tone that gives no addition reaction with methylmagnesium halide. We have investigated the behavior of the isomeric ketone, 3-methyl-3-ethyl-2-hexanone, when it reacts in a suitable apparatus[3] with methylmagnesium bromide. We have found that 3-methyl-3-ethyl-2-hexanone reacts with methylmagnesium bromide in the same manner as 3,3-diethyl-2-pentanone.

Experimental

All melting points are uncorrected.

Preparation of Methylethyl-*n*-propylacetic Acid.—The acid was prepared by treating the Grignard reagent, dissolved in diethyl ether, of 3-methyl-3-chlorohexane (prepared from methylethyl-*n*-propyl carbinol by a method that avoided distillation of the tertiary chloride[4]) with carbon dioxide under 50 lb. pressure for twenty-four hours with shaking. Attempts to prepare the acid by bubbling a stream of carbon dioxide gas through the Grignard reagent solution or by the reaction of the Grignard reagent with Dry Ice gave only traces of acid. When the acid was extracted from the reaction mixture in the usual manner and purified by distillation, a 25% yield, based on the tertiary chloride, was obtained as an average of six quarter-mole preparations. The fraction boiling 81–83° at 1 mm. was retained. The literature reports the b. p. of the acid as 215–220° at atmospheric pressure.[5]

Anal. Calcd. for $C_8H_{16}O_2$: neut. equiv., 144. Found: neut. equiv., 143.9.

Preparation of Methylethyl-*n*-propylacetyl Chloride.—From 50 g. of acid and 60 g. of thionyl chloride was obtained 52 g., 80% yield, of the acid chloride, b. p. 174–175° at 730 mm. The acid chloride reacted vigorously with aniline to produce an anilide, m. p. 80–81°.

Anal. Calcd. for $C_{14}H_{21}ON$: N, 6.35. Found: N, 6.08.

Preparation of 3-Methyl-3-ethyl-2-hexanone.—A solution of 40 g. of acid chloride (0.25 *M*) in anhydrous ether was added to a solution of dimethylcadmium prepared from a 0.5 *M* solution of methylmagnesium bromide in diethyl ether.[6] After processing in the usual fashion, the ketone was purified by distillation through a 10-plate Penn State type column.[7] From this reaction was obtained 34 g., 47% yield, of the ketone. The properties of the ketone are summarized in Table I. The ketone yielded on prolonged heating a 2,4-dinitrophenylhydrazone,[8] m. p. 80–81°.

Anal. Calcd. for $C_{15}H_{22}O_4N_4$: mol. wt., 322; N, 17.38. Found: mol. wt. (cryoscopic), 348; N, 17.01.

TABLE I

PROPERTIES OF 3-METHYL-3-ETHYL-2-HEXANONE

	Calcd.	Found
B. p., °C. (86 mm.)	...	108–110
d_{30}	...	0.8313
$n^{30}D$	...	1.4222
$[M]_D$	43.77	43.51
Anal. % Carbon	76.17	76.21
Hydrogen	12.68	12.69

Reaction with Methylmagnesium Bromide.—Determinations of addition and enolization were made in a suitable apparatus,[3] using 0.002 *M* quantities of ketone with excess methylmagnesium bromide. The methane gas liberated corresponded to 99% enolization and no addition.

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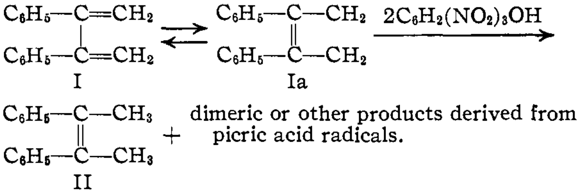
Reduction of 2,3-Diphenylbutadiene to *cis*-Dimethylstilbene by Reaction with Picric Acid

BY AHMED MUSTAFA

In an investigation of the susceptibility of 2,3-diphenylbutadiene (I) to dimerization, (I) was heated in the presence of a relatively large amount of picric acid as a polymerization inhibitor[1] in benzene solution. *cis*-Dimethylstilbene (II) m.p. 67–68°, was isolated from the reaction mixture in 36% yield, and identified by mixed m.p. with two authentic specimens, prepared by two different methods.[2,3] Further confirmation of the structure of II derived from I in this manner was obtained by its hydroxylation with performic acid to 2,3-diphenylbutandiol-2,3 which was identical (mixed m.p.) with a known sample,[4] and was oxidized to acetophenone (identified as the semicarbazone) by chromic acid in acetic acid.

1,4-Diphenyl-1,3-butadiene gave a deep red color on treatment with picric acid, apparently due to the formation of a molecular compound, and no reduction product was isolated.

