a solid residue which was recrystallized from ether to afford 75 mg. II in the form of thick hexagonal prismatic plates, double, m. p. 118–120° and 127–129°; $[\alpha]^{19}\mathrm{D}$ $+ 155.6° \pm 3°$ ($c = 0.649$ in chloroform). A mixed m. p. determination with the product described above gave no depression. The mother liquors yielded 10 mg. of prisms, m. p. 122–126°; total yield 85 mg. or 56%. The Keller–Kiliani reaction gave results identical with those recorded above.

Methylation of II.—A sample of II was methylated following Purdie's procedure. The product III crystallized from ether–pentane in thin prisms, m. p. 98–99°, not depressed on admixture of an authentic specimen[1] of the methyl ether.

Reduction of VI with LiAlH$_4$.—150 mg. of VI (m. p. 147°)[9] was dissolved in 40 ml. of anhydrous ether. This solution was added slowly to a well-stirred and mildly refluxing solution of 500 mg. of LiAlH$_4$ in 50 ml. of anhydrous ether. The reaction was run for one hour and then worked up as described above. The product was recrystallized from ether–pentane, giving hexagonal plates, m. p. 111–112°; $[\alpha]^{22}\mathrm{D} + 107.3 \pm 2°$ ($c = 0.941$ in chloroform).[10] Admixture of an authentic sample[11] of VII caused no depression of the m. p. The yield was 129 mg. or 86%.

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[9] H. R. Bolliger and D. A. Prins, *Helv. Chim. Acta*, **28**, 465 (1945).

[10] Value previously[4] recorded: $[\alpha]^{12}\mathrm{D} +95.0 \pm 1°$ ($c = 2.904$ in chloroform).

[11] Kindly furnished by Prof. T. Reichstein, Basel.

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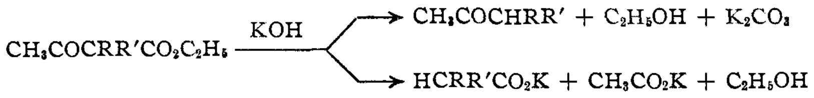
Preparation of Ketones from α,α-Disubstituted Acetoacetic Esters

BY W. B. RENFROW AND G. B. WALKER

α,α-Disubstituted acetoacetic esters undergo two competing reactions with alkali.



$$\mathrm{CH_3COCRR'CO_2C_2H_5} \xrightarrow{\mathrm{KOH}} \begin{cases} \longrightarrow \mathrm{CH_3COCHRR'} + \mathrm{C_2H_5OH} + \mathrm{K_2CO_3} \\ \longrightarrow \mathrm{HCRR'CO_2K} + \mathrm{CH_3CO_2K} + \mathrm{C_2H_5OH} \end{cases}$$

The ketonic cleavage is favored by a low concentration of alkali,[1] but maximum yields of ketones vary widely with the nature of the groups R and R′. Esters in which both R and R′ are methyl, ethyl or *n*-butyl groups give 60–84% yields[2,3] of ketones, but we have found that when R was an *n*-butyl group and R′ was either an *i*-butyl or *s*-butyl group the yields of ketones were very low (10%) and yields of disubstituted acetates were high even when the alkali concentration was kept at a minimum by adding it slowly to refluxing solutions of the esters in aqueous methanol.

After it was found that other hydrolysis procedures[2,4] were also unsatisfactory, the pyrolysis of *t*-butyl esters[5] of these dibutyl-substituted β-keto acids was investigated. By this method corresponding ketones have been obtained in good yield.

We have incidentally prepared several disubstituted ethyl acetates by alcoholysis[6] of α,α-disubstituted acetoacetic esters.

Experimental

Boiling and melting temperatures were determined with partial immersion thermometers. Yields, physical properties and analytical data for new liquids are listed in Table I.

Preparation and Ketonic Cleavage of *t*-Butyl Acetoacetates.—*t*-Butyl acetoacetate has been prepared by self-condensation of *t*-butyl acetate with sodium *t*-butoxide,[7] sodium amide or *i*-propylmagnesium bromide.[8] We have found sodium hydride to be a better condensing agent. Sodium hydride (9.6 g., 0.40 mole) was added to *t*-butyl acetate[9] (62 g., 0.53 mole) and the mixture refluxed from an oil-bath maintained at 90–110° for three and one-half hours. The bath temperature was then raised to 140° and heating continued for two hours longer. The mixture became almost solid. The reaction mixture was cooled to room temperature and treated with ice (70 g.) and concentrated hydrochloric acid (35 ml.). The organic layer was separated, washed with 5% sodium bicarbonate, dried and distilled through 18 cm. of glass helices. The *t*-butyl acetoacetate (27.7 g., 66% yield) boiled 81–82° at 15 mm. The reaction time could be shortened to two and one-half hours by using a ratio of two moles of ester to one mole of hydride, but the resulting yield of *t*-butyl acetoacetate was only 50%. We were unable to make all of the sodium hydride react when a ratio of one mole of ester to one mole of sodium hydride was used.

