

ing from a pinacol type reduction. Fieser² has shown that a similar high-melting product obtained by the Clemmensen reduction of β -benzoylpropionic acid has this type of structure.

Anal. Calcd. for $C_{22}H_{22}O_4$: C, 75.38; H, 6.34; sapon. equiv., 175. Found: C, 75.32, 75.33; H, 6.42, 6.71; sapon. equiv.,³ 171, 181.

The starting material was recovered unchanged by acidifying and warming the saponification mixture.

(2) "Organic Syntheses," Vol. XV, John Wiley and Sons, Inc., New York, N. Y., 1935, p. 65.

(3) Redemann and Lucas, *Ind. Eng. Chem., Anal. Ed.*, **9**, 521 (1937).

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ESTERS OF DIACETONE ALCOHOL¹

The acetate, propionate and butyrate of diacetone alcohol were formed by refluxing 4 moles of the alcohol and 2 moles of the anhydride for six hours. The cooled reaction mixture was shaken with ice water, the aqueous layer was neutralized with solid, and the oily layer with a solution of bicarbonate. The combined oily layers were thoroughly washed with water and dried over calcium chloride. Fractional distillation under reduced or atmos-

(1) From the thesis of Herbert E. Ungnade for the M.S. degree, August, 1934.

pheric pressure gave a 70% or better yield of mesityl oxide and a 10-15% yield of the ester of diacetone alcohol. Use of acetic acid instead of the anhydride gave an undiminished yield of mesityl oxide but only a 3% yield of the acetate. The esters are pleasant smelling oils with excellent solvent properties.

The following numerical data as to their properties were determined.

Ester	Acetate	Propionate	Butyrate	
B. p. {	°C.	171-173	182-184	192-193
	Mm.	742	742	742
	°C.	72-73	80-81	97-98
	Mm.	10	8	12
d_{25}^{25}		0.9811 ^a	0.9680	0.9536
	n_D^{20}	1.4229	1.4256	1.4270
M_D^{20} {	Calcd.	40.80	45.4	50.0
	Found	40.85	45.4	50.0
Acid, {	Calcd.	37.97	42.99	47.28
	% Found	37.82 38.07	42.99 43.20	47.31 47.43
Semicarbazones				
M. p. °C.	137.5-138	144.5-145	110.4-110.8	
N, % {	Calcd.	19.53	18.34	17.24
	Found	19.49 19.33	18.40 18.52	16.82 17.00
^a d_{25}^{25} .				

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COMMUNICATION TO THE EDITOR

THE NITRATION OF ALIPHATIC HYDROCARBONS *Sir:*

While the nitration of hydrocarbons is one of the oldest reactions known, it is still one of the least understood. Recently nitration of simple saturated hydrocarbons has been carried out in the vapor phase at elevated temperatures,¹ a reaction said to involve free radicals.² Since little is known about the mechanism of this nitration in the liquid phase, we wish to report that nitration of *levo*-3-methyl-octane yields *levo*-3-methyl-3-nitro-octane.³

The mechanism of this nitration is still not clear. However a survey of the literature reveals the following pertinent facts:

(1) Haas, Hodge and Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936).
(2) McCleary and Degering, *ibid.*, **30**, 64 (1938); Seigle and Haas, *ibid.*, **31**, 648 (1939).

(3) It is not yet possible to say whether or not partial racemization occurred.

A. Tertiary hydrogen atoms are generally the most easily replaced.⁴

B. Nitration of neohexane proceeds without rearrangement yielding 3,3-dimethyl-2-nitrobutane.⁵

C. Nitration of camphane (caged structure) yields secondary nitro compounds in place of the expected tertiary,⁶ indicating an inversion mechanism.⁷

For the empirical equation $C_9H_{20} + NO_2 \rightarrow C_9H_{19}NO_2 + H$, several mechanisms can be advanced:

1. Replacement by removal of the hydrogen as a proton. This would appear implausible from (A) above. The well-known electron-repelling

(4) Konowalov, *Ber.*, **28**, 1855 (1895).

(5) Markownikov, *Chem. Zentr.*, **70**, II, 473 (1899); *Ber.*, **33**, 1906 (1900).

(6) Nametkin, *J. Russ. Phys.-Chem. Soc.*, **47**, 409 (1915).

(7) Bartlett and Knox, *THIS JOURNAL*, **61**, 3184 (1939).

character of tertiary groups might be expected to make such replacement more, not less difficult than replacement of secondary or primary hydrogen.

2. Replacement by removal of the hydrogen as a negative ion. This mechanism is unlikely because of the absence of rearrangement as in (B).