A possible mechanism for the reduction of I to *cis*-dimethylbutadiene (II) proceeds through the intermediate di-radical (Ia).[5] Ia could be reduced to II by successive reaction with picric acid molecules, with the formation of radicals derived from picric acid which lead to dimeric or other products.



$$\begin{matrix} C_6H_5\text{—}C\text{=}CH_2 \\ | \\ C_6H_5\text{—}C\text{=}CH_2 \\ \text{I} \end{matrix} \rightleftarrows \begin{matrix} C_6H_5\text{—}C\text{—}CH_2 \\ \| \\ C_6H_5\text{—}C\text{—}CH_2 \\ \text{Ia} \end{matrix} \xrightarrow{2C_6H_2(NO_2)_3OH}$$

$$\begin{matrix} C_6H_5\text{—}C\text{—}CH_3 \\ \| \\ C_6H_5\text{—}C\text{—}CH_3 \\ \text{II} \end{matrix} + \text{dimeric or other products derived from picric acid radicals.}$$

The isolation of II from this reaction is of interest since it supports the idea that picric acid and similar polynitro compounds such as trinitrobenzene may function as polymerization retarders or inhibitors by transfer of ring hydrogen atoms to the free radical intermediates in the chain reaction.

Experimental[6]

1,4-Dibromo-2,3-diphenylbutadiene.—This compound was prepared by a modification of a procedure described

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(3) Lehman and Basch, *Ind. Eng. Chem.*, *Anal. Ed.*, **17**, 428 (1945).

(4) Whitmore and Williams, THIS JOURNAL, **55**, 406 (1933).

(5) Haller and Bauer, *Compt. rend.*, **148**, 130 (1909).

(6) Marvel and Caverly, *Rec. trav. chim.*, **55**, 518 (1936).

(7) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

(8) McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1945, p. 199.

(1) Frank and Adams, THIS JOURNAL, **68**, 908 (1946).

(2) Ott, *Ber.*, **61**, 2136 (1928).

(3) Allen, Eliot and Bell, *Can. J. Res.*, **17B**, 75 (1939).

(4) Lucas and Legagneur, *Bull. soc. chim.*, (4) **45**, 718 (1929).

(5) Such radicals are represented as intermediates in addition polymerization by Staudinger, *Ber.*, **58**, 1075 (1925); *Ann.*, **488**, 1 (1931).

(6) Melting points are corrected.

by Allen, Eliot and Bell.[3] 2,3-Diphenylbutanediol-2,3 (56 g.) containing 0.03 g. of phenyl-β-naphthylamine was placed in a 500-ml. flask cooled in an ice–salt-bath and 170 ml. of acetyl bromide was added slowly. After the vigorous reaction was over (thirty minutes), the reaction mixture was heated on a water-bath for three hours, when no more evolution of hydrogen bromide was observed. The excess of acetyl bromide was removed under reduced pressure and the oily residue was cooled, dissolved in ether, and washed with sodium carbonate solution and with water. After drying over sodium sulfate the ether was distilled and 17 ml. of bromine in 50 ml. of dry chloroform was added dropwise with continuous shaking to a solution of the oily residue in 100 ml. of dry chloroform. The chloroform was removed under reduced pressure and the solid mass obtained on cooling the residue was filtered, washed with cold hexane and crystallized from ethyl alcohol; yield 34 g. (40%) of dibromide, m. p. 147–148°. I was prepared from the dibromide by the procedure described previously.[3]

Reaction of 2,3-Diphenylbutadiene with Picric Acid.—A solution of 2.5 g. (0.012 mole) of (I) and 1.5 g. (0.006 mole) of picric acid in 50 ml. of benzene was heated under slow reflux in a nitrogen atmosphere under a positive pressure of 7 cm. of mercury for seven days. The benzene was distilled under reduced pressure and the reddish-brown residue was extracted with two 50-ml. portions of ether. The ether solution was washed several times with aqueous sodium bicarbonate, then with water, and dried over sodium sulfate. The ether was distilled and a solution of the residue in 15 ml. of hexane was cooled in a freezing mixture. The colorless crystals which separated (0.9 g.) were recrystallized from methyl alcohol; m. p. and mixed m. p. with known samples of *cis*-dimethylstilbene[2,3] 67–68°.

Anal. Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 92.3; H, 7.8.

In a similar experiment in which 50 ml. of xylene was the solvent, after seven days refluxing 0.75 g. (30%) of crude (II) was isolated, which after recrystallization melted at 66°.