Alkylation of *t*-butyl acetoacetate with *n*-butyl bromide by the potassium *t*-butoxide method[10] gave *t*-butyl α-*n*-butylacetoacetate. Further alkylation of this product with *i*-butyl or *s*-butyl iodides by the same method gave the α,α-disubstituted acetoacetic esters. The disubstituted esters underwent some decomposition to ketones, carbon dioxide and *i*-butylene when fractionated, so they were purified by distillation from an ordinary Claisen flask.

The *t*-butyl acetoacetates were cleaved to ketones by mixing with 5% of their weight of *p*-toluenesulfonic acid and heating on a boiling water-bath until evolution of gas had ceased (about one hour). The liquids were then extracted with saturated sodium bicarbonate, dried over sodium sulfate and distilled. Semicarbazones of the new ketones were prepared and crystallized from ethanol–water. These semicarbazones have the same empirical formula. Calcd. for $C_{12}H_{25}ON_3$: C, 63.39; H, 11.09. 3-(2-Methylpropyl)-2-heptanone semicarbazone, m. p. 121°; C, 63.37; H, 11.15. 3-(2-Butyl)-2-heptanone semicarbazone, m. p. 127°; C, 63.64; H, 11.10.

Cleavage of Disubstituted Ethyl Acetoacetates to Disubstituted Ethyl Acetates.—Ethyl acetoacetates with the following substituents in the two alpha positions were cleaved: di-*n*-butyl, *n*-butyl-*i*-butyl, *n*-butyl-*s*-butyl, di-*i*-butyl. In a typical experiment, the acetoacetic ester (0.25 mole) was refluxed with a solution of sodium (0.125 g.-atom) in absolute ethanol (125 ml.) for five hours. Some of the alcohol (100 ml.) was removed by distillation and the residue poured into ice-water containing hydrochloric acid (0.12 mole). The layers were separated, the aqueous layer extracted with benzene and the combined organic layers fractionated through 18 cm. of glass helices. For further characterization, these esters were saponified and the acids converted to anilides *via* the acid chlorides. Melting points and analytical data for new anilides are

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[1] Wislicenus, *Ann.*, **190**, 257 (1878).

[2] Connor and Adkins, THIS JOURNAL, **54**, 3420 (1932).

[3] Renfrow, *ibid.*, **66**, 144 (1944).

[4] Hudson and Hauser, THIS JOURNAL, **63**, 3163 (1941); Newman, *ibid.*, **63**, 2431 (1941); Heller and Hoffman, *Ber.*, **62**, 871 (1929); James, *Ann.*, **231**, 244 (1885).

[5] This reaction has been used in a similar way by Hauser and co-workers, THIS JOURNAL, **66**, 1286 (1944); **69**, 2326 (1947).

[6] Beckham and Adkins, *ibid.*, **56**, 1119 (1934).

[7] Fisher and McElvain, *ibid.*, **56**, 1766 (1934).

[8] Hudson, Shivers and Hauser, *ibid.*, **65**, 2051 (1943).

[9] "Organic Syntheses," **24**, 18 (1944), Acetic Anhydride Method. Failure to dry this ester thoroughly (either over "Drierite" or by distillation) led to seriously depleted yields of *t*-butyl acetoacetate.

[10] Renfrow and Renfrow, *ibid.*, **68**, 1801 (1946).

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
$CH_3(CH_2)_3\underset{(CH_3)_2CHCH_2}{\underset{\mid}{C}}(COCH_3)CO_2C(CH_3)_3$	74	140	1.4359	.9150	71.07	70.72	11.18	11.10
$CH_3(CH_2)_3\underset{C_2H_5CHCH_3}{\underset{\mid}{C}}(COCH_3)CO_2C(CH_3)_3$	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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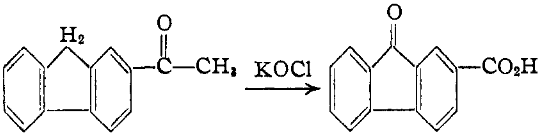
Oxidation of a Methylene Group with Hypochlorite

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).