

by gravity and the filter paper washed with water. The filtrate was titrated with silver nitrate by means of an electrometric titrimeter.

Anal. Calcd. as moles of hydrochloric acid per mole of DDT: 4-hour irradiation, 0.39; 8-hour irradiation, 0.67; 16-hour irradiation, 0.88.

1,1,4,4-Tetrakis-(*p*-chlorophenyl)-1,2,3-butatriene (III).—A suspension of 100 mg. of II (from irradiated DDT) in 50 ml. of 2 *N* alcoholic potassium hydroxide was refluxed for two hours. The mixture was poured into 150 ml. of water and filtered by gravity when precipitation was completed. The yellow reaction product was washed with water, and the washings were added to the filtrate. The reaction product was dissolved in 50 ml. of benzene and shaken with water. The aqueous extracts were added to the filtrate.

The benzene solution was concentrated to 5 ml. on the steam-bath, and the yellow-orange needles that separated were recrystallized and dried in vacuum at room temperature. The product melted at 288° with decomposition, and no lowering of melting point could be observed when it was mixed with III prepared in accordance with Brand and Bausch.⁵

The filtrate from the original precipitation together with the washings was neutralized with concentrated nitric acid, and then a 3-ml. excess was added. The solution was titrated with 0.1 *N* silver nitrate with an electrometric titrimeter.

Anal. Calcd. for C₂₂H₁₈Cl₆: 2 moles Cl, 13.40 mg. Cl. Found: 13.65 mg. Cl.

4,4'-Dichlorobenzophenone (IV).—A solution of 45 mg. of III (from irradiated DDT) and 50 mg. of chromic anhydride in 5 ml. of acetic acid was refluxed for two hours. The solution was poured into 50 ml. of water and the reaction product filtered and recrystallized from alcohol. The product weighed 27 mg. and melted at 145–146°. No depression of melting point was observed when the product was mixed with authentic 4,4'-dichlorobenzophenone.

The ketone yielded an oxime of melting point 134–135°. Dittrich⁸ gives the melting point as 135°.

Summary

It has been shown that ultraviolet light catalyzes the decomposition of DDT.

One of the decomposition products is 4,4'-dichlorobenzophenone when air is present. In the absence of air 2,3-dichloro-1,1,4,4-tetrakis-(*p*-chlorophenyl)-2-butene is formed. This compound, through loss of hydrogen chloride and subsequent oxidation, may be converted into 4,4'-dichlorobenzophenone.

(8) M. Dittrich, *Ann.*, **264**, 177 (1891).

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

Catalytic Reduction of Aromatic Ketones

By E. C. HORNING AND D. B. REISNER¹

The problem of reducing β -aroylpropionic acids to the corresponding γ -arylbutyric acids in convenient fashion and in good yield has led to continued investigation of classical chemical methods for the reduction of an aryl keto group to a methylene group. This work has led to the development of greatly improved procedures in the form of the Clemmensen–Martin–Sherman procedure² and the Wolff–Kishner–Huang method.³ Modifications of these procedures can be applied to the reduction of aliphatic and alicyclic carbonyl groups as well, and these methods are of particular value because of this degree of generality.

The reduction of a carbonyl group adjacent to an aromatic nucleus does not present a difficult problem in terms of reactivity; the conversion of keto groups of this kind to the corresponding alcohols has been observed under a variety of mild catalytic hydrogenation conditions, and it is known that compounds of the benzyl alcohol type will undergo catalytic hydrogenolysis with ease to yield a fully reduced system. The fact that catalytic methods are not widely used for the reduction of such carbonyl groups to methylene groups is apparently due to the circumstance that appropriate catalytic conditions have not been established in many instances. We have found that certain types of carbonyl compounds can be reduced eas-

ily and in good yield by catalytic means, but that it is not always possible to predict in advance what effect structural changes will have upon the reduction. For example, 6-acetoxycoumaran-3-one can be reduced easily to 6-acetoxycoumaran, but under the same conditions the reduction of 6-hydroxycoumaran-3-one proceeds very slowly to give a mixture which includes products resulting from reduction of the aromatic ring.⁴