Structure of *cis*-Dimethylstilbene Derived from I.—II prepared from I by the above procedure (0.83 g.) was added to a solution of 5 ml. of 30% hydrogen peroxide in 15 ml. of 88% formic acid with stirring and heated at 45–50° for forty minutes. The mixture was allowed to stand overnight at room temperature and poured into 100 ml. of ice water. The oily product was separated and crystallized on standing for several hours. After filtering and washing with cold water, 0.4 g. of crude 2,3-diphenylbutanediol-2,3 was obtained, m. p. 114–116°. After two recrystallizations from benzene–petroleum ether the yield was 0.29 g. (30%), m. p. and mixed m. p. with an authentic sample[4] 117–118°.

2,3-Diphenylbutanediol-2,3 prepared in this way (0.4 g.) in 5 ml. of glacial acetic acid was oxidized by portionwise addition of 0.5 g. of chromic anhydride during ten minutes. The mixture was heated on a water-bath for one hour and poured into cold water. The product was isolated by extraction with ether, which was washed with sodium carbonate solution and dried over sodium sulfate, and then distilled at atmospheric pressure. It was proved to be acetophenone by conversion to the semicarbazone, m. p. and mixed m. p. with a known sample 202°.

cis-Dimethylstilbene prepared from I was also identified by oxidation to acetophenone (identified as the semicarbazone) by direct treatment with chromic acid in acetic acid according to the procedure by Lévy[7] for oxidizing *trans*-dimethylstilbene.

Reaction of 1,4-Diphenyl-1,3-butadiene with Picric Acid.—These reactants formed a deep red solution on heating in benzene or xylene solution under the conditions described for 2,3-diphenylbutadiene. Red crystals separated from the solutions, which on exposure to air and on treatment with alcohol became yellow and yielded 1,4-diphenyl-1,3-butadiene and picric acid. Formation of an unstable molecular compound from 1,4-diphenyl-1,3-butadiene and *s*-trinitrobenzene has been described by Briegleb and Kambeitz.[8]

Acknowledgment.—The author expresses his gratitude to Dr. Arthur C. Cope for his interest in this investigation.

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[7] Lévy, *Bull. soc. chim. France*, [4] **29**, 889 (1921).

[8] Briegleb and Kambeitz, *Z. physik. Chem.*, **32B**, 305 (1936).

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On the Nature of the Reaction between Ascorbic Acid and Formaldehyde[1]

BY F. J. REITHEL AND R. P. WITHER

In a recent publication[2] evidence was presented to show that mixtures of ascorbic acid and formaldehyde solutions yield carbon dioxide as a reaction product. Under the proper conditions one mole of carbon dioxide is produced per mole of ascorbic acid.

Previous workers[3] studying the reaction between ascorbic acid and formaldehyde ascribed the disappearance of the reducing properties of ascorbic acid to an addition reaction with formaldehyde. It occurred to us that the phenomena observed might be explained more fully by postulating the oxidation of ascorbic acid by formaldehyde. It has been shown[4] that solutions of dehydroascorbic acid liberate carbon dioxide under conditions similar to those employed by us.

In the following experiments the rates of carbon dioxide evolution from dehydroascorbic acid and ascorbic acid–formaldehyde solutions were compared using the Warburg apparatus. All solutions were saturated with carbon dioxide before use. After gas and temperature equilibration the contents of the side arm were tipped into the body of the flask and the carbon dioxide evolution followed manometrically. The results are summarized in Table I. The data indicate that the rate of evolution of carbon dioxide from the ascorbic acid–formaldehyde mixture is nearly identical with that from the solution of dehydroascorbic acid. Similar data exist for other reaction mixtures in which the concentration of ascorbic acid was varied from 4.8×10^{-2} to 4.8×10^{-3} M and the formaldehyde concentration was varied from 0.2 to 1.8 M. In all cases the rate of carbon dioxide evolution was similar to controls containing dehydroascorbic acid. The use of iodine as an oxidizing agent also yielded results similar to those presented.

In addition to this evidence it has been found that the effect of temperature on the rate of car-

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[1] This paper is abstracted from the thesis of R. P. Wither presented to the faculty of the University of Oregon in August, 1948 in partial fulfillment of the requirements for the degree of Master of Arts in Chemistry. This work was aided by a grant from the Graduate Research Council of the Oregon State System of Higher Education.

[2] Reithel and West, THIS JOURNAL, **70**, 898 (1948).

[3] Snow and Zilva, *Biochem. J.*, **37**, 630 (1943).

[4] West and Rinehart, *J. Biol. Chem.*, **146**, 105 (1942).