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Studies on Peroxy Compounds

XXI. The Preparation of 3-Substituted Levulinic Esters *

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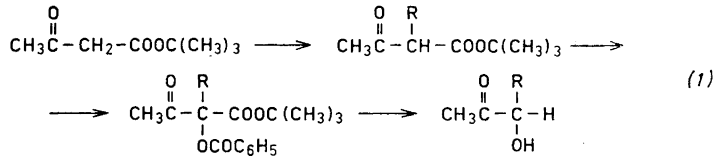
Submitted in honour of the sixtieth birthday of our teacher, Professor *Arne Fredga*

Heating a tertiary β-ketoester with *p*-toluenesulphonic acid easily causes elimination of the carbo-*t*-butoxy group without side reactions. Starting from derivatives of *t*-butyl acetoacetate, a convenient method for the preparation of 3-alkylsubstituted levulinates is described. 3-Benzoyloxy derivatives of ethyl levulinates were also prepared by reacting benzoyl peroxide with the sodium compounds of different mixed succinates. An attempt to prepare a compound of the acyloin-type by alcoholysis of a benzoyloxy compound only gave an unsaturated ester.

In a series of papers Lawesson *et al.* have recently studied the reaction between benzoyl peroxide and sodium compounds of so-called active methylene compounds. It was found that the benzoyloxy group is easily introduced into diethyl malonates giving O-benzoyltartronates [1], from which diethyl tartronates and tartronic acids could be prepared. Ethyl benzoyloxycyanoacetates [2] were also easily prepared. These compounds are of potential interest in connection with studies on amino acid precursors. β-Ketoesters [3] and β-diketones [4] also react smoothly to give the corresponding benzoyloxy derivatives. *t*-Butyl



(1)

I

* Part XX. Lawesson, S.-O. and Berglund, C. *Arkiv Kemi* **17** (1961) 485.

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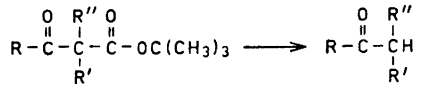
acetoacetate, which is easily prepared from diketene and *t*-butyl alcohol, has been investigated and a novel method of preparing acyloins [5] has been developed according to scheme (1).

The carbo-*t*-butoxy group is easily split off from the *α*-benzoyloxy derivative, I, on heating with *p*-toluenesulphonic acid and, generally, the *β*-carbonyl compound, II, is readily transformed into III under the same conditions (for pertinent references, see Frisell and Lawesson [6]).

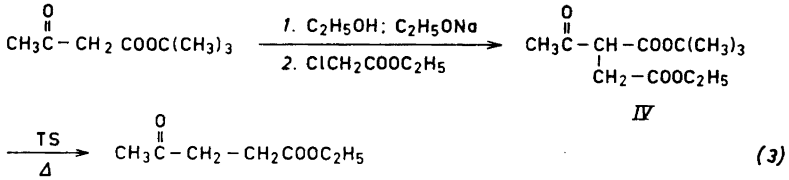


(2)

II III

As an extension of the benzoyl peroxide project [1–5] described in this paper, some work is recorded here on ethyl levulinates with special reference to the preparation of 3-substituted derivatives.

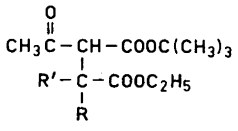
Treibs and Hintermeier [7] prepared ethyl levulinate by reacting the sodium compound of *t*-butyl acetoacetate with ethyl chloroacetate in ethanol as solvent, whereby 1-acetyl-1-carbo-*t*-butoxy-2-carbethoxy-ethane, IV, was first formed. By decomposing IV, ethyl levulinate, V, was obtained in high yields.



(3)

V

As the oxygen-oxygen bond in benzoyl peroxide is smoothly ruptured when the sodium compound of a so-called active methylene compound is allowed to react with this peroxide, the acetyl succinate, IV, and related compounds should be suitable starting materials for such work, especially as we were interested in extending the new acyloin method [5]. We therefore prepared succinates (VI, a—e)



VI

VI *a*: R=R′=H VI *d*: R=R′=CH_3

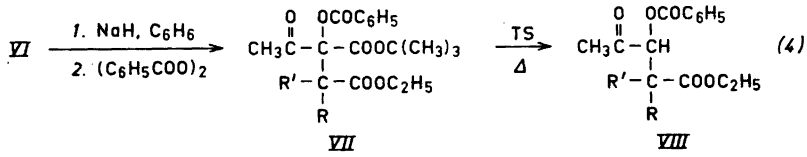
VI *b*: R=H; R′=CH_3 VI *e*: R=H; R′=n-C_6H_{13}