In the case of ketoacids, catalytic reduction with a palladium–carbon catalyst appears to proceed with particular ease in acetic acid at 65°. Two examples of the reduction of β -aroylpropionic acids are described; on a scale of about 0.1 mole the reduction was completed in about thirty or forty minutes, and the product was isolated easily in good yield. There was no apparent change in the rate of reduction during this period, and no attempt was made to isolate an intermediate reduction stage. For acids of this kind, this method may be superior to the procedures now in general use.

The reduction of *o*-benzoylbenzoic acid proceeded smoothly and rapidly to give *o*-benzylbenzoic acid in 95% yield.

The reduction of benzoin, under the same conditions, occurred very much less readily. The rate of reduction was rapid at first, but the time required for completion was much longer (about eight hours) and slightly less than the theoretical

(1) Research Corporation Research Assistant, 1948.

(2) Fieser, *et al.*, *This Journal*, **70**, 3197 (1948).

(3) Huang, *ibid.*, **68**, 2487 (1946).

(4) Horning and Reisner, *ibid.*, **70**, 3619 (1948).

amount of hydrogen was taken up. The product, 1,2-diphenylethane, was isolated easily in crystalline form by dilution of the solvent with water. In this case, both oxygenated functional groups were converted to methylene groups.

Acknowledgment.—We are indebted to the Research Corporation for a grant-in-aid of this work.

Experimental

All melting points are corrected.

Palladium-Carbon Catalyst.—A 5% palladium-carbon catalyst was prepared according to the general method of Hartung.⁵ The palladium was obtained from J. Bishop and Company, in a 10% solution, and was deposited on Norit.

γ -(*p*-Tolyl)-butyric Acid.—A mixture of 20.0 g. of β -(*p*-toluyl)-propionic acid,⁶ 3.0 g. of 5% palladium-carbon catalyst, and 40 ml. of acetic acid was shaken with hydrogen (initial pressure, 40 lb.) in a Parr hydrogenation apparatus at approximately 65°. The reduction (100% absorption) was completed in about twenty-five minutes. No further absorption occurred on continued shaking. The catalyst was removed by filtration and washed with acetic acid. The solvent was removed by distillation at atmospheric pressure; the distillation was continued under reduced pressure to yield 14.7 g. (79%) of γ -(*p*-tolyl)-butyric acid, b. p. 124–134° (0.3–0.5 mm.), m. p. 54–56° (reported, m. p. 61–62°, 92%, Clemmensen-Martin method).⁷

γ -(*p*-Anisyl)-butyric Acid.—The reduction of 20.8 g. of β -(*p*-anisoyl)-propionic acid⁸ was carried out in 125 ml. of acetic acid with 3.0 g. of 5% palladium-carbon catalyst at approximately 65°. About forty minutes was required

for the reduction (100% absorption). After removal of the catalyst, the solution was added to 200 ml. of water. The mixture was chilled and filtered to provide 14.5 g. (75%) of colorless γ -(*p*-anisyl)-butyric acid, m. p. 61–62° (reported, Clemmensen-Martin method, m. p. 59–60°, 65%⁹; m. p. 60–61°, 85%⁷; Wolff-Kishner-Huang method, 75%¹⁰).

***o*-Benzylbenzoic Acid.**—The reduction of 27.6 g. of *o*-benzylbenzoic acid was carried out in 40 ml. of acetic acid with 3.0 g. of palladium-carbon catalyst at approximately 65°. About seventy-five minutes was required for completion of the reaction. After removal of the catalyst, the solution was poured into 200 ml. of water, and the mixture chilled for twelve hours. Filtration and drying *in vacuo* yielded 24.5 g. (95%) of colorless *o*-benzylbenzoic acid, m. p. 111–113° (reported, m. p. 113–114.2°, 75%, Clemmensen method).¹¹ The product was completely soluble in warm sodium bicarbonate solution.

