613. *Experiments on the Synthesis of Carbonyl Compounds. Part IV.**

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The use of acid anhydrides in the synthesis of ketones by the debenzylation process (Bowman, *J.*, 1950, 325) leads to moderate yields of ketones and keto-acids. Whilst other types of carbonyl compounds including amino-ketones, keto-nitriles, and keto-aldehydes have been prepared in the usual manner from the requisite acid chloride with varying degrees of success, all attempts to employ arylmalonic esters proved abortive.

In Part II (*J.*, 1950, 325) a new and apparently general method of synthesis of saturated ketones was described comprising the following steps :

$$\underset{\text{(I.)}}{R\cdot CH(CO_2Et)_2} \xrightarrow[CH_2Ph\cdot OH]{Na-} R\cdot CNa(CO_2\cdot CH_2Ph)_2 \xrightarrow{R'\cdot COCl} R'\cdot CO\cdot CR(CO_2\cdot CH_2Ph)_2$$

$$\xrightarrow{H^+} R'\cdot CO\cdot CR(CO_2H)_2 \xrightarrow{-2CO_2} \underset{\text{(II.)}}{R'\cdot CO\cdot CH_2R}$$

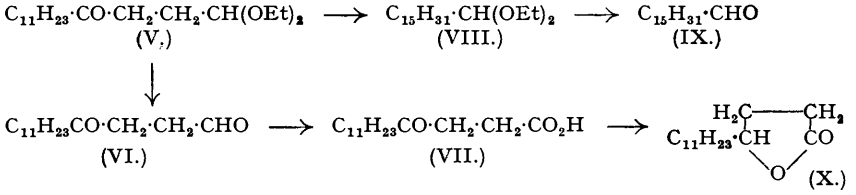
This paper reports the use of reagents other than acid chlorides, and the preparation of other types of carbonyl compounds. Use of hexanoic, succinic, β-methylglutaric, and glutaric anhydrides in place of the chlorides, and two simple alkylmalonic esters (I; R = n-C_6H_{13} and n-$C_{12}H_{25}$), gave the desired products but the yields were much inferior, except with glutaric anhydride. Undoubtedly one of the main reasons for the lower yields was the difficulty of decomposing the viscous condensation products which separated from the reaction medium.

* Part III, *J.*, 1950, 329.

The use of phthalimido-acid chlorides for the preparation of α-amino-ketones was even less successful, only poor yields of the hydrobromides of 2-aminodecan-3-one (II; R′ = $CHMe{\cdot}NH_2$, R = C_6H_{13}) and 1-aminononan-2-one (II; R′ = $CH_2{\cdot}NH_2$, R = C_6H_{13}) being obtained.

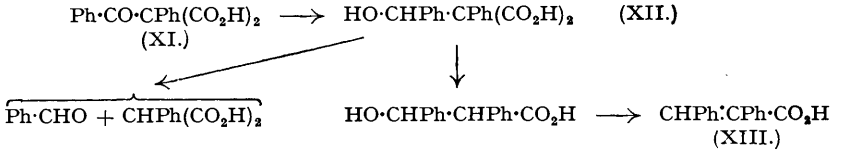
In a further variation, the readily accessible ethyl 2-cyanoethylmalonate (R = $CH_2{\cdot}CH_2{\cdot}CN$) (U.S.P. 2,461,336) and decanoyl chloride afforded 1-cyanopentadecan-4-one (III) which on reductive cyclisation over Raney nickel W7 at atmospheric pressure furnished 2-undecylpiperidine (IV), both in excellent yield (cf. Henecka, *Ber.*, 1949, **82**, 104).

With the exception of the β-compounds, aliphatic keto-aldehydes are almost unknown, and their preparation by our method was therefore studied, using the readily accessible ethyl 2 : 2-diethoxyethylmalonate. After preliminary difficulties this ester and decanoyl chloride gave (60%) yields of 4-ketopentadecanal diethyl acetal (V). Hydrolysis with dilute mineral acid



then furnished the free aldehyde (VI). Oxidation of this by alkaline potassium permanganate yielded the keto-acid (VII), and Wolff–Kishner reduction (Huang-Minlon modification, *J. Amer. Chem. Soc.*, 1946, **68**, 2487) of (V) furnished the hexadecanal acetal (VIII) which was hydrolysed to *n*-hexadecanal (IX) (isolated as its oxime). These structures were confirmed by synthesis of the keto-acid (VII) from decanoyl chloride and ethyl ethane-1 : 1 : 2-tricarboxylate. Reduction of (vii) by the Ponndorf method gave the γ-lactone (X).

