodium sulfate, since calcium chloride converts acetophenon-pinakon into a white resinous mass, probably through dehydration and polymerization. The ether extract thus dried is filtered and left to evaporate and the syrup remaining as a residue extracted with cold petrol ether. The residue insoluble in petrol ether is allowed to stand, whereupon a considerable portion of acetophenon-pinakon slowly crystallizes out. The product is best recrystallized from petrol ether.

In the preparation of acetophenon-pinakon from diacetyl and phenyl bromide, Grignard's reagent was prepared using 12 g. of magnesium ribbon and 85 g. of phenyl bromide dissolved in 300 cc. of dry ether. The flask containing the reagent was cooled in ice water and through a reflux condenser 20 g. of diacetyl, dissolved in an equal amount of dry ether, slowly added. The reaction product was allowed to stand for an hour, occasionally heated to the boiling point, and finally poured upon chipped ice. The mixture was acidified with dilute sulfuric acid and extracted with ether. From the ether extract the pinakon was recovered as above.

In the preparation of acetophenon-pinakon from benzil and methyl iodide Grignard's reagent was prepared by dissolving 25 g. of magnesium ribbon in 150 g. of methyl iodide dissolved in 500 cc. of dry ether. The flask containing the reagent was attached to a reflux condenser, cooled by means of ice water, and through the top of the condenser gradually added 90 g. of finely powdered benzil. This mixture was allowed to stand for one hour, during which time it was occasionally heated to the boiling point. The reaction product was then slowly and with constant stirring poured upon chipped ice. The resulting mixture was acidified with dilute sulfuric acid, extracted with ether, and the ether extract dried over fused sodium sulfate. After filtering the ether was evaporated and from the residue the pinakon was recovered as above. The yield was about 60 g.

The dehydration of the pinakon was carried out according to the method mentioned by Thoerner and Zinke.[1] One part of the pinakon is heated with three parts of acetic anhydride in a sealed tube for three hours at a temperature of 180°. The mixture is diluted with water, neutralized with sodium carbonate and subjected to a steam distillation. The hydrocarbon carried over with the steam readily crystallizes and is easily recrystallized from alcohol. Its melting point was found to be 49°. The readiness with which it spontaneously changes into a resinous material has already been mentioned, likewise the fact that satisfactory derivatives were not prepared.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

DIPHENYLTETRACHLOROPHTHALIDE AND SOME OF ITS DERIVATIVES.

BY W. R. ORNDORFF AND MISS R. R. MURRAY.

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The tetrachlorophthalic acid used in this investigation was a commercial product purified by the method of Delbridge.[2] The acid had a faint yellow color but melted at 255–257° and an analysis[3] showed that it was pure.

Subst., 0.1731; cc. 0.1 N $AgNO_3$, 22.19.

Calc. for $C_8H_2O_4Cl_4.{}^1/_2H_2O$: Cl, 45.33. Found: Cl, 45.46.

Tetrachlorophthalic anhydride was prepared from the acid by heating 120 hours in a water oven at a temperature of about 100°, previous work[4] having shown that this was sufficient time for its complete conversion into the anhydride.

Diphenyltetrachlorophthalide.—This substance was first prepared by the action of aluminum chloride on tetrachlorophthalyl chloride in benzene solution. The tetrachlorophthalyl chloride was prepared, with some changes, according to the method of Graebe.[5] One molecule of the acid and 3.5 molecules of phosphorus pentachloride were heated in a flask connected with an upright condenser to 150–160° on a metal bath for 30 hours. The phosphorus oxychloride was then distilled off and the residue, which did not pass over at 125° under atmospheric pressure, was distilled under reduced pressure. A pale yellow liquid was obtained which immediately solidified to a pale yellow solid. This was recrystallized from benzene,

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[1] *Loc. cit.*

[2] *Am. Chem. J.*, 41, 414 (1909).

[3] *Ibid.*, 41, 397 (1909).

[4] *Ibid.*, 41, 359 (1909).

[5] *Ann.*, 238, 328 (1887).