1,2-Diphenylethane.—The reduction of 21.2 g. of benzoin was carried out in 200 ml. of acetic acid with 3.0 g. of 5% palladium-carbon catalyst at 65°; the rate of hydrogen absorption slowed gradually and stopped after about eight hours at 92% of completion. The catalyst was removed and the solution was poured into 300 ml. of water. The product crystallized immediately; after chilling, filtration yielded 13.5 g. (74%) of 1,2-diphenylethane, m. p. 49–50° (reported,¹² 51.5–52.5°).

Summary

A method for the catalytic reduction of certain aryl ketones is described. The keto group is reduced to a methylene group in acetic acid solution at 65° with a palladium-carbon catalyst.

(9) Fieser, *et al.*, *ibid.*, **70**, 3200 (1948).

(10) Dauben and Adams, *ibid.*, **70**, 1759 (1948).

(11) Bradlow and VanderWerf, *ibid.*, **69**, 1254 (1947).

(12) Cannizzaro and Rossi, *Ann.*, **121**, 251 (1862).

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(5) "Organic Syntheses," **26**, 77 (1946).

(6) "Organic Syntheses," Coll. Vol. II, **82** (1943).

(7) Martin, *THIS JOURNAL*, **58**, 1438 (1936).

(8) Fieser and Hershberg, *ibid.*, **58**, 2314 (1936).

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Allylic Chlorides. V. Relative Reactivities with Sodium Ethoxide in Ethanol

BY LEWIS F. HATCH AND HAROLD E. ALEXANDER

The relative reactivities of various allylic chlorides with potassium iodide in acetone have been reported^{1,2} which indicate that both position isomerism and geometrical configuration have an effect on the rate of reaction. Although the reaction between sodium ethoxide and several allylic chlorides has been reported,^{1,3} no effort had been made to ascertain if this reaction is influenced by geometrical configuration until the recent work of Andrews and Kepner.⁴ Young and Andrews⁵ had, however, suggested that this might be the case.

The present study was made to extend previously reported investigations on the sodium ethoxide reaction to determine the effects of substituents on the rate of reaction, and also to

confirm the observation of Andrews and Kepner pertaining to the lack of influence of geometrical isomerism.

Materials

1-Chloro-1-propene.—A mixture of *cis* and *trans* 1-chloro-1-propene (Research Chemicals, San Jose, California) was distilled to obtain a fraction with a boiling range of 34–35°. This fraction, being intermediate in boiling range between the two isomers (*cis* 32.0–32.2°; *trans* 36.7°), was assumed to contain both isomers.

Allyl chloride⁶ boiling at 44.3° was used without further purification; n_D^{25} 1.4109.

Methallyl chloride⁶ was redistilled and a fraction boiling at 70.9–71.0° was used.

2-Bromo-3-chloro-1-propene obtained from Halogen Chemicals of Columbia, S. C., was distilled at 150 mm. pressure. The fraction used boiled at 61.5°; n_D^{25} 1.4967.

2,3-Dichloro-1-propene⁶ was distilled at 150 mm. pressure and a fraction boiling at 48° was used; n_D^{25} 1.4578; d_4^{25} 1.2004; *MR* (calcd.) 25.32, (obsd.) 25.16.

1,3-Dichloropropene.—A mixture of the two isomers of 1,3-dichloropropene⁶ was fractionated. The low boiling

(1) Tamele, Ott, Marple and Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941).

(2) Hatch, Gordon and Russ, *THIS JOURNAL*, **70**, 1093 (1948).

(3) Young and Andrews, *ibid.*, **66**, 421 (1944).

(4) Andrews and Kepner, *ibid.*, **70**, 3456 (1948).

(5) Furnished by Shell Chemical Co., San Francisco, California.