Attention was next directed to the use of arylmalonic esters and, although we have already described the successful use of an aromatic acid chloride and an alkylmalonate (*loc. cit.*), the results in this case were disappointing. Thus, although *m*-anisoyl chloride and dibenzyl sodiophenylmalonate appeared to react normally to give an aroylmalonate, hydrogenolysis of the latter did not stop abruptly at the amount of hydrogen necessary for debenzylation but proceeded slowly further giving a product from which, after decarboxylation, a small yield of *m*-anisyl phenylketone was obtained. Further, benzoyl chloride and the benzyl ester gave no deoxybenzoin although a small quantity of α-phenylcinnamic acid (XIII) was isolated; in this case hydrogenation proceeded until 2·5 mols. of hydrogen had been taken up. Two possible



explanations for the failures come to mind. (1) Reduction of the carbonyl group in the intermediate aroylmalonic acid (XI) might give the unstable hydroxy-acid (XII) which when heated could either lose water to give (XIII) or be hydrolysed to benzaldehyde and phenylmalonic acid. However, in reduction of simpler compounds such as ethyl benzoyl-*iso*propyl- and -phenyl-malonate and benzoylmethanetricarboxylate no significant absorption of hydrogen took place under the conditions used in the ketone synthesis. (2) The product of interaction

(XIV.) $Ph{\cdot}CO_2{\cdot}C(O{\cdot}CH_2Ph){:}CPh{\cdot}CO_2{\cdot}CH_2Ph$ $PhCO_2{\cdot}C(OH){:}CPh{\cdot}CO_2H$ (XV.)

of aroyl chlorides and sodioarylmalonates might consist mainly of the *O*-aroyl derivative (XIV) which would undergo debenzylation to the acid (XV) which could suffer further hydrogenolysis

or, later, hydrolysis to its progenitors.* Although we have no proof that either mechanism takes place we consider it likely that both occur to a significant extent.

We report in the Experimental section some comparative work on variations of the reaction conditions, etc. Two experimental points emerged. First, commercial ethyl methyl ketone is an excellent solvent for the hydrogenation. Secondly, the hydrogenolysis and decarboxylation may be carried out in one step, without sacrifice of yield, by passage of hydrogen through a solution of the benzylacyl-esters in boiling ethyl methyl ketone in the presence of palladised strontium carbonate until evolution of carbon dioxide was complete, a technique which is particularly advantageous on a large scale. During these experiments *n*-tetradecan-6-one and hexadecan-8-one were obtained in a pure condition and characterised as the derived hydantoins (Henze, *J. Amer. Chem. Soc.*, 1942, **64**, 522).

Experimental.

General Method (cf. Part II).—A solution of the requisite malonic ester (1 mol.) and benzyl alcohol (1 mol. per carbethoxy-group of the malonic ester) in benzene (AnalaR) was added to "foamed" sodium ethoxide (1 mol.) in a vacuum and, when dissolution was complete, dry air was admitted. The mixture was distilled through a Fenske column until ester interchange was complete. The acid chloride (0·95 mol.) was then added to the cooled solution and after 30 minutes' refluxing the product was worked up as described previously (*loc. cit.*), hydrogenated in dry ethyl acetate in the presence of 10% palladised strontium carbonate (*ca.* 1 g. per 2 l. of hydrogen), and finally decarboxylated in the usual manner.

Reactions with Acid Anhydrides.—(1) *Hexanoic anhydride.* A solution of the anhydride (19 g., 0·1 mol.; b. p. 107—108°/0·5 mm.) in dry benzene (50 ml.) was added slowly with shaking to a solution of dibenzyl sodiododecylmalonate (0·1 mol.) in benzene, whereupon heat was evolved. The mixture was then refluxed for 0·25 hour and the resulting very viscous mass allowed to cool and decomposed by shaking it vigorously with aqueous acetic acid. After debenzylation and decarboxylation in the usual manner, the product was dissolved in light petroleum (b. p. 40—60°), and acidic material removed by neutralisation with aqueous sodium hydroxide solution. Evaporation of the organic extract furnished pure n-*nonadecan-6-one* (9·2 g., 33%) which separated from light petroleum (b. p. 40—60°) at 0° as colourless plates, m. p. 49° (Found: C, 80·7; H, 13·1. $C_{19}H_{38}O$ requires C, 80·9; H, 13·4%). It formed a *semicarbazone*, prisms (from ethanol), m. p. 66° (Found: N, 12·1. $C_{20}H_{41}ON_3$ requires N, 12·4%).

