1]heptane (IV),[3] if hydrogenation over copper chromite at high temperature and pressure were to convert II and III as it does the γ-nitropimelic esters.

Diethyl β-nitromethylglutarate (II) was obtained by the condensation of nitromethane with diethyl glutaconate in the presence of benzyltrimethylammonium hydroxide in 51% yield. Ethyl β-carbethoxy-δ-nitrovalerate (III) was obtained in lower yield by the condensation of nitromethane with diethyl itaconate in the presence of either diethylamine or diisopropylamine. Very little mono-condensation product could be isolated when benzyltrimethylammonium hydroxide was used as the condensing agent. Neither II nor III yielded any 1-azabicyclo[2.2.1]heptane (IV) when subjected to hydrogenation in dioxane over copper chromite at 350 atm. and 260°.[2]

In the condensation of nitroethane with diethyl itaconate in the presence of diisopropylamine to give ethyl β-carbethoxy-δ-nitrocaproate, a solid product was also isolated which was identified unequivocally as diisopropylamine nitrite. The nitrous acid salt of diisopropylamine was shown to be the result of a reaction between the amine and nitroethane alone, since an excess of the nitroethane converted diisopropylamine to the salt in excellent yield. The formation of *nitrite* ion during the reaction of nitroparaffins with strong alkali was observed by Dunstan and Dymond,[4] but Lippincott[5] has claimed that *nitrate* ion is produced in the self-condensation of nitroethane in the presence of diethylamine. The direct production of a readily isolable nitrite derivative during the nitrous acid elimination reaction of a simple nitroparaffin appears to be unique, and diisopropylamine should serve as a most useful base for the study of this reaction. Where the elimination of nitrous acid from an aliphatic nitro derivative has been described previously, the nitro group invariably was attached to the carbon *beta* to a strongly negative group.[6,7]

Experimental

Diethyl β-Nitromethylglutarate.—To a stirred solution of 31 g. (0.5 mole) of nitromethane and 10 g. of benzyltrimethylammonium hydroxide (40% aqueous)[8] in 75 ml. of dioxane was added 31 g. (0.17 mole) of diethyl glutaconate.[9] The solution was kept at 65° for sixty hours. It was then cooled and neutralized with 6 *N* hydrochloric acid, and an equal volume of ethylene dichloride was added. The ethylene dichloride layer was washed with water and the more volatile components were removed by distillation at atmospheric pressure. The residue was fractionated *in vacuo* and the diethyl β-nitromethylglutarate was collected at 118–120° (0.5 mm.); n^{20}_D 1.4482; d^{20}_4 1.1492; yield, 21 g. (51%).

Anal. Calcd. for $C_{10}H_{17}NO_6$: N, 5.67; MR_D, 57.32. Found: N, 5.43; MR_D, 57.61.

Ethyl β-Carbethoxy-δ-nitrovalerate.—A solution of 50 g. (0.27 mole) of diethyl itaconate (prepared in 95% yield from itaconic acid, Chas. Pfizer Co., through the use of an ethyl ester column), 61 g. (1.0 mole) of nitromethane and 35 g. (0.34 mole) of diisopropylamine was allowed to stand at 25° for sixteen days. The solution was neutralized with 6 *N* hydrochloric acid, and 100 ml. of ethylene dichloride was added. The ethylene dichloride layer was washed twice with 150-ml. portions of water. The solvent was removed and the residue was fractionated *in vacuo*. Diethyl itaconate (23.5 g.), b. p. 79–82° (2 mm.), was recovered and 8.6 g. (25% yield on the basis of unrecovered itaconic ester) of ethyl β-carbethoxy-δ-nitrovalerate was obtained; b. p. 126–130° (1.5 mm); n^{20}_D 1.4472; d^{20}_4 1.1394.

Anal. Calcd. for $C_{10}H_{17}NO_6$: N, 5.67; MR_D, 57.32. Found: N, 6.08; MR_D, 58.00.

