TABLE I

YIELDS AND PHYSICAL PROPERTIES OF SOME NEW LIQUIDS

	Yield, %	B. p., °C. at 10 mm.	n^{25}_D	d^{25}_{25}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$CH_3(CH_2)_3CH(COCH_3)CO_2CH_3$[a]	67	105	1.4276	0.9723	62.76	62.56	9.37	9.42
$[CH_3(CH_2)_3]_2C(COCH_3)CO_2CH_3$[b]	80	130	1.4393	.9410	68.38	68.14	10.57	10.58
$CH_3(CH_2)_3CH(COCH_3)CO_2C(CH_3)_3$	75	110	1.4248	.9208	67.25	67.15	10.35	10.34
$CH_3(CH_2)_3\underset{(CH_3)_2CHCH_2}{\underset{\vert}{C}}(COCH_3)CO_2C(CH_3)_3$	74	140	1.4359	.9150	71.07	70.72	11.18	11.10
$CH_3(CH_2)_3\underset{C_2H_5CHCH_3}{\underset{\vert}{C}}(COCH_3)CO_2C(CH_3)_3$	50	139	1.4390	.9218	71.07	70.88	11.18	11.22
$CH_3(CH_2)_3CH(COCH_3)CH_2CH(CH_3)_2$	84	88	1.4237	.8215	77.58	77.30	13.02	13.10
$CH_3(CH_2)_3CH(COCH_3)CH(CH_3)C_2H_5$	75	88	1.4290	.8334	77.58	77.23	13.02	12.96
$CH_3(CH_2)_3CH(CO_2C_2H_5)CH_2CH(CH_3)_2$	82	96	1.4184	.8553	71.95	71.81	12.08	12.05
$CH_3(CH_2)_3CH(CO_2C_2H_5)CH(CH_3)C_2H_5$	74	98	1.4234	.8716	71.95	71.82	12.08	11.91
$[(CH_3)_2CHCH_2]_2CHCO_2C_2H_5$	78	88	1.4163	.8491	71.95	71.84	12.08	12.24
$CH_3(CH_2)_3CH(CO_2H)CH_2CH(CH_3)_2$	74	137	1.4288	.8916	69.75	69.70	11.71	11.82
$CH_3(CH_2)_3CH(CO_2H)CH(CH_3)C_2H_5$	50	138	1.4331	.9029	69.75	70.07	11.71	11.72
$[(CH_3)_2CHCH_2]_2CHCO_2H$	74	132	1.4260	.8849	69.75	69.56	11.71	11.78

[a] Prepared from methyl acetoacetate, sodium methoxide in methanol and *n*-butyl iodide. [b] Prepared from preceding compound by potassium *t*-butoxide method (ref. 10). Ketonic cleavage of this compound with both basic and acidic reagents gave practically the same results as were obtained with the ethyl ester.

listed below. These anilides all have the same empirical formula. Calculated for $C_{16}H_{25}ON$: C, 77.68; H, 10.19. 2-*n*-Butylcaproanilide, m. p. 106°; C, 77.71; H, 10.22. 2-(2-Methylpropyl)-caproanilide, m. p. 91°; C, 77.59; H, 10.15. 2-(2-Butyl)-caproanilide, m. p. 90°; C, 77.75; H, 10.22. 4-Methyl-2-(2-methylpropyl)-valeranilide, m. p. 108°; C, 77.75; H, 10.21.

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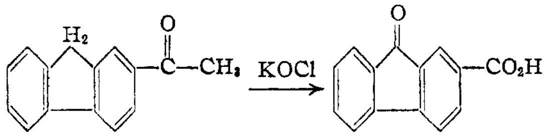
Oxidation of a Methylene Group with Hypochlorite

BY ROBERT W. SCHIESSLER AND NELSON R. ELDRED[1]

In an attempt to prepare fluorene-2-carboxylic acid (I) from 2-acetylfluorene (II) by the haloform reaction, fluorenone-2-carboxylic acid (III) was formed.



II III

Such oxidation of a methylene group to a carbonyl group with hypochlorite apparently has not been reported previously.