(2) *Succinic anhydride.* A solution of succinic anhydride (10 g., 0·1 mol.) in boiling benzene (100 ml.) was added quickly to a refluxing solution of dibenzyl sodio-*n*-hexylmalonate (0·1 mol.), and the mixture refluxed for a further 0·5 hour. The resulting thick sludge was cooled and decomposed with dilute sulphuric acid. The product of debenzylation and decarboxylation was heated to 200° to complete the decarboxylation of unchanged malonic acid and then distilled, yielding 4-*ketoundecanoic acid* as a colourless oil, b. p. 160—164°/1·5 mm. (4 g., 20%) which solidified immediately and then separated from light petroleum (b. p. 40—60°) in clusters of colourless needles, m. p. 80° (Found: C, 65·8; H, 10·1. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·0%).

(3) *β-Methylglutaric anhydride.* Prepared as in the previous experiment from the anhydride (12·8 g., 0·1 mol.) and dibenzyl sodio-*n*-dodecylmalonate (0·1 mol.), 5-*keto*-3-*methyloctadecanoic acid* was obtained as a colourless oil, b. p. 196—198°/0·2 mm. (10 g., 32%) which readily solidified and formed colourless plates, m. p. 57·5°, from light petroleum (b. p. 40—60°) (Found: C, 73·4; H, 11·6. $C_{19}H_{36}O_3$ requires C, 73·1; H, 11·5%). Its p-*bromophenacyl* ester crystallised from light petroleum (b. p. 60—80°) in colourless needles, m. p. 71° (Found: C, 63·4; H, 8·2. $C_{27}H_{41}O_4Br$ requires C, 63·6; H, 8·1%).

(4) *Glutaric anhydride.* The viscous, semi-fluid mass resulting from the interaction of the anhydride (11 g., 0·088 mol.) and dibenzyl sodio-*n*-hexylmalonate (0·1 mol.) in benzene was cooled and rendered homogeneous by addition of dry acetone. Decomposition of the sodium salt was then accomplished as in the previous experiment but more readily on account of the lower viscosity of the organic phase. Isolation, debenzylation, decarboxylation, and subsequent distillation furnished 5-*ketododecanoic acid* as a colourless oil, b. p. 140—145°/0·3 mm. (11·5 g., 60%). The keto-acid separated from ethyl acetate–light petroleum (b. p. 40—60°) as thin rectangular plates, m. p. 70° (Found: C, 67·3; H, 10·3. $C_{12}H_{22}O_3$ requires C, 67·3; H, 10·2%). The p-*phenylphenacyl* ester crystallised from moist ethanol (norite) in colourless laminae, m. p. 103—104° (Found: C, 76·5; H, 7·9. $C_{26}H_{32}O_4$ requires C, 76·5; H, 7·9%).

Amino-ketones.—(1) 2-*Aminodecan*-3-*one hydrobromide.* Oxalyl chloride (16 ml.) was added to a suspension of phthaloylalanine (17·5 g., 0·08 mol.) in dry AnalaR benzene (170 ml.), and since no evident reaction occurred the reaction mixture was heated to the b. p. whereupon a smooth evolution of hydrogen chloride took place and after 1 hour all the solid had dissolved. After 2·5 hours' refluxing, the mixture was slowly distilled through a short Fenske column until the vapour temperature reached 79°, whereafter the remaining solvent was removed under reduced pressure. The resulting acid chloride, which was an almost colourless viscous oil, was dissolved in fresh benzene (100 ml.) and added to a solution of dibenzyl sodio-*n*-hexylmalonate (0·1 mol.) in benzene. The product was isolated, debenzylated, and decarboxylated in the usual manner, the resulting oil diluted with water, and the mixture neutralised with alkali to phenolphthalein. The crude phthalimido-ketone which was isolated

* We are grateful for a suggestion by a Referee that *O*-acylation may predominate in such cases on account of the resulting tendency for the enolate to stabilise itself by conjugation with the benzene ring, *e.g.*, $EtO_2C{\cdot}CPh{:}C(OEt){\cdot}O^-$.

by extraction with benzene–ethyl acetate, was a viscous yellow oil. As it did not crystallise it was hydrolysed by boiling hydrobromic acid (50 ml.; 48%) and acetic acid (50 ml.) for 10 hours. Evaporation to *ca.* 30 ml. gave, on cooling, phthalic acid (2·5 g.; m. p. 200°). The filtrate was decolorised with norite and then evaporated to dryness, furnishing the *hydrobromide* as a crystalline mass (5·2 g., 24%) readily soluble in water, insoluble in ether, but fairly soluble in ethyl acetate from which it separated as colourless, prismatic rods, m. p. 78° after softening at 70° (Found: N, 5·3; Br, 31·4. $C_{10}H_{22}ONBr$ requires N, 5·6; Br, 31·7%).