VI *c*: R=H; R′=C_2H_5

by reacting the sodium compound of *t*-butyl acetoacetate with the appropriate *α*-bromoester. Using ethyl alcohol as solvent, we did not observe any re-esterifi-

action of the *t*-butyl ester. Much lower yields were found when benzene was used as solvent. The succinates VI, a—e, are all rather stable compounds and could be distilled without any observable decomposition. VI (R=H; R′=C_6H_5), however, decomposed on attempted distillation.

The procedure for the subsequent reaction with benzoyl peroxide in benzene was the same as that earlier described [1] and in all cases quantitative yields of benzoic acid were isolated and no gas evolution was observed. No attempts were made to isolate the new products either by crystallization or distillation. Instead, after the usual work-up, catalytic amounts of *p*-toluenesulphonic acid were added and the carbo-*t*-butoxy group eliminated in the usual way. The 3-benzoyloxy levulinates were obtained in high yields. These were stable and did not show any tendency to decompose on distillation.



VIII a: R=R′=H VIII d: R=R′=CH_3

VIII b: R=H; R′=CH_3 VIII e: R=H; R′=n-C_6H_{13}

VIII c: R=H; R′=C_2H_5

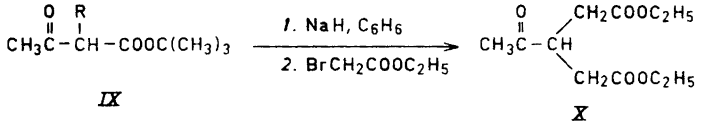
Having a series of benzoyloxy compounds VIII available, we investigated the possibility of preparing compounds of the acyloin type. It is known that the free acyloin is easily prepared from O-benzoylacyloins by hydrolysis with a base [5]. However, in our case, only small amounts of ethyl acetylacrylate were isolated by alcoholysis of VIII a, indicating that a 1,2-elimination had occurred.

Levulinic ester is the simplest member of γ-ketoesters and is especially attractive as a chemical intermediate because of its various reactive centres. The chemistry of levulinic acid and its esters is not well investigated although their uses as chemical intermediates, solvents, emulsifiers, plasticizers, pharmaceuticals etc. are well known. We have prepared some 3-alkylsubstituted levulinic esters as the starting material for further investigations. Using *t*-butyl acetoacetate instead of ethyl acetoacetate, the elimination of the *t*-butyl ester group under mild conditions is possible without hydrolysis of the ethyl ester group.

Alkylsubstituted *t*-butyl acetoacetates (in the form of the sodium compounds) reacted smoothly with ethyl bromoacetate and some other α-bromoesters and the corresponding levulinic esters were isolated in high yields. In one case, the levulinic ester was hydrolyzed to 3-hexyl levulinic acid which is thought to be a degradation product [8] of Antimycin A_1. A mixed melting point with the 2,4-dinitrophenylhydrazone of the named degradation product * was not depressed and the infrared spectra were superimposable.

* We are grateful to Professors E. E. van Tamelen and F. M. Strong for supplying a sample of this compound.

By reacting the sodium compounds of *t*-butyl iso-propyl acetoacetate and *t*-butyl *sec*-butylacetoacetate with ethyl bromoacetate, either in ethanol or benzene, the expected product was not formed and only diethyl *β*-acetylglutarate could be isolated. At present no explanation can be presented for this unusual observation.



IX a: R = i-C_3H_7

IX b: R = sec-C_4H_9

It was shown that the starting materials actually were IX a and IX b by decomposing them in the presence of *p*-toluenesulphonic acid and isolating the corresponding ketones in high yields. The identity of *β*-acetylglutarate, X, was shown by an unequivocal synthesis.

EXPERIMENTAL

The reactions between benzoyl peroxide and the sodium derivatives were carried out in an atmosphere from which moisture was excluded. Benzoyl peroxide was recrystallized at low temperature from chloroform and methanol. The infrared spectra were recorded on an Infracord. The analyses were made at the Analytical Department of Uppsala University. Boiling and melting points are not corrected.

