[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, FORDHAM UNIVERSITY]

Applicability of Palladium Synthetic High Polymer Catalysts

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The preparation of highly active palladium and platinum synthetic high polymer catalysts was presented in an earlier paper.[2] Their general superiority over other types of noble metal catalysts is now further exemplified by the hydrogenation of furfural, quinone, benzil, cinnamic aldehyde, *m*-bromonitrobenzene, chaulmoogric and propiolic acids. The procedure for the hydrogenation has been described elsewhere.[2] The data obtained are summarized in Table I.

TABLE I

SUMMARY OF THE HYDROGENATIONS OF VARIOUS COMPOUNDS[j]

Compound	Catalyst	Moles H_2/mole compound	Time	Products
Benzil, 1 g.	Pd–PAME[a]	2	80 min.	Hydrobenzoin
Benzil, 2 g.	Pd–PAME[a]	3.18	30 hours	Dibenzil
m-Bromonitrobenzene (1 g.)	Pd–PVA[b]	4	15 min.	Aniline
m-Bromonitrobenzene (2 g.)	Pd–PVA[b]	7	65 hours	Cyclohexylamine
Chaulmoogric acid, 1 g.	Pd–PAME[c]		60 min.	Corresponding hydrogenated product[d]
Cinnamic aldehyde, 2 cc.	Pd–PVA[e]	1.39	120 min.	Not isolated
Cinnamic aldehyde (5.075 g.)	Pd–PAME[f]	2.31	10 hours	Hydrocinnamic aldehyde Hydrocinnamic alcohol Propylbenzene
Cinnamic aldehyde (5.015 g.)	Pd–MMA[g]	2.38	45 hours	
Furfural, 1 cc.	Pd–PAME[h]	3	8 hours	Not isolated
Propiolic acid (1.175 g.)	Pd–PVA[b]	1	15 min.	Acrylic acid
Quinone, 1.08 g.	Pd–PVA[i]	1	5 min.	Hydroquinone

[a] 15 mg. Pd, 400 mg. PAME, 50 cc. glacial acetic acid. [b] 10 mg. Pd, 250 mg. PVA, du Pont RH-391, 50 cc. of 50% alcohol. [c] 10 mg. Pd, 400 mg. PAME, 50 cc. glacial acetic acid (warm). [d] Spec. rotation: before reduction + 43°, after, 0.0°. [e] 10 mg. Pd, 250 mg. PVA, 50 cc. of 50% alcohol. [f] 25 mg. Pd, 400 mg. PAME, 50 cc. glacial acetic acid. [g] 25 mg. Pd, 400 mg. MMA, 50 cc. glacial acetic acid. [h] 10 mg. Pd, 400 mg. PAME, 50 cc. glacial acetic acid. [i] 10 mg. Pd, 250 mg. PVA, I. G. product, 50 cc. of 50% alcohol, neutral medium. [j] For a more complete summary see ref. 2.

With benzil it was found that using Pd–PAME the reduction of hydrobenzoin to dibenzil takes place without intermediate formation of phenylbenzilcarbinol. In the case of *m*-bromonitrobenzene,[3] the reduction of the nitro group took place simultaneously with complete dehalogenation, the final product being cyclohexylamine which was obtained in theoretical yield. Cinnamic aldehyde, as well as furfural, was distilled in an atmosphere of nitrogen prior to use. From the former we isolated and identified hydrocinnamic aldehyde, hydrocinnamic alcohol and propylbenzene. The reported impossibility[4] of reducing quinone in acid solution has been overcome by the Pd–PVA catalyst. With a reaction mixture containing 1.08 g. of quinone and 0.25 cc. of concd. hydrochloric acid in 50 cc. of 50% alcohol catalyst solution containing 10 mg. of palladium and 250 mg. PVA (du Pont RH-391), the absorption of hydrogen at the end of ten minutes was 95 cc. The obtained hydroquinone was sublimated and identified.

As a result of our experiments certain compounds have been reduced for the first time over palladium. Among these transformations may be listed that of benzil to dibenzil, *m*-bromonitrobenzene to cyclohexylamine, and quinone to hydroquinone in acid solution. The superiority of PAME over MMA catalysts has been demonstrated in the reduction of cinnamic aldehyde.

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Summary

The effectiveness and superiority of synthetic high polymer palladium catalysts has been demonstrated in a number of typical and difficult hydrogenations.

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[2] Louis D. Rampino and F. F. Nord, THIS JOURNAL, **63**, 2745 (1941).

[3] Wheeler and McFarland, *Am. Chem. J.*, **19**, 366 (1897).

[4] O. Neunhoeffer and W. Pelz, *Ber.*, **72**, 433 (1939); E. F. Rosenblatt, THIS JOURNAL, **62**, 1092 (1940).