

The mixed melting point with 2,2',4-triacetoxybenzophenone was depressed.

Anal. Calcd. for  $C_{19}H_{16}O_7$ : C, 64.0; H, 4.5. Found: C, 64.2; H, 4.3.

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DEPARTMENT OF PURE AND APPLIED CHEMISTRY  
ROYAL TECHNICAL COLLEGE  
SALFORD, LANCs, ENGLAND

## The Stobbe Condensation on *p*-Methoxy-*m*-methylisobutyrophenone

MILTON D. SOFFER AND ANN DONALDSON<sup>1</sup>

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The substances described were prepared in preliminary experiments directed toward 7-hydroxy-1,6-dimethyl-4-isopropyl-naphthalene whose unambiguous synthesis,<sup>2</sup> serving to confirm the structure of the sesquiterpene copaene,<sup>3</sup> was accomplished while this work was in progress. We therefore wish merely to record the results of these experiments which were discontinued at that time. The products obtained are intermediates in an adaptation of the general "tetralone" scheme developed by Johnson and coworkers.<sup>4</sup> Methyl *o*-cresyl ether readily entered into the Friedel-Crafts reaction with isobutyryl chloride to produce *p*-methoxy-*m*-methylisobutyrophenone. The use of carbon disulfide which gives inferior results with similar phenolic ethers in the reaction with succinic anhydride,<sup>5</sup> gave good yields in the present case. The crystalline acid ester, 3-carbomethoxy-4-(*p*-methoxy-*m*-tolyl)-5-methyl-3-hexenoic acid, was obtained in the Stobbe condensation with dimethyl succinate and sodium hydride. The assignment of the ethylenic linkage to the 3 position is in accord with the infrared absorption spectrum which exhibited in addition to the carboxyl band (5.79  $\mu$ ) the maxima characteristic of the conjugated ester carbonyl and double bond (5.82, 6.11  $\mu$ ).<sup>6</sup> The diacid was also prepared by saponification. Upon recrystallization from hot benzene-petroleum ether a small amount of a lower melting substance was isolated which is apparently the corresponding cyclic anhydride. A similar behavior has been noted for

$\gamma,\gamma$ -di-*p*-methoxyphenylitaconic acid,<sup>7</sup> which is a close electronic and steric analog.

### EXPERIMENTAL<sup>8</sup>

*p*-Methoxy-*m*-methylisobutyrophenone.<sup>9</sup> To a well stirred ice-cooled mixture of 135.8 g. (1.04 moles) of anhydrous aluminum chloride and 160 ml. of dry carbon disulfide, 111 g. (1.04 moles) of carefully fractionated isobutyryl chloride<sup>10</sup> was added slowly, followed by 91.0 g. (0.745 mole) of *o*-methyl cresyl ether. The ether must be added cautiously to keep the copious evolution of gas under control. The mixture was stirred at 0° for 15 hr. and allowed to warm up to room temperature. Following cautious treatment with 400 ml. of ice and water, and 200 ml. of concentrated hydrochloric acid, most of the carbon disulfide was removed at reduced pressure. The product was extracted with ether, washed thoroughly with 5% sodium hydroxide, water, and dried over magnesium sulfate and freed from solvent. The residual oil from two such runs was distilled roughly under nitrogen and fractionated through a five-plate modified Widmer column to give 231 g. (81%) of the colorless ketone, b.p. 110–115° at 0.5 mm., m.p. 22–23°.

The *semicarbazone* was readily obtained in pyridine-methanol, melting at 143–145° after one recrystallization from aqueous methanol, and finally at 144–145°;  $\lambda_{\text{max}}^{\text{Nujol}}$  5.92  $\mu$ .<sup>11</sup>

Anal. Calcd. for  $C_{13}H_{19}O_2N_3$ : C, 62.62; H, 7.68. Found: C, 62.75, 62.70; H, 7.55, 7.55.

