

tion rate as revealed by the decline of the toluene yield. It appears therefore that here the dehydrogenation rate is even more affected by the poisoning action than the cyclization, but the decline still runs parallel to that of the cyclization.

The interpretation given to the results discussed leads to the conclusion that both reactions, dehydrogenation and cyclization, are affected by the poisoning of the catalyst. Where the poisoning action is due to accumulation of polymer, which is probably the reason for the decline of activity in the course of a run, the two reactions are affected to much the same extent. When water and particularly when ethylene is the poison the dehydrogenation rate is repressed even more than that of cyclization, but the decline is still parallel.

These conclusions are contrary to the views of Taylor and Fehrer mentioned previously. It follows that their further deductions concerning the relation of the two reactions and the seat of catalytic action need revision. In their view, because of the very different effect of catalyst poisons on the two reactions, the two reactions take place on different active centers of the catalyst. The present interpretation leads to the opposite conclusion—which also appears the simpler—that, because of the close relationship revealed by the parallel effect of poisons on both reaction rates, it seems likely that they proceed on identical centers of the catalyst surface.

MANCHESTER OIL REFINERY, LTD.
MANCHESTER, ENGLAND

RECEIVED JUNE 30, 1945

Methylation of Methyl 6-Hydroxydehydroabietate

BY HAROLD H. ZEISS

Methyl 6-hydroxydehydroabietate can be satisfactorily methylated with dimethyl sulfate in an ethereal solution of methylmagnesium chloride.¹ It has been reported that methylation with dimethyl sulfate in alcoholic alkali gives small or vanishing yields. This difficulty was attributed to the steric hindrance exerted by the adjacent isopropyl group, although this explanation appeared surprising in view of the reactivity of the 6-position of the dehydroabietic structure.

It has now been found that the use of dimethyl sulfate in aqueous alcoholic alkali gives a good yield with ease and rapidity.

Experimental

To a solution of 3 g. of methyl 6-hydroxydehydroabietate (m. p. 158–159°) in 60 ml. of ethanol and 42.5 ml. of 1% aqueous sodium hydroxide 1 g. of dimethyl sulfate is added at room temperature and the turbid mixture refluxed for two and one-half hours. Ten ml. of 12% sodium hydroxide is then added to destroy the excess dimethyl sulfate. After distilling off the alcohol and cooling, the

residue is extracted with several portions of ether and the extract washed with water until neutral. Replacement of the ether with ethanol and the addition of water to turbidity gives broad white plates of methyl 6-methoxydehydroabietate in a pure state. The yield in three crops has been 2.1 g. (68%); m. p. 65–66°.

The method was repeated with another 3 g. of methyl 6-hydroxydehydroabietate (m. p. 158–159°). From this run methoxy ester of the same m. p. was obtained again in 68% yield.

RIDBO LABORATORIES, INC.
PATERSON 3, NEW JERSEY

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NEW COMPOUNDS

Some Polysubstituted Benzene Derivatives

3-Benzoylmesitonitrile.—A mixture of 10.1 g. of 3-bromomesityl phenyl ketone,¹ 4.5 g. of cuprous cyanide and 6 ml. of pyridine was heated for twelve hours under reflux in a metal bath maintained at 220–225°. The hot reaction mixture was poured into a dilute ammonium hydroxide solution and, after several hours, a mixture of 100 ml. of ether and 70 ml. of benzene was added to the resulting tarry mass. The organic layer, after being washed with dilute ammonium hydroxide and with water, was filtered. Removal of the solvent left the nitrile as an oily residue which crystallized when allowed to stand with methanol. It was recrystallized from methanol; m. p. 107–108°; yield 83%.

Anal. Calcd. for C₁₇H₁₅ON: C, 81.90; H, 6.07. Found: C, 81.70; H, 6.18.

1,2-Di-(2,4,6-triisopropylbenzoyl)-ethylene.—A solution of 76.5 g. of fumaryl chloride in 100 ml. of dry carbon disulfide was added gradually over a period of one and one-half hours to a mixture of 245 ml. of 1,3,5-triisopropylbenzene, 300 ml. of carbon disulfide and 140 g. of anhydrous aluminum chloride. The reaction mixture was stirred continuously during the period of addition and for two hours afterward. It was poured on a mixture of 1 kg. of ice and 100 ml. of concentrated hydrochloric acid. Removal of the solvent left the 1,2-di-(2,4,6-triisopropylbenzoyl)-ethylene as a gummy, red solid. It separated from acetone in yellow needles; m. p. 190.5–192°; yield 47%.

Anal. Calcd. for C₃₄H₄₈O₂: C, 83.55; H, 9.90. Found: C, 83.40; H, 9.76.

1,2-Di-(2,4,6-triisopropylbenzoyl)-ethane.—A suspension of 9.7 g. of 1,2-di-(2,4,6-triisopropylbenzoyl)-ethylene in 150 ml. of ethanol was shaken with 0.05 g. of platinum oxide in an Adams hydrogenation machine. One mole of hydrogen was absorbed. Acetone was added to bring the product into solution and the catalyst was removed by filtration. The filtrate evidently contained the expected enediol, 1,4-di-(2,4,6-triisopropylphenyl)-1,3-butadiene-1,4-diol, for it rapidly turned yellow when exposed to the air. It continued to give a positive indophenol test for about twenty minutes. Dilution of the solution with water precipitated the 1,2-di-(2,4,6-triisopropylbenzoyl)-ethane in the form of white crystals. These gave a negative indophenol test. The diketone crystallized from methanol in colorless hexagonal plates; m. p. 140–141°.

Anal. Calcd. for C₃₄H₅₀O₂: C, 83.21; H, 10.27. Found: C, 83.37; H, 10.42.

N-Methylmesitamide.—A solution of 27.5 g. of mesityl chloride in 20 ml. of low-boiling petroleum ether was added dropwise, with stirring, to 100 ml. of a 35% methylamine solution. The reaction mixture was kept ice cold during the addition and was stirred at room temperature for one

(1) (a) Campbell and Todd, *THIS JOURNAL*, **62**, 1287 (1940); (b) Campbell, U. S. Patent 2,359,826; (c) L. F. Fieser, "Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1944, p. 994.

(1) Hyde and Adams, *THIS JOURNAL*, **50**, 2503 (1928).