

THE PHENACYL, *p*-PHENYLPHENACYL AND *p*-NITROBENZYL ESTERS OF CERTAIN UNEVEN NUMBERED FATTY ACIDS

The general method of preparation consisted in dissolving 150 mg. of the fatty acid in 4 cc. of 95% ethyl alcohol, titrating to phenolphthalein with 0.5 *N* sodium hydroxide and just reacidifying by the addition of a crystal of the fatty acid so that the solution becomes colorless; 150 mg. of the phenacyl bromide was then added and the mixture refluxed for one and one-half hours. Two recrystallizations from 95% ethyl alcohol were sufficient to purify the derivatives of the acids from tridecyl upward, while two to three crystallizations from approximately 65% ethanol were required for the lower derivatives.

The melting points were taken with a Fisher melting point apparatus<sup>1</sup> using a thermometer calibrated against a set of Anschütz thermometers corrected by the Bureau of Standards, the temperature being raised at the rate of one degree in about two minutes.

Acid <sup>a</sup>	Ester	M. p. <sub>2</sub> (cor.), C.	Empirical formula	Analysis, %			
				C	H	Found C	Found H
Pelargonic	Phenacyl	oil					
	<i>p</i> -Phenylphenacyl	70.8–71.3	C <sub>23</sub> H <sub>28</sub> O <sub>3</sub>	78.36	8.01	78.29	8.34
	<i>p</i> -Nitrobenzyl	oil					
Undecylic	Phenacyl	oil					
	<i>p</i> -Phenylphenacyl	79.5–80	C <sub>25</sub> H <sub>32</sub> O <sub>3</sub>	78.87	8.48	78.85	8.62
	<i>p</i> -Nitrobenzyl	oil					
Tridecyl	Phenacyl	45.0–45.5	C <sub>21</sub> H <sub>22</sub> O <sub>3</sub>	75.84	9.71	75.97	9.81
	<i>p</i> -Phenylphenacyl	86.5–87	C <sub>27</sub> H <sub>36</sub> O <sub>3</sub>	79.36	8.89	79.42	8.73
	<i>p</i> -Nitrobenzyl	oil					
Pentadecylic	Phenacyl <sup>b</sup>	53.6	C <sub>23</sub> H <sub>36</sub> O <sub>3</sub>	76.61	10.07	76.34	10.25
	<i>p</i> -Phenylphenacyl	91.3–91.8	C <sub>29</sub> H <sub>40</sub> O <sub>3</sub>	79.76	9.24	79.55	9.50
	<i>p</i> -Nitrobenzyl	39.5–40	C <sub>22</sub> H <sub>25</sub> O <sub>4</sub> N	69.97	9.35	70.16	9.71
Margaric	Phenacyl	60.0–60.5	C <sub>25</sub> H <sub>40</sub> O <sub>3</sub>	77.26	10.38	77.16	10.50
	<i>p</i> -Phenylphenacyl	95.3–95.8	C <sub>31</sub> H <sub>44</sub> O <sub>3</sub>	80.11	9.55	79.76	9.67
	<i>p</i> -Nitrobenzyl <sup>c</sup>	48.5–49.0	C <sub>24</sub> H <sub>33</sub> O <sub>4</sub> N	71.05	9.70	70.84	10.06

<sup>a</sup> Heptico *p*-nitrobenzyl ester was obtained only as an oil. <sup>b</sup> This ester melts at 53.6° only if heated rapidly; if heated in the normal way it melts several degrees lower. <sup>c</sup> Lyons and Reid [THIS JOURNAL, 39, 1737 (1917)] reported an attempt to prepare this ester, but, as they could not get consistent melting points, abandoned the experiment.

(1) H. L. Fisher, "Laboratory Manual of Organic Chemistry," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1934, p. 28.

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NITRO DERIVATIVE OF 2-BROMO-4-AMINO-1,3-DIMETHYLBENZENE

2-Bromo-4-acetylamino-6-nitro-*m*-xylene.—Two grams of 2-bromo-4-acetylamino-*m*-xylene<sup>1</sup> was dissolved in 20 g. of concentrated sulfuric acid and treated with 0.75 g. of concentrated nitric acid below 15°. After ten minutes, the solution was poured into ice water. The precipitate was collected, washed with water, and recrystallized from dilute alcohol. It was obtained as small white needles, m. p. 171–172°. Yields on 30-g. quantities of starting material were consistently above 90%.

(1) Noelting, Braun, and Thesmar, *Ber.*, 34, 2242 (1901).

*Anal.* Calcd. for C<sub>10</sub>H<sub>11</sub>O<sub>2</sub>N<sub>2</sub>Br: N, 9.76. Found: N, 9.83.

2-Bromo-4-amino-6-nitro-*m*-xylene.—Thirty grams of 2-bromo-4-acetylamino-6-nitro-*m*-xylene was refluxed with 50% sulfuric acid until all had dissolved. The solution was poured into cold water and neutralized with ammonia water. The precipitate was collected, washed with water, and recrystallized from alcohol after decolorization with Norit. It formed yellow needles, m. p. 129–130°, with extensive sublimation.

*Anal.* Calcd. for C<sub>8</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>Br: N, 11.44. Found: N, 11.67.

The structure of both compounds was proved by conversion of the latter into 2-bromo-4-nitro-*m*-xylene, by reduction of the diazonium sulfate with alcohol. The product, isolated by steam distillation, was obtained in colorless, waxy needles of plastic consistency, m. p. 56.5–58°, after several decolorizations and recrystallizations from alcohol. No depression was observed when a mixed

melting point was taken with 2-bromo-4-nitro-*m*-xylene obtained from 2-amino-4-nitro-*m*-xylene by the method of Noelting, Braun, and Thesmar.<sup>1</sup> The color of the compound obtained by their method is light yellow.

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γ,γ'-DI-*p*-TOLYL-γ,γ'-SUBERODILACTONE

The reduction of 50 g. of β-*p*-toluylpropionic acid with 75 g. of zinc dust in 200 cc. of boiling 80% acetic acid for six hours yielded, in addition to the main product, γ-*p*-toluyl-γ-butyrolactone (m. p. 67–68°),<sup>1</sup> 2.5 g. of glistening white plates, m. p. 275–276°, which separated from the reaction mixture on cooling. This material has been identified as γ,γ'-di-*p*-toluyl-γ,γ'-suberodilactone, result-

(1) Gergel and Wagner (*Ann.*, 482, 74 (1930)) obtained the same product by reduction with sodium amalgam, m. p. 69°.

ing from a pinacol type reduction. Fieser<sup>2</sup> has shown that a similar high-melting product obtained by the Clemmensen reduction of  $\beta$ -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.,<sup>3</sup> 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 ALCOHOL<sup>1</sup>

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 <sup>a</sup>	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
<sup>a</sup> $d_{25}^{25}$ .				

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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,<sup>1</sup> a reaction said to involve free radicals.<sup>2</sup> 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.<sup>3</sup>

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.<sup>4</sup>

B. Nitration of neohexane proceeds without rearrangement yielding 3,3-dimethyl-2-nitro-butane.<sup>5</sup>

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

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).