Reduction of III to fluorene-2-carboxylic acid by the modified Wolff–Kishner method[2] was found to be more convenient and to give higher yields than the two-step method using alcoholic potassium hydroxide and zinc dust, followed by phosphorus and iodine in acetic acid.[3]

Several attempts were made to oxidize fluorene to fluorenone with potassium hypochlorite. Under conditions comparable to the successful conversion of II to III, no fluorenone was formed. However, a small yield of fluorenone was realized when a solution of fluorene in chlorobenzene was refluxed with a potassium hypochlorite solution. Under these conditions the hypochlorite probably was being converted to chlorate.[4]

The hypochlorite method for oxidation of 2-acetylfluorene to fluorenone-2-carboxylic acid is more convenient than the method using sodium dichromate,[3] for the procedure is simpler and more rapid, yields are comparable, and recoveries are better.

Experimental

Fluorenone-2-carboxylic Acid.—2-Acetylfluorene (35 g.) was vigorously stirred for one hour with 500 ml. of 15% potassium hypochlorite.[5] After cooling, the unreacted material (II) was filtered off and the product precipitated from the filtrate with hydrochloric acid. When dried, the bright yellow crystalline product melted with decomposition at 333–335°. The yield was 22.6 g. or 60%. There was recovered 10.2 g. (28%) of 2-acetylfluorene. No fluorene-2-carboxylic acid could be isolated by selective solubility in ethanol.

Fluorene-2-carboxylic Acid.—By the method of Ray and Rieveschl,[3] 22 g. of fluorenone-2-carboxylic acid was reduced to yield 5 g., 25% yield, of fluorene-2-carboxylic acid, m. p. 265–274° with decomposition.

By the modified Wolff–Kishner reduction,[2] 26 g. of the keto acid was reduced, yielding 10.5 g., 43% yield of fluorene-2-carboxylic acid, m. p. 271–275° *without decomposition*. (Neutral equivalent: calcd., 210; found 207, 208.)

Fluorenone.—A solution of fluorene (20 g.) in 100 ml. of chlorobenzene was stirred vigorously for forty-eight hours with a refluxing solution of potassium hypochlorite.[4,5] The organic layer was separated, washed with water, and the chlorobenzene evaporated off. The solid residue was dissolved in 150 ml. of hot ethanol, which deposited two large crops of fluorene after cooling. Evaporation of the

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[1] Research Fellow, American Petroleum Institute Project 42.

[2] Whitmore, Herr, Clarke, Rowland and Schiessler, THIS JOURNAL, **67**, 2059 (1945).

[3] Ray and Rieveschl, THIS JOURNAL, **65**, 836 (1943).

[4] Bhaduri, *Z. anorg. Chem.*, **13**, 385 (1897).

[5] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 428 (1943).

mother liquors yielded a small quantity of dark oil which reacted with 3 ml. of 100% hydrazine hydrate in 2 ml. of ethanol. The mixture solidified on cooling. After repeated recrystallization from hot ethanol, *ca.* 1.0 g. of fluorenone was isolated as the hydrazone (m. p. 148–149°; mixed m. p. 148–149°).

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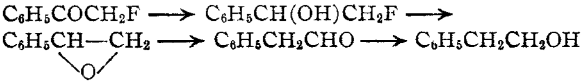
Reduction of Phenacyl Fluoride with Aluminum Isopropoxide[1]

BY WILLIAM E. TRUCE AND B. H. SACK

The original purpose of this investigation was to prepare ω-fluorostyrene by reduction of phenacyl fluoride with aluminum isopropoxide, followed by dehydration of the resulting fluorohydrin.

Phenacyl fluoride was prepared by acylating benzene with fluoroacetyl chloride[2] in the presence of aluminum chloride. After this portion of the work had been completed our attention was called to the publication of similar results.[3] However, the authors did not report the yield of phenacyl fluoride obtained nor that phenacyl chloride was an important by-product.

Phenacyl fluoride was treated with aluminum isopropoxide and isopropyl alcohol according to the procedure given for the reduction of benzophenone.[4] The product contained no fluorine. On the basis of previous results where halogen-free carbinols and ethers were obtained as reduction products of certain α-bromoketones,[4] 2-phenyl-1-ethanol was considered as a possible reduction product of phenacyl fluoride. The failure of the α-naphthylurethan of this alcohol to alter the melting point of the same derivative of an authentic sample of 2-phenyl-1-ethanol led to the conclusion that the reduction product was 2-phenyl-1-ethanol. It may have been formed by the following sequence of reactions[4]



$$C_6H_5COCH_2F \longrightarrow C_6H_5CH(OH)CH_2F \longrightarrow C_6H_5\underset{\diagdown O \diagup}{CH-CH_2} \longrightarrow C_6H_5CH_2CHO \longrightarrow C_6H_5CH_2CH_2OH$$