When an aqueous solution of the hydrobromide was mixed with a slight excess of sodium cyanate in water, an oil separated which solidified on being warmed. 5-n-*Heptyl*-4 : 5(? 3 : 4)-*dihydro*-2-*keto*-4-*methylglyoxaline* crystallised from aqueous ethanol in colourless tablets, m. p. 242° (Found: N, 13·9. $C_{11}H_{20}N_2O$ requires N, 14·3%).

(2) 1-*Aminononan*-2-*one hydrobromide*. From phthaloylglycine chloride (12·5 g., 0·09 mol.; m. p. 82—84°) (Sheenan and Frank, *J. Amer. Chem. Soc.*, 1949, **71**, 1859) and dibenzyl sodio-*n*-hexylmalonate (0·1 mol.) as in the previous experiment, crude *phthalimidononan*-2-*one* was obtained as a viscous oil which slowly solidified (11·5 g.). Although insoluble in light petroleum (b. p. 40—60°) it crystallised, albeit with much loss, from a mixture of that solvent and benzene in yellow prisms, m. p. 44—46°. Removal of the colour could only be effected by repeated crystallisation from light petroleum (b. p. 40—60°)–ethyl acetate, eventually furnishing colourless prisms, m. p. 48° (Found: N, 4·8. $C_{17}H_{21}O_3N$ requires N, 4·8%). The mother-liquors from the crystallisations were evaporated to dryness, to give crude material which was hydrolysed as in the previous experiment. 1-*Aminononan*-2-*one hydrobromide* formed colourless leaflets (from ethyl acetate containing a trace of ethanol) which sintered at 90°, gave a clear mass at *ca.* 120°, and completely liquified at 190° with decomposition (Found: N, 5·8. $C_9H_{10}ONBr$ requires N, 5·9%).

1-*Cyanopentadecan*-4-*one*.—*n*-Dodecanoyl chloride (38 g., 0·17 mol.; b. p. 124°/2 mm.) and dibenzyl sodio-2-cyanoethylmalonate (0·2 mol.) yielded, by the general procedure, a crude product which was boiled with benzene (150 ml.)–ethanol (50 ml.) containing toluene-*p*-sulphonic acid (0·2 g.), under a Fenske column fitted with a Dean and Stark separator until esterification was complete. The cooled solution was washed with potassium hydrogen carbonate solution and water. After the drying (Na_2SO_4) and evaporation of the solvent, the residue was distilled, yielding a fore-run (b. p. 70—150°) and then the *keto-nitrile* as a colourless oil, b. p. 150—154°/0·4 mm. (30 g., 78%), which rapidly solidified and had f. p. 30°. It separated from 96% methanol at 0° in colourless glistening plates, m. p. 30·6—30·8° (Found: C, 76·4; H, 11·4. $C_{16}H_{29}ON$ requires C, 76·4; H, 11·6%).

This (2 g.) with boiling sodium hydroxide (3 ml.; 10N)–ethoxyethanol (10 ml.) (1 hour) gave, after dilution with water and acidification, a quantitative yield of 5-*ketohexadecanoic acid* which separated from light petroleum (b. p. 80—100°) containing a few drops of ethyl acetate as colourless plates (1·7 g.), m. p. 84·5—85·5° (Found: C, 71·4; H, 10·9. $C_{16}H_{30}O_3$ requires C, 71·1; H, 11·1%). Its p-*bromophenacyl* ester crystallised from ethanol in clusters of needles, m. p. 89° (Found: C, 61·4; H, 7·4. $C_{24}H_{35}O_4Br$ requires C, 61·7; H, 7·5%).

2-*Undecylpiperidine*.—The foregoing nitrile (7·5 g.) was hydrogenated in ethanol (100 ml.) in the presence of Raney nickel W7 (Adkins and Billica, *J. Amer. Chem. Soc.*, 1948, **70**, 695) (*ca.* 5 g.) at 50°/1 atm. until absorption of hydrogen ceased (3 mols.). After removal of the catalyst, the filtrate was distilled, yielding the *base* as a colourless oil, b. p. 118—119°/0·3 mm., n_D^{20} 1·4615 (6·5 g., 91%) (Found: C, 80·3; H, 13·7. $C_{16}H_{33}N$ requires C, 80·3; H, 13·8%). Its *hydrochloride* was very sparingly soluble in water but separated from aqueous ethanol in colourless needles, m. p. 138° (Found: N, 5·1. $C_{16}H_{34}NCl$ requires N, 5·05%).

