

VERSUCHE

Trichlormethansulfenylchlorid und Phenylmagnesiumbromid. Die beiden Verbindungen wurden in Ätherlösung in wechselnden Mengenverhältnissen bei Temperaturen zwischen -70° und $+34^{\circ}$ miteinander umgesetzt. Die stark exotherme Reaktion lieferte keine definierten Produkte.

Trichlormethylphenylsulfid und Phenylmagnesiumbromid. Zu einer Lösung von 20,0 g (0,088 Mol) Trichlormethylphenylsulfid in Äther wurden unter Rühren in Stickstoffatmosphäre 148 ml einer 1,78-molaren ätherischen Phenylmagnesiumbromidlösung (0,264 Mol) zugegeben. Anschliessend wurde noch 2 Stunden gekocht, mit Eiswasser und Salzsäure zersetzt und wie üblich aufgearbeitet. Zwischen $80^{\circ}/0,4$ mm und $96^{\circ}/0,4$ mm gingen 7,8 g (47 % der Theorie) Diphenylsulfid über. $n_D^{20} = 1,6236$ (Literatur 1,6312). Das Sulfon schmolz zwischen 122° und 127° (Literatur 128°), der Mischschmelzpunkt mit authentischem Diphenylsulfon (F: 127°) war 123° – 127° . Das Produkt war mit Diphenyl (von der Bereitung des Grignardreagenz) verunreinigt, das sich nicht vollständig abtrennen liess.

Trichlormethylphenylsulfid und 1-Naphthylmagnesiumbromid. Die Umsetzung wurde wie oben durchgeführt, zur besseren Lösung der Grignardverbindung wurde etwas Benzol zugesetzt. Zwischen $211^{\circ}/11$ mm und $225^{\circ}/11$ mm gingen 7,0 g (33 % der Theorie) 1-Naphthylphenylsulfid über. Die Substanz schmolz nach Umkristallisieren aus Alkohol zwischen 37° und 39° (Literatur $41,8^{\circ}$). Das Sulfon schmolz zwischen 97° und 99° (Literatur $99,5^{\circ}$ – $100,5^{\circ}$). Das Produkt war mit Dinaphthyl-(1,1') verunreinigt.

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Studies on Peroxy Compounds VI.* A Novel Method for the Preparation of Acyloins

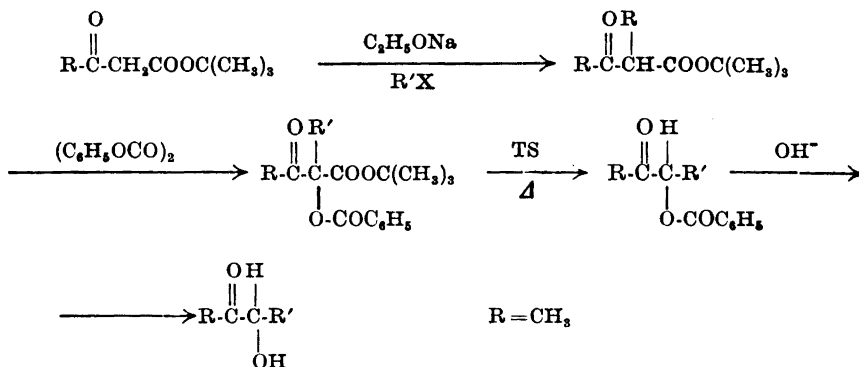
SVEN-OLOV LAWESSON and
SUSANNE GRÖNWALL

Department of Organic Chemistry, Chemical Institute, University of Uppsala, Uppsala, Sweden

In connection with our current studies of the reaction between benzoyl peroxide and sodium compounds of so called active methylene compounds¹, we have recently completed a project on ethyl acetoacetate and ethyl benzoylacetate. Inspired by the work of Treibs and Hintermeier² we directed our attention to *t*-butyl acetoacetate which is easily prepared in high yields from *t*-butyl alcohol and diketene. First we synthesized a series of α -alkyl and α -aralkyl substituted homologues of *t*-butyl acetoacetate with sodium ethoxide in ethanol as condensation agent. The benzoyloxy group is then easily introduced into the α -position of the ester by reacting its sodium compound with benzoyl peroxide in an inert solvent at 0 – 4°C . The benzoate, however, decomposes upon distillation. By reacting the crude ester with a catalytic amount of *p*-toluenesulphonic acid (TS) the carbo *t*-butoxy group is eliminated, and a benzoyl derivative of the corresponding acyloin is obtained. Hydrolysis may then give the acyloin according to the following formulas.