Starting material

t-Butyl acetoacetate and alkylated derivatives thereof were prepared according to Lawesson *et al.*[5] *t*-Butyl isopropylacetoacetate, a new compound, was prepared as described below. The *α*-bromo carboxylic esters were purchased from Schuchardt, Munich, and used without further purification. Bromoacetone was prepared according to *Organic Syntheses*[9].

t-Butyl isopropylacetoacetate. To a sodium alcoholate solution, prepared from 6.9 g of sodium in 150 ml of ethyl alcohol, 47.4 g (0.3 mole) of *t*-butyl acetoacetate were added. After 15 min 51 g (0.3 mole) of isopropyliodide was added during 30 min and the mixture then refluxed for 7.5 h. The excess ethanol was then immediately stripped off at reduced pressure and the remaining solution poured into water. The water phase was twice extracted with ether. The combined ether extracts were washed with water until neutral and then dried over sodium sulphate. Distillation gave the main fraction at b.p. 90°C/11 mm Hg as a colourless liquid. Yield 47.4 g (79 %), n_D^{20} = 1.4238. (Found: C 65.83; H 10.06. Calc. C 65.97; H 10.07).

Preparation of succinic esters

VI a. Sodium alcoholate was prepared from 6.9 g (0.3 mole) of sodium in 150 ml of ethanol to which 47.4 g (0.3 mole) of *t*-butyl acetoacetate were added. Thereafter 50.3 g (0.3 mole) of ethyl bromoacetate were added dropwise during 15 min and gentle reflux was maintained for 30 min. The ethanol was then stripped off, the remaining solution poured into water + acid. The water phase was extracted with ether several times. The combined ether extracts were washed with water until neutral, dried over sodium sulphate and distilled. The main fraction was a colourless liquid with b.p. 106°C/0.6 mm Hg; n_D^{20} = 1.4338. Yield 58 g (79 %). (Found: C 59.00; H 8.32. Calc.: C 59.00; H 8.25).

When ethyl chloroacetate was used instead of ethyl bromoacetate, the diester was obtained in 62—69 % yield.

VI b. 0.4 mole of sodium ethoxide was prepared in 200 ml of absolute ethanol, and 63 g (0.4 mole) of *t*-butyl acetoacetate were added. After the exothermic reaction had ceased, 72.4 g (0.4 mole) of ethyl *a*-bromopropionate were added and gentle reflux was maintained for 45 min. The ethanol was distilled off and the work-up was performed as above. A colourless liquid was obtained with b.p. 90—92°C/0.3 mm Hg; n_D^{20} = 1.4342. Yield 87.4 g (85 %). (Found: C 60.23; H 8.57. Calc.: C 60.44; H 8.59).

When the sodium compound of *t*-butyl acetoacetate was prepared in benzene from sodium hydride, the following reaction with ethyl *a*-bromoproprionate gave only VI b in 28 % yield.

VI c. The diester was prepared as above from 6.9 g (0.3 mole) of sodium in 150 ml of ethanol, 47.4 g (0.3 mole) of *t*-butyl acetoacetate and 58.5 g (0.3 mole) of ethyl *a*-bromobutyrate (gentle reflux for about 2 h). Distillation gave a colourless liquid with b.p. 120—123°C/0.7 mm Hg; n_D^{02} = 1.4389. Yield 59.6 g (73 %).

VI d. The ester was prepared from 4.6 g (0.2 mole) of sodium in 100 ml of ethanol, 31.6 g (0.2 mole) of *t*-butyl acetoacetate and 39 g (0.2 mole) of ethyl *a*-bromo-isobutyrate (refluxed for 5 h). The usual work-up gave a colourless liquid with b.p. 120—123°C/0.7 mm Hg; n_D^{20} = 1.4433. Yield 13.8 g (25 %).

VI e. The diester was prepared from 79.0 g (0.5 mole) of *t*-butyl acetoacetate and 125.5 g (0.5 mole) of ethyl *a*-bromocaprylate in the usual way (refluxed for 3 h). A colourless liquid with b.p. 130—131°C/0.6 mm Hg; n_D^{20} = 1.4428. Yield 99.1 g (60 %). (Found: C 65.64; H 9.79; Calc.: C 65.82; H 9.82).

