

formation of small amounts of diacetate $\text{CF}_3\text{CH}_2\text{C}(\text{CF}_3)(\text{OAc})_2$. The monoacetate is transformed into $\text{CF}_3\text{COCH}_2\text{CF}_3$ in 99% yield by alcoholysis

with butanol, while the diacetate does not undergo alcoholysis cleanly.

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Investigations on the Mechanism of Catalytic Hydrogenations. XV. Studies with Colloidal Iridium

BY W. P. DUNWORTH AND F. F. NORD

I. Introduction

Results on the application of synthetic polymers in obtaining highly effective colloidal platinum, palladium and rhodium catalysts, studies on their physical properties and on the mechanism of their action have been reported by this laboratory in the past.¹ In the present paper observations will be communicated which were made with the aid of a colloidal iridium catalyst supported by polyvinyl alcohol (PVA).

More than three decades ago the preparation of colloidal iridium utilizing sodium protalbinat and sodium lysalbinat as protective colloids was reported.² Aside from the contents of these papers only scanty information is available on colloidal iridium and no systematic kinetic study has been made on hydrogenations with such a catalyst attempting to apply more recent developments in theoretical chemistry.

II. Experimental

Preparation of the Iridium-PVA Catalyst.—To 40 cc. of distilled water was added 50 cc. of a 4% aqueous PVA solution. Then 10 cc. of a 0.5% (of iridium) solution of potassium iridium chloride and 1.1 cc. of a 20% (by weight) aqueous solution of sodium hydroxide is added with stirring to bring about a change of the color of the solution from deep red to straw yellow. The covered contents of the beaker are then placed on the steam-bath for fifteen minutes. Due to this heating, the straw-colored solution assumed an opaque brownish black color. The solution is then allowed to cool to room temperature, measured, and, if necessary, distilled water is added to bring the total volume to 100 cc. Hereafter the solution is shaken with hydrogen at atmospheric pressure for twenty minutes and is then immediately neutralized with 10% acetic acid. The catalyst is now ready for use. Twenty cc. of this preparation contain 10 mg. of iridium.

Hydrogenation of Organic Substances.—In these experiments a constant mole fraction (usually 0.01 mole) of the substrate was dissolved in 100 cc. of 76% ethanol and 1 cc. of 10% sodium hydroxide. Then 20 cc. of the catalyst preparation was added to the ethanol-substrate solution and the mixture was placed in a vessel where it was shaken with hydrogen at atmospheric pressure and room temperature.

III. Results and Discussion

The first compound used as a substrate for hy-

drogenation with our colloidal iridium catalyst was nitrobenzene.³ Complete reduction of 1/100 of a mole was effected in twenty minutes. The rate of the hydrogenation was found to be minimum in acid solution and maximum in alkaline solution.

While the catalyst was found to be useful for the reduction of nitrobenzene, it was noticed that it was ineffective for the hydrogenation of benzoic acid, benzaldehyde, phenyl cyanide, styrene, or allyl alcohol when the operation was carried on for twice as long a period of time as was required to completely reduce the same mole fraction of nitrobenzene.

It was also observed that elemental sulfur, hydrogen sulfide, thiophene, and allyl thiourea rendered the catalyst ineffective for the reduction of nitrobenzene.

However, since evidence has been presented showing that the mechanism of hydrogenation using colloidal palladium differs from that using colloidal rhodium,¹¹ and ¹² it was decided to study the mechanism of hydrogenation using colloidal iridium. For these reductions meta and para substituted nitrobenzene derivatives were chosen. The results of these experiments are recorded in the following tables.

TABLE I NITROBENZENE COMPOUNDS SUBSTITUTED IN THE <i>meta</i> POSITION		TABLE II NITROBENZENE COMPOUNDS SUBSTITUTED IN THE <i>para</i> POSITION	
Substituent	Hydrogen uptake in 5 minutes, cc.	Substituent	Hydrogen uptake in 5 minutes, cc.
Cl	220	CHO	225
Br	210	Cl	212
OCH ₃	160	Br	205
H	160	CN	185
CH ₃	142	H	160
CHO	105	NO ₂	105 (0.5 total)
NH ₂	102	OCH ₃	56
CN	86	COOH	55
NO ₂	80 (0.5 total)	CH ₃	49
COOH	19	NH ₂	38

The only relationship which we could discern between the rate of hydrogenation with colloidal iridium and a property which is inherent in the molecules, was that between the dipole moment of nitrobenzenes substituted in the meta position by

(1) F. F. Nord and co-workers, *THIS JOURNAL*, (a) **63**, 2745 (1941); (b) **63**, 3268 (1941); (c) **64**, 2721 (1942); (d) **65**, 429 (1943); (e) **65**, 2121 (1943); (f) **66**, 2126 (1944); (g) *Proc. Natl. Acad. Sci., U. S.*, **29**, 246 (1943); (h) *Experientia*, **3**, 489 (1947); (i) *J. Colloid Sci.*, **3**, 363 (1948); (j) **3**, 377 (1948).