The 2,4-dinitrophenylhydrazone crystallized from aqueous methanol in yellow blades, m.p. 151–152°.

3-Carbomethoxy-4-(*p*-methoxy-*m*-tolyl)-5-methyl-3-hexenoic acid. The Stobbe condensation<sup>4</sup> was run in dry benzene using 9.6 g. (0.05 mole) of the foregoing ketone, 26.1 (0.18 mole) of dimethyl succinate, and 2.9 g. (0.12 mole) of granular sodium hydride. The reactants were mixed all at once under dry nitrogen in an apparatus provided for entry and exit of gases and measurement of evolved hydrogen. It was necessary to add a few drops of methanol and to reflux the mixture for a few minutes to induce a steady evolution of hydrogen, which then continued at room temperature for approximately 26 hr.

Excess acetic acid was added cautiously, followed finally by water and ether, and the product was isolated by extraction with a 5% solution of sodium bicarbonate followed by acidification and re-extraction with ether. Drying over magnesium-sulfate and removal of solvent left a semi-crystalline solid, m.p. 95–105° from which one pure stereoisomer was obtained by successive recrystallization from benzene-petroleum ether (b.p. 30–60°), water, and hexane; 3.37 g. (22%); m.p. 120–121°;  $\lambda_{\text{max}}^{\text{Nujol}}$  5.79, 5.82, 6.11  $\mu$ .<sup>11</sup>

Anal. Calcd. for  $C_{18}H_{21}O_5$ : C, 66.65; H, 7.24; neut. equiv., 306.4. Found: C, 66.88, 67.28; H, 7.44, 7.30; neut. equiv., 306.4, 309.0.

In separate experiments in which more methanol was used in priming, or glass marbles were added for pulverizing action,<sup>12</sup> the initial heating period was not required and the

(7) W. S. Johnson and M. W. Miller, *J. Am. Chem. Soc.*, **72**, 511 (1950).

(8) Temperature readings are uncorrected.

(1) From the M.A. thesis of Ann Donaldson, 1949.

(2) L. H. Briggs, N. S. Gill, F. Lyons, and W. I. Taylor, *J. Chem. Soc.*, 1098 (1949).

(3) L. H. Briggs and W. I. Taylor, *J. Chem. Soc.*, 1338 (1947).

(4) W. S. Johnson and G. H. Daub, *Org. Reactions*, VI, 34 (1951); W. S. Johnson and A. R. Jones, *J. Am. Chem. Soc.*, **69**, 792 (1947).

(5) L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, **58**, 2314 (1936).

(6) R. S. Rasmussen and R. R. Brattain, *J. Am. Chem. Soc.*, **71**, 1073 (1949).

(9) The orientation of the acyl function is assigned by analogy [cf. reference 5; G. Stadnikoff and A. Baryschewa, *Ber.*, **61**, 1996 (1928); W. P. Campbell and M. D. Soffer, *J. Am. Chem. Soc.*, **64**, 417 (1942)].

(10) R. E. Kent and S. M. McElvain, *Org. Syntheses*, **25**, 58–60 (1941).

(11) We are indebted to Mr. Philip Sadtler of Samuel

(12) N. Green and F. B. LaForge, *J. Am. Chem. Soc.*, **70**, 2287 (1948).

rate of gas evolution was markedly increased but the yield of pure product was somewhat decreased (13–16%).

*3-Carboxy-4-(p-methoxy-m-tolyl)-5-methyl-3-hexenoic acid.* The crude diacid (16.5 g., m.p. 114–116°) was refluxed for 6.5 hr. in 10% sodium hydroxide. The semicrystalline product isolated in the usual way (13 g., 83%) gave on recrystallization from benzene-petroleum ether (b.p. 90–100°) 9.5 g. of one relatively pure stereoisomer, m.p. 155–156°. Further recrystallization from the same solvent, aqueous methanol, and benzene-hexane gave the pure diacid, m.p. 162–163°. The same product was obtained in a preliminary experiment on the pure half ester.