The preparation of ethyl *a*-bromocaprylate

88 g (0.74 mole) of redistilled thionyl chloride were placed in a 500 ml three-necked flask, fitted with a stirrer, a dropping funnel and a reflux condenser. After heating the chlorinating agent till gentle reflux, 97.5 g (0.68 mole) of newly distilled caprylic acid were added dropwise during 30 min. Gentle reflux was maintained for a further 30 min, whereafter 0.5 g of red phosphorus were added. After heating till reflux 40 ml (124 g, 0.78 mole) of bromine were added dropwise during 2 ½ h and the mixture was then refluxed for a further 4 ½ h. After cooling, the mixture was poured into the dropping-funnel and in the flask were placed 100 ml of ethanol, to which the mixture was added during on hour. Gentle reflux was maintained for 3 h. Ether was added to the mixture and after washing with sodium bicarbonate and water and drying over sodium sulphate, the ether was stripped off. Distillation gave a colourless liquid with b.p. 118—119°C/11 mm Hg; n_D^{20} = 1.4545. Yield 132.7 g (77 %). (Found: C 47.80; H 7.62. Calc.: C 47.82; H 7.63).

The preparation of ethyl 2-alkyl-3-benzoyloxy-levulinates

VIII a. 4.8 g (0.2 mole) of sodium hydride, covered with 200 ml of dry benzene were placed in a three-necked flask, fitted with a stirrer, reflux condenser and dropping funnel. 48.8 g (0.2 mole) of VI a were added dropwise and when all sodium hydride had been consumed the flask was cooled in an ice-water bath, 36.3 g (0.15 mole) of benzoyl peroxide in 300 ml of benzene were then added during 45 min. After one hour the peroxide test was negative; the mixture was poured out onto water, and the benzene phase separated. The water layer was extracted many times with ether, the combined organic phases washed neutral whit water and dried over sodium sulphate. The solvents were then stripped off and to the remaining solution 0.25 g of *p*-toluenesulphonic acid were added. The distillation vessel was connected to a water pump and warmed on an oil-bath maintained at a temperature of 160°C. When the decomposition was complete (constant pressure) the product was distilled. The main fraction was a pale yellow liquid with b.p. 137—139°C/0.2 mm Hg. n_D^{20} = 1.5022. Yield 33.1 g (86 %). (Found: C 63.30; H 6.19. Calc.: C 63.62; H 6.10). From the water phase 18 g of benzoic acid were isolated.

VIII b. This compound was prepared from 77.4 g (0.3 mole) of VI b and 7.2 g (0.3 mole) of sodium hydride in 225 ml of benzene and 48.4 g (0.2 mole) of benzoyl peroxide

in 400 ml of benzene. The reaction was complete after one hour. The product, which was weakly yellow, had b.p. 142–145°C/0.4 mm Hg. n_D^{20} = 1.4980. Yield 35 g (63 %). (Found: C 64.41; H 6.63. Calc.: C 64.73; H 6.52). Isolated benzoic acid = 24 g.

VIII c. The levulinate was prepared from 54.4 g (0.2 mole) of VI c, 4.8 g (0.2 mole) of sodium hydride and 36 g (0.15 mole) of benzoyl peroxide in a total volume of 450 ml benzene. After the usual work-up, the product was obtained with b.p. 147–150°C/0.4 mm Hg; n_D^{20} = 1.4960. Yield 19.4 g (44 %). (Found: C 65.94; H 6.98. Calc.: C 65.74; H 6.90).

VIII d. The sodium compound of VI d was prepared from 1.4 g (0.06 mole) of sodium hydride and 16.4 g (0.06 mole) of VI d in 75 ml of benzene. 9.7 g (0.04 mole) of benzoyl peroxide in 100 ml of benzene were added and after one hour all peroxides hade been consumed. The work-up gave quantitative yields of benzoic acid and the main product with b.p. 141–144°C/0.3 mm Hg; n_D^{20} = 1.5098. Yield 6.5 g (56 %). (Found: C 65.17; H 6.92. Calc.: C 65.74; H 6.90).

VIII e: The levulinate was prepared as above from 98.4 g (0.3 mole) of VI e and 7.2 g (0.3 mole) of sodium hydride in 225 ml of benzene and 48.4 g (0.2 mole) of benzoyl peroxide dissolved in 400 ml of benzene. No gas was evolved. 20.3 g (84 %) of benzoic acid were isolated and the product had b.p. 169–171°C/0.4 mm Hg; n^{20} = 1.4888. Yield 50.5 g (73 %). (Found: C 68.78; H 8.25. Calc.: 68.94; H 8.10).