Experimental

Preparation of Phenacyl Fluoride.—Into a mixture of 117 g. (1.50 moles) of benzene, 198 g. (1.50 moles) of technical anhydrous aluminum chloride, and 300 ml. of carbon disulfide, surrounded by ice-water, was added 114 g. (1.32 moles) of fluoroacetyl chloride (b. p. 71° (755 mm.), $n^{27}D$ 1.3835). The addition was carried out dropwise with stirring over a period of five hours. The reaction mixture was allowed to warm up to room temperature and stirred for an additional four hours. The contents were poured into a mixture of ice and hydrochloric acid and then extracted twice with ether. This solution was treated with Drierite, the ether removed, and a vacuum rectification was carried out through a two-foot, helix-packed column. The yield of phenacyl fluoride was 46%, b. p. 94–95° (12 mm.), m. p. 27–28°.

Anal. Calcd. for C_8H_7FO: F, 13.77. Found: F, 13.78, 13.82; Cl, trace.

Phenacyl benzoate was prepared by refluxing a mixture of 1.0 g. of sodium benzoate, 5 cc. of water, 5 cc. of ethyl alcohol and 1.0 g. of phenacyl fluoride, for six hours. After chilling overnight an oil precipitated and after standing several days a small crop of long needles formed. These were recrystallized from 95% ethyl alcohol; m. p. 117–118° (lit. value 117–117.5°).[5]

The residue from the distillation of phenacyl fluoride amounted to 34 g. On recrystallization from methyl alcohol it melted at 56–57° and did not depress the melting point an authentic sample of phenacyl chloride.

Reduction of Phenacyl Fluoride.—Thirty-two grams (0.23 mole) of phenacyl fluoride was added to a mixture of 47 g. (0.23 mole) of aluminum isopropoxide in 235 cc. of isopropyl alcohol (distilled from calcium oxide) in a flask connected to a Hahn partial condenser. The solution was refluxed at such a rate that four to eight drops were distilled per minute. After thirteen hours the distillate showed a negative acetone test when treated with 2,4-dinitrophenylhydrazine reagent. The excess isopropyl alcohol was removed under reduced pressure. The residue was allowed to cool and was then hydrolyzed with cold, dilute hydrochloric acid (80 cc. of concd. acid and 400 cc. of water). The organic material was extracted with ether and, after removal of the ether, it was distilled, the material boiling at 97–102° (8 mm.) being collected; weight 16.3 g., $n^{26.8}D$ 1.5238, d^{20}_4 1.024. The α-naphthyl urethan, prepared according to directions given by Shriner and Fuson,[6] melted at 116–117°. It did not depress the melting point of the α-naphthyl urethan of an authentic sample of 2-phenyl-1-ethanol.

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[1] Abstracted from the M.S. thesis of B. H. Sack.

[2] Truce, THIS JOURNAL, **70**, 2828 (1948).

[3] Gryszkiewicz-Trochimowski, Sporzynski and Wnuk, *Rec. trav. chim.*, **66**, 419 (1947).

[4] Wilds, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Chap. 5.

[5] Zincke, *Ann.*, **216**, 308 (1882).

[6] Shriner and Fuson, "Identification of Organic Compounds," 3rd edition, John Wiley and Sons, New York, N. Y., 1940, p. 163.

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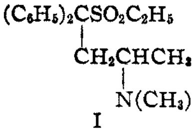
The Resolution of Ethyl 1,1-Diphenyl-3-dimethylaminobutyl Sulfone

BY B. F. TULLAR, W. WETTERAU AND S. ARCHER

In a previous paper[1] it was reported that the sulfone, I, exhibited strong analgesic action. For pharmacological reasons it became desirable to resolve this compound into its optical antipodes.



$$(C_6H_5)_2C(SO_2C_2H_5)CH_2CH(CH_3)N(CH_3)_2$$

I

The yield of ethyl benzohydryl sulfone was somewhat improved by using benzohydryl bromide rather than the chloride as the starting material. The sulfone was alkylated with dimethylaminoisopropyl chloride and sodium hydride rather than sodium amide as the condensing agent. The yield of pure I was 45% and about 29% of

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[1] Klenk, Suter and Archer, THIS JOURNAL, **70**, 3846 (1948).