(2) C. Paal and co-workers, *Ber.*, **50**, 722 (1917), and previous papers in this series.

(3) F. F. Nord, *ibid.*, **52**, 1705 (1919).

ortho, para directing groups and the log of the hydrogen uptake. However, this relationship may be fortuitous.

Since the rate of hydrogenation varies with the nature of the substituent groups we conclude that the colloidal iridium catalyst causes the hydrogen to add to the nitro group in an ionic form as was found to be the case with rhodium.^{1b}

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IV. Summary

1. A method has been described for the preparation of an iridium-polyvinyl alcohol catalyst.

2. A kinetic study of hydrogenations carried out with this catalyst has been undertaken.

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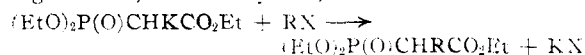
[CONTRIBUTION FROM THE RUSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE]

Alkylation of Triethyl Phosphonoacetate and Related Esters

BY GENNADY M. KOSOLAPOFF AND J. STEPHEN POWELL

A number of years ago Arbuzov and his co-workers discovered the possibility of alkylation of triethyl phosphonoacetate in a manner analogous to that used for alkylation of dialkyl malonates.¹ However, no further investigations of this useful reaction existed until the present, while the work of Arbuzov and Razumov covered but a few examples. A more thorough study of the possibilities of this reaction was undertaken in this Laboratory in order to provide the necessary intermediates for the synthesis of "phosphono" analogs of naturally occurring amino acids and to clear up several points of identification of phosphonocarboxylic acids which have been left from the work of Arbuzov and Razumov, as well as from some earlier studies of Michaelis.

Triethyl phosphonoacetate may be alkylated readily, *via* its potassium derivative, in satisfactory yields, especially when a relatively high-boiling solvent, such as xylene, is used.



Furthermore, it has been found that dialkylation is also feasible and several disubstituted compounds were readily prepared. This finding was useful in the final identification of the oxidation product of the "diacetonephosphinic" acid of Michaelis,² which was provisionally given the structure of dimethylphosphonoacetic acid by Anschütz, Klein and Cermak.³

While triethyl phosphonoacetate reacts quite readily with potassium metal on heating, the mono-alkylated esters react even more readily and their metal derivatives are obtainable without external heating. These react with alkyl halides to yield the dialkylated esters. The separation of the alkylation products is not a difficult

task when the alkyl groups employed are fairly large, but the methylated derivatives present a particularly difficult problem, since the mono-methylated derivative boils at essentially the same temperature as the unsubstituted ester; the dimethylated ester boils lower than these and may be separated rather readily. The monomethylated product, reported by Arbuzov and Razumov,¹ was stated to yield on hydrolysis a free acid, the melting point of which was reported as 119–132°; the paper of Arbuzov and Dunin¹ described the acid as a hygroscopic sirup. These unsatisfactory results are readily explainable by contamination of the monomethylated ester with, probably, small amounts of the starting material. Our results were similar to those of Arbuzov and his co-workers. The only other reference to this acid is given by Nylen,⁴ who obtained the acid by hydrolysis of the triethyl ester, which in turn was secured by the reaction of triethyl phosphite with ethyl α -bromopropionate in an extremely poor yield; Nylen's acid also had an unsatisfactory melting point (75–95°) and was admittedly impure. Nylen mentioned that his triethyl methylphosphonoacetate lost a considerable part of its phosphorus content during hydrolysis in the form of phosphorous acid. Neither Arbuzov and Razumov nor the present investigation confirm such dephosphonation of the ester prepared by alkylation of triethyl potassiumphosphonoacetate. The appearance of phosphorous acid during hydrolysis of Nylen's product is explainable by the contamination of the desired ester, in the course of its preparation, by tetraethyl hypo- and pyrophosphates, which form a rather difficultly separable mixture which boils in the range of the methylphosphonoacetate. The formation of the hypo- and pyrophosphates is a common side reaction in the interaction of secondary halides with reagents of the phosphite class and appears to involve the formation of $(\text{RO})_2\text{PO}$, which dimerizes and also undergoes oxidation-reduction reactions.⁵

(1) Arbuzov and Razumov, *J. Russ. Phys.-Chem. Soc.*, **61**, 628 (1929). A previous communication by Arbuzov and Dunin (*Ber.*, **60**, 291 (1927)) stated that such a reaction had been carried out but gave no information whatever about the procedure used or results obtained.

(2) Michaelis, *Ber.*, **17**, 1273 (1884); **18**, 898 (1885); **19**, 1009 (1886).

(3) Anschütz, Klein and Cermak, *ibid.*, **77**, 726 (1911).

(4) Nylen, *ibid.*, **57**, 1023 (1924).

(5) Chuvanne and Rumpf, *Compt. rend.*, **225**, 1322 (1947).