Ethanolysis of VIII a. Sodium alcoholate was prepared from 4.6 g (0.2 mole) of sodium in 100 ml of ethanol. 52.8 g (0.2 mole) of ethyl 3-benzoyloxy levulinate were added dropwise during 15 min. A brown-red precipitate was formed immediately and the mixture stirred for 45 h at room temperature. The mixture was then poured onto water and this phase was extracted 5 times with ether. The combined extracts were washed until neutral with water, dried over sodium sulphate and distilled. A product with b.p. 78–80°C/8 mm Hg was obtained, n_D^{20} = 1.4500, yield 6.2 g (22 %) and was indentified as ethyl 3-acetylacrylate. The 2,4-dinitrophenylhydrazone had m.p. 148–149.5°C and the mixed m.p. with the authentic hydrazone was not depressed on admixture. 16.6 g of the starting material (VIII a) were recovered and from the water phase 17.8 g of benzoic acid was isolated.

Preparation of substituted levulinic esters

General procedure. Sodium hydride, covered with dry benzene, was placed under nitrogen in a three-necked flask fitted with a reflux condenser, a stirrer and a dropping funnel. The β-ketoester was added slowly and the sodium hydride was then consumed (in most cases heat was applied). The α-bromoester was then added quickly and the mixture heated under gentle reflux until nearly neutral. The benzene phase was poured into water, the benzene phase separated and the water phase extracted three times with ether. The combined organic phases were washed with water until neutral, dried over sodium sulphate and finally the solvents were stripped off. To the remaining solution 0.25 g of *p*-toluenesulphonic acid were added and the distillation vessel connected to a water pump and warmed on an oilbath, maintained at a temperature of about 150°C. When the decomposition was complete (constant pressure) the product was distilled. Before the final distillation, the product was always taken up in ether and washed with sodium bicarbonate to remove acidic substances.

Ethyl 3-benzyl levulinate. 49.6 g (0.2 mole) of *t*-butyl benzylacetoacetate were added to 4.8 g (0.2 mole) of sodium hydride covered with 150 ml of benzene. 33.5 g (0.2 mole) of ethyl bromoacetate were added and the mixture refluxed for 3 h. After the usual work-up, distillation gave the main fraction as a colourless liquid, b.p. 121–122°C/0.4 mm Hg. Yield 41.1 g (88 %); n_D^{20} = 1.5028. (Found: C 71.44; H 7.73. Calc.: C 71.77; H 7.74).

Ethyl 3-allyl levulinate was prepared from 4.8 g (0.2 mole) of sodium hydride covered with 150 ml of benzene, 40 g (0.2 mole) of redistilled *t*-butyl allyl acetoacetate and 33.5 g (0.2 mole) of ethyl bromoacetate. The product was obtained after the usual work-up and was a colourless liquid with b.p. 67–69°C/0.4 mm Hg. n_D^{20} = 1.4444. Yield 32.5 g (88 %). (Found: C 65.12; H 8.75. Calc.: C 65.19; H 8.75).

Ethyl 3-ethyl levulinate. The sodium compound was prepared from 4.8 g (0.2 mole) of sodium hydride, covered with 150 ml of benzene and 36 g (0.2 mole) of *t*-butyl ethyl acetoacetate. 33.5 g (0.2 mole) of ethyl bromoacetate were added and after reflux for

2.5 h the usual work-up was performed. The main fraction was a colourless liquid and had b.p. 58—60°C/0.4 Hg; n_D^{20} = 1.4312. Yield 29.5 g (86 %). (Found: C 62.34; H 9.34; Calc.: C 62.76; H 9.36).

Ethyl 2-methyl-3-benzyllevulinate. The sodium compound was prepared from 4.8 g (0.2 mole) of sodium hydride and 49.6 g (0.2 mole) of *t*-butyl benzyl acetoacetate. 36.2 g (0.2 mole) of ethyl *a*-bromopropionate were added and after reflux for 5 h the usual work-up gave a colourless liquid with b.p. 125—127°C/0.4 mm Hg; n_D^{20} = 1.5072. Yield 33.4 g (67 %). (Found: C 72.28; H 7.82. Calc.: C 72.55; H 8.12).

Ethyl 2-phenyllevulinate. Sodium alcoholate was prepared from 4.6 g (0.2 mole) of sodium in 100 ml of ethanol and (0.2 mole) of *t*-butyl acetoacetate were added. 48.6 g (0.2 mole) of ethyl *a*-bromophenylacetate were then added during 15 min and the mixture refluxed for 4 h. After the usual work-up, attempted distillation of the diester showed that it decomposed slowly. The carbo-*t*-butoxy group was therefore eliminated by adding TS. The main fraction had b.p. 136—139°C/0.6 mm Hg; n_D^{20} = 1.5038. Yield 30 g (68 %). (Found: C 70.32; H 7.32. Calc.: C 70.89; H 7.32). After some time the liquid crystallized and recrystallization from petrol ether gave needles with m.p. 40—41°C.

