ing from a pinacol type reduction. Fieser[2] 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; sapn. equiv., 175. Found: C, 75.32, 75.33; H, 6.42, 6.71; sapn. equiv.,[3] 171, 181.

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

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[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 ALCOHOL[1]

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 atmospheric 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^{20}_D		1.4229	1.4256	1.4270
M^{20}_D	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^{28}_{25}.

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

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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:

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

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[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.

[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).