3. Replacement by removal of the hydrogen as an atom. If direct replacement without inversion occurs, then inactive products would be expected due to the formation of an isolated organic free radical.⁸ However a one-step acceptor-donor inversion mechanism, suggested in (C), analogous to that involving ions, need not cause racemization. At present we favor this latter view, in spite of possible objections on thermodynamic grounds. It appears to be consistent with the electron-repelling character of tertiary groups and the ease of replacement of tertiary hydrogen, as well as the absence of rearrangement as in (B). In addition it is in harmony with the results reported by Price and Schwarcz on the chlorination of cyclic dibasic acid esters.⁹ Further work on this type of nitration is now in progress.

Experimental Part

Eleven grams of *levo*-3-methyloctane, b. p. 142–143° (760 mm.), α_D^{25} -6.5° ,¹⁰ n_D^{25} 1.4045, was prepared as described by Levene and Marker,¹¹ except that the intermediate bromide was prepared from the corresponding carbinol with dry hydrogen bromide at 120–130°, and the

(8) Compare Brown, Kharasch and Chao, from a paper presented to the Division of Organic Chemistry at Detroit, Michigan, September, 1940. Abstract of papers, pages 57–59.

(9) Price and Schwarcz, Cincinnati Meeting, Abstracts, pp. 18–19.

(10) Homogeneous, 1-dm. tube.

(11) Levene and Marker, *J. Biol. Chem.*, **91**, 77 (1931).

crude hydrocarbon was hydrogenated with Adams platinum catalyst before fractionation. The nitration was carried out in a sealed tube with gentle shaking for twelve hours at 130° using 90 cc. of nitric acid, d. 1.075. The hydrocarbon layer was added to 10 cc. of ether, dried over anhydrous sodium sulfate, the ether evaporated, and the unreacted hydrocarbon (2 cc.) removed by fractionation at 25 mm. through a small bore reflux column of approximately 8 plates, equipped with a gold-plated spiral.

The residue was extracted three times with 15 cc. of a 15% aqueous alcoholic (3-1) potassium hydroxide solution, each extraction lasting 30 minutes with frequent agitation.¹² The yellow-orange alkaline layer was then extracted once with ether, the ether washed with water, and combined with the alkali-insoluble portion, dried over anhydrous sodium sulfate, the ether evaporated, and the tertiary nitro compound fractionated through the above mentioned Podbielniak-type column. To ensure freedom from any secondary or primary nitro compounds, fraction 2 (see below in Table I) was re-extracted thrice in the same way with 15 cc. of a 10% aqueous alcoholic (3:1) potassium hydroxide solution, whereby this time the alkaline solution remained colorless. The product was fractionated as before. The optical activity was virtually unchanged.

TABLE I

Distillation	First		Second			
	Fraction	1	2	Residue	1	Residue
Vol., cc.	0.3	3.0	1.5	2.0	0.5	
Time, min.	15	45	..	40	..	
Reflux ratio	50/1	50/1	..	50/1	..	
Temp., ° C.	100–106.5	106.5–107	..	106.5–107	..	
Press., mm.	15	15	..	15	..	
n_D^{25}	1.4340	
α_D^{25}	-0.65 ¹⁰	..	-0.70 ¹⁰	..	
Nitro- gen, % } Found	..	8.1	
	..	8.2 ¹²	

(12) Compare Konawalov, *Chem. Zentr.*, **77**, II, 312 (1906); also Seigle and Haas, ref. 2.

(13) Analysis run on inactive material.

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NEW BOOKS

Electrochemistry and Electrochemical Analysis. By HENRY J. S. SAND, D.Sc., Ph.D., F.I.C., Lately Head of the Department of Inorganic and Physical Chemistry and Lecturer on Electrolytic Analysis at the Sir John Cass Technical Institute, London. Volume II. Gravimetric Electrolytic Analysis and Electrolytic Marsh Tests. Chemical Publishing Co., Inc., 148 Lafayette St., New York, N. Y., 1940. 1x + 149 pp. Illustrated. 12.5 × 19 cm. Price, \$2.00.

Dr. Sand is known particularly for his work in the field of electrolytic analysis. The scope of this book is indicated by the author's statements: "Exhaustiveness has

not been aimed at" . . . "particular attention has been devoted to the methods for separating metals by control of the cathode potential" . . . "simplified by the introduction of what may be described as high resistance voltmeters in place of the potentiometer." Yet no method which would compete with the more usual methods of analysis seems to have been omitted. No theory is included.

The chapter on "Apparatus" seems somewhat elaborate. The author seems to anticipate all of the problems of the novice. In his discussions of "Technique" he shows the work of an experimentalist who is thoroughly familiar with the pitfalls. His methods of detecting small amounts