With certain limitations, it would be possible to prepare *t*-butyl esters of different β -keto acids according to well-known methods, and therefore the synthetic route outlined above appears to be general for the preparations of acyloins. As a full paper will be published at a later date,

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only one series of experiments is described here.

*Preparation of t-butyl- α -*n*-amyl acetoacetate.* To a sodium alcoholate solution prepared from 6.9 g of sodium in 150 ml of absolute ethyl alcohol, 47.4 g (0.3 mole) of *t*-butyl acetoacetate is added. After 10 min, 45.3 g (0.3 mole) of redistilled *n*-amyl bromide is added dropwise during 25 min and thereafter the mixture is refluxed for half an hour. The excess of ethanol is then immediately stripped off at reduced pressure, and the remainder poured onto water. The water phase is twice extracted with ether, and the combined ether extracts washed with water until neutral and then dried over sodium sulphate. Distillation gives the main fraction at b.p. 120–122°/10 mm Hg (Found: C 67.85; H. 10.57; Calc. C 68.38; H 10.59) $n_D^{20} = 1.4308$. Weight 46 g, yield 67 %.

The purity of the product has been verified by gas chromatographic analysis. When the *t*-butyl ester is heated, *isobutylene* rapidly splits off, and its incomplete combustion causes the low carbon yield percentage.

Preparation of octan-2-one-O-benzoyl-3-ol. In a 1 l three-necked flask, fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel, is placed 4.8 g of sodium hydride and covered with 200 ml of dry benzene. 45.6 g (0.2 mole) of *t*-butyl- α -*n*-amyl acetoacetate is added dropwise to the sodium hydride, and after 2 h of rapid stirring almost all hydride has reacted, the evolution of hydrogen has ceased and a clear solution is formed. Then the flask is cooled in an ice-water bath to about 0° and 36.3 g (0.15 mole) of benzoyl peroxide in 200 ml of dry benzene is added dropwise through the dropping funnel during 45 min. After another 15 min, the peroxide test is negative and the porridge-like mixture is poured into water.

The benzene phase is separated, the water phase extracted once with ether and the combined organic extracts washed neutral with water; 15.2 g of benzoic acid is isolated. From the organic phase, solvents and excess of starting material are distilled off. To the residue, 0.25 g *p*-toluene sulphonic acid is added. The distillation vessel is connected to a water pump and warmed on an oil bath maintained at a temperature of 160°C. When the decomposition is complete (constant pressure), the product is distilled. The main fraction is obtained at b.p. 114–115°/0.1 mm Hg. (Found: C 72.55; H 8.19. Calc. C 72.55; H 8.12). $n_D^{20} = 1.4959$. Weight 31 g, yield 83 %.

Preparation of octan-2-one-3-ol. In a flask fitted with a mechanical stirrer and a reflux condenser is placed 27 g of octan-2-one-O-benzoyl-3-ol and 200 ml of 10 % sodium hydroxide solution. Gentle heat is applied (inner temperature of the flask 60°C); after one hour's violent stirring, the mixture becomes homogeneous and turns a deep yellow colour. It is then extracted three times with ether and the organic layers are poured together, washed neutral with water and dried over sodium sulphate. 13 g of benzoic acid is obtained from the water phase. By vacuum distillation, 8 g of octan-2-one-3-ol at b.p. 93–94°/12 mm Hg is obtained (Found: C 66.57; H 11.03. Calc. 66.63; H 11.18). $n_D^{20} = 1.4340$, yield 51 %.

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