The preparation of 2-hexyllevulinic acid

a) *Ethyl 2-hexyllevulinate.* 92 g of VI e were decomposed in the presence of *p*-toluenesulphonic acid and gave 56 g of ethyl 2-hexyllevulinate, n_D^{20} = 1.4418, b.p. 95—97°C/0.4 mm Hg.

b) *2-Hexyllevulinic acid.* 45.6 g of ethyl 2-hexyllevulinate were mixed with 225 ml of 2 M sodium hydroxide solution and the solution was refluxed for 1 ½ h. After cooling, the water phase was acidified and exracted three times with ether. The combined extracts were washed once with water and dried over sodium sulphate. Distillation gave a colourless liquid with b.p. 145°C/0.4 mm Hg; n_D^{20} = 1.4502. Yield 26.4 g (66 %). (Found: C 66.11; H 10.08. Calc.: C 65.97; H 10.07).

The 2,4-dinitrophenylhydrazone of the acid was prepared in the usual waya nd recrystallized from ethanol + acetone to a constant melting point 123—124°C. The mixed m.p. with the degradation product was not depressed. (Found: C 53.76; H 6.43; N 14.68. Calc.: C 53.70; H 6.36; N 14.72).

Attempts to prepare ethyl 3-sec-butyl levulinate. 42.8 g (0.2 mole) of *t*-butyl sec-butyl acetoacetate were added to 4.8 g (0.2 mole) of sodium hydride in 150 ml of benzene. Thereafter, when all hydride was consumed, 33.5 g (0.2 mole) of ethyl bromoacetate were added and the mixture was refluxed for 3 h. The following work-up was performed in the usual way. Distillation gave a colourless product with b.p. 114—116°C/0.3 mm Hg. n_D^{20} = 1.4435. This product was identified as diethyl *β*-acetyl glutarate. Yield 20.2 g (88 %). (Found: C 57.27; H 7.89. Calc. for $C_{11}H_{18}O_5$: C 57.38; H 7.88).

Attempts to prepare t-butyl 3-isopropyl levulinate. 40 g (0.2 mole) of *t*-butyl isopropyl acetoacetate were added to 4.8 g (0.2 mole) of sodium hydride, covered with 150 ml of benzene. After the sodium compound had been formed, 33.5 g (0.2 mole) of ethyl isopropylacetoacetate were added quickly and the mixture was refluxed for 6 h. The work-up gave a product, identified as diethyl *β*-acetylglutarate, with b.p. 115°—118°C/0.3 mm Hg. n_D^{20} = 1.4438. Yield 15.4 g (67 %).

Decomposition of t-butyl sec-butylacetoacetate. 42.8 g (0.2 mole) of IX b were heated to 150°C in the presence of 0.25 g of *p*-toluenesulphonic acid. After the gas evolution ceased, distillation gave a product with b.p. 144—145°C. Yield 18.9 g (83 %). The semicarbazone (from ethanol) had m.p. 120—122°C; lit.[10] 120°C.

Decomposition of t-butyl isopropylacetoacetate. 40 g (0.2 mole) of IX a were decomposed as above. Methyl isobutyl ketone was obtained with b.p. 117°—119°C (lit.[11] 119°C). The 2,4-dinitrophenylhydrazone was prepared and recrystallized from ethanol. M.p. 84—85°C (lit.[11] 95°). (Found: C 51.37; H 5.79; N 19.92. Calc. for $C_{12}H_{16}O_4N_4$: C 51.42; H 5.75; N 19.99).

The preparation of diethyl β-acetylglutarate. Sodium alcoholate was prepared from 6.9 g (0.3 mole) of sodium and 150 ml of ethanol. 73.2 g (0.3 mole) of VI a were added and after another 15 min 50.3 g (0.3 mole) of ethyl bromoacetate were added dropwise and refluxed for 3 h. The alcohol was stripped off and the remainder worked up in the

usual way. After decomposing the product at 150°C distillation gave a colourless liquid with b.p. 120–121°C/0.3 mm Hg. n_D^{20} = 1.4435. Yield 41.4 g (60 %). (Found: C 56.94; H 7.82. Calc.: C 57.38; H 7.88).

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