Ethyl β-Carbethoxy-δ-nitrocaproate.—A solution of 93 g. (0.5 mole) of diethyl itaconate, 50 g. (0.66 mole) of nitroethane, and 50 g. (0.5 mole) of diisopropylamine was allowed to stand at 25°. After one week crystals appeared on the wall of the flask and continued to form for two weeks. After forty days the crystalline solid was collected, washed with ethylene dichloride and dried (28 g.). The solution and the ethylene dichloride washings were combined and an additional 200 ml. of ethylene dichloride was added. From this point, the product was worked up in the manner described for ethyl β-carbethoxy-δ-nitrovalerate. The ethyl β-carbethoxy-δ-nitrocaproate distilled at 138–142° (2 mm.); n^{20}_D 1.4455; d^{20}_4 1.1123; yield, 31 g. (40% yield on the basis of unrecovered itaconic ester).

Anal. Calcd. for $C_{11}H_{19}NO_6$: N, 5.36; MR_D, 61.94. Found: N, 5.58; MR_D, 62.58.

The crystalline product which separated was recrystallized from acetone and was freed from final traces of moisture by boiling toluene over the colorless needles, m. p. 140°.

Anal. Calcd. for $C_6H_{16}N_2O_2$: C, 48.62; H, 10.63. Found: C, 48.45; H, 10.77.

The infrared spectrum indicated the presence of strong hydrogen bonding. Acidification of the needles caused the evolution of nitrous fumes. Alkali liberated a base which formed a picrate as needles, m. p. 145–146°, which caused no depression in the melting point (145–146°) of an authentic sample of diisopropylamine picrate. The nitrous acid salt of diisopropylamine has been reported as melting at 140°.[10] An authentic sample of this compound was prepared by passing nitrous acid fumes through a dry toluene solution of diisopropylamine. After recrystallization from acetone and drying under toluene, the diisopropylamine nitrite melted at 140° and gave no depression in melting point with the compound isolated from the original reaction mixture.

Diisopropylamine nitrite likewise was produced in over 80% yield when nitroethane and diisopropylamine, in 2:1 molar ratio, were allowed to stand at 25°. The reaction is being investigated further.

---

[3] Prelog and Cerkovnikov, *Ann.*, **525**, 292 (1936); Prelog, Cerkovnikov and Ustriceo, *ibid.*, **535**, 37 (1938); Prelog, Heimbach and Rezek, *ibid.*, **545**, 231 (1940).

[4] Dunstan and Dymond, *J. Chem. Soc.*, **59**, 410 (1891).

[5] Lippincott, THIS JOURNAL, **62**, 2604 (1940).

[6] Kloetzel, *ibid.*, **70**, 3571 (1948).

[7] van Tamelen and Van Zyl, *ibid.*, **71**, 835 (1949).

[8] Bruson, U. S. Patent 2,342,119 (February 22, 1944); U. S. Patent 2,390,918 (December 11, 1945).

[9] Lochte and Pickard, THIS JOURNAL, **68**, 721 (1946).

[10] Heilbron and Bunbury, "Dictionary of Organic Compounds," Vol. 1, Eyre and Spottiswoode, London, 1943, p. 875.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED JANUARY 14, 1949

3-Methyl-3-ethyl-2-hexanone

BY CHAS. T. LESTER AND JOHN R. PROFFITT, JR.[1]

Whitmore and Lewis[2] have reported that 3,3-diethyl-2-pentanone is the smallest aliphatic ke-

---

[1] Community Trust Fellow, 1945–1946.

[2] Whitmore and Lewis, THIS JOURNAL, **64**, 1618 (1942).

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.

Acknowledgment.—We are indebted to A. E. Robinson and E. C. Suratt for density determination and carbon and hydrogen analysis.

DEPARTMENT OF CHEMISTRY
EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA

RECEIVED JANUARY 22, 1949

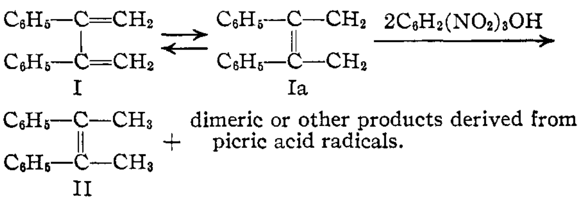
Reduction of 2,3-Diphenylbutadiene to *cis*-Dimethylstilbene by Reaction with Picric Acid

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.



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

---

(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.