*Anal.* Calcd. for  $C_{14}H_{18}O(COOH)_2$ : neut. equiv., 146.2. Found, neut. equiv., 146.6, 146.8.

From the preceding benzene petroleum ether mother liquors there was isolated 1.0 g. of crystalline material m.p. 119–120° which has the composition of  $\gamma$ -(*p*-methoxy-*m*-tolyl)- $\gamma$ -isopropylitaconic anhydride. The melting point changes on exposure to air, apparently by absorption of moisture. A pure sample was prepared by repeated recrystallization from benzene-petroleum ether; m.p. 121–121.5°.

*Anal.* Calcd. for  $C_{18}H_{18}O_4$ : C, 70.05; H, 6.61. Found: C 70.33, 70.59; H, 6.53, 6.81.

DEPARTMENT OF CHEMISTRY  
SMITH COLLEGE  
NORTHAMPTON, MASS.

## Glycol Esters of 3-Alkoxypropionic Acids

JOHN W. LYNN

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The probability that glycol esters of 3-alkoxypropionic acids would be useful as plasticizers and lubricants prompted the synthesis of a number of these materials.

While the preparation of numerous monohydric esters of 3-alkoxypropionic acids by the base-catalyzed addition of an alcohol to an alkyl acrylate has been previously reported,<sup>1,2</sup> the synthesis of a glycol ester appears to be novel.

TABLE I  
3-ALKOXYPROPIONIC ACIDS:  $R-O-CH_2CH_2CO_2H$

R	B.P., <sup>3</sup> °C.	Mm.	$n_D^{20}$
$CH_2=CHCH_2-$	110	5	1.4383
$(CH_2CH_2)_2CHCH_2-$	144	10	1.4301
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	142	5.5	1.4350

  

R	$d_4^{20}$	Purity, % <sup>a</sup>	Yield, %
$CH_2=CHCH_2-$	1.0562	98.1	73
$(CH_2CH_2)_2CHCH_2-$	0.9641	95.8	85
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	0.9248	99.7	82

<sup>a</sup> Based on titration with 0.1N sodium hydroxide.

(1) M. B. Dixon, C. E. Rehberg, and C. H. Fisher, *J. Am. Chem. Soc.*, **70**, 3733 (1948).

(2) C. E. Rehberg, M. B. Dixon, and C. H. Fisher, *J. Am. Chem. Soc.*, **69**, 2966 (1947).

(3) All temperatures are uncorrected.

TABLE II  
GLYCOL ESTERS OF 3-ALKOXYPROPIONIC ACIDS:  $(ROCH_2CH_2CO_2)_2R'$

R	R'	B.P., °C./mm.	$n_D^{20}$	$d_4^{20}$	Purity, <sup>a</sup> %	Yield, %	Calcd., %		Found, %	
							C	H	C	H
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	$-CH_2CH_2-$	154/0.2 <sup>b</sup>	1.4439	0.9582	98.8	75	67.0	10.7	66.9	10.6
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	$O(CH_2CH_2)_2$	180/0.2 <sup>b</sup>	1.4464	0.9747	101	81	65.8	10.5	65.5	10.4
$CH_3(CH_2)_3(CH_3CH_2)CHCH_2-$	$-(CH_2)_6-$	181/0.25 <sup>b</sup>	1.4472	0.9455	100	94	67.8	11.1	68.1	10.8
$(CH_3CH_2)_2CHCH_2-$	$-(CH_2CH(CH_3)O)-_2$	Residue	1.4431	0.9860	98.5	99	63.5	10.2	63.5	10.4
$CH_2=CHCH_2-$	$-CH_2CH_2-$	180/0.8	1.4533	1.0876	104.6	16	58.7	7.74	58.3	7.45

<sup>a</sup> Based on saponification and titration with 0.1N hydrochloric acid. <sup>b</sup> Falling film molecular still.