Ethyl 2 : 2-*Diethoxyethylmalonate*.—Previous preparations of the diethyl ester (Perkin and Sprankling, *J.*, 1899, **75**, 13) required the use of pressure equipment but this may be avoided by the following modification: Bromacetal (177 g., 0·9 mol.), prepared in high yield (83—91%) by Bedoukian's method (*J. Amer. Chem. Soc.*, 1944, **66**, 651), was added to a solution of ethyl sodiomalonate (1·25 mols.) in ethanol (400 ml.) containing sodium iodide (2 g.), and the resulting mixture refluxed for 6 hours. Ethanol was removed by distillation with stirring until the bath-temperature reached 160° and refluxing was then continued for a further 3 hours. The thoroughly cooled mixture was then added to water (500 ml.) containing acetic acid (70 ml.), and the product isolated with benzene in the usual manner. Distillation through a Vigreux column furnished unchanged starting materials and then the product as a colourless oil, b. p. 124—125°/2 mm. 114 g., 40%).

Preliminary experiments on the conversion of this material into its dibenzyl ester yielded a dark material, probably owing to the presence of free aldehyde. Accordingly, the ester (100 g.) was purified by slow distillation with a mixture of benzene (200 ml.) and ethanol (50 ml.) containing toluene-*p*-sulphonic acid (0·2 g.) through a Fenske column for 4 hours to convert the free aldehyde into acetal. Anhydrous potassium carbonate (2 g.) was added to the cooled solution, with shaking, followed by water (100 ml.). The ester was then isolated and distilled as before.

4-*Ketopentadecan*-1-*al Diethyl Acetal*.—The foregoing purified ester-acetal (27·6 g., 0·1 mol.) was converted into the sodium derivative of the corresponding dibenzyl ester by means of sodium (2·3 g.; 0·1 mol.) and benzyl alcohol (21·6 g., 0·2 mol.) in benzene (200 ml.) in the usual manner. Decanoyl chloride (20 g., 0·09 mol.) was then added, the mixture refluxed for 30 minutes, and the product isolated, debenzylated, and decarboxylated as described above. Early experiments in which the product was freed from acidic contaminants by neutralisation with alkali yielded a mixture of aldehyde and acetal which were difficult to separate by fractional distillation. Accordingly, the crude product was refluxed with benzene (150 ml.) and ethanol (100 ml.) containing dry hydrogen chloride (1 g.), with azeotropic separation of water, for 8 hours and the product isolated as in the previous experiment. Distillation

furnished the original esters (b. p. 60—158°) and then the *keto-acetal* as a colourless oil, b. p. 158—160°/0·3 mm. (16 g., 60%), which solidified and had f. p. 20—21°. It separated from light petroleum (b. p. 40—60°) at −5° in colourless plates, m. p. 23° (Found: C, 72·9; H, 12·2. $C_{19}H_{38}O_3$ requires C, 72·6; H, 12·1%).

Hydrolysis by boiling N-hydrochloric acid for a few minutes yielded 4-*ketopentadecanal* as a solid which crystallised from light petroleum (b. p. 40—60°) at −10° in colourless plates, m. p. 46° (Found: C, 74·7; H, 11·4. $C_{15}H_{28}O_2$ requires C, 75·0; H, 11·6%). The latter reduced both Tollens' reagent and Fehling's solution, formed a *disemicarbazone*, prisms (from ethyl acetate), m. p. 160° (Found: N, 23·4. $C_{13}H_{34}N_6O_2$ requires N, 23·7%), and was oxidised by warm aqueous potassium permanganate–potassium hydrogen carbonate to the corresponding keto-acid (m. p. 92°), identical with the acid synthesised below.

The keto-acetal (5 g.), potassium hydroxide (4·5 g.), hydrazine hydrate (10 ml.; 50%), and 2 : 2′-dihydroxydiethyl ether (30 ml.) were refluxed for 1·5 hours, whereafter the temperature of the mixture was raised to 200° by distillation and kept at that temperature for a further 4 hours. The cooled solution was diluted with water, and the product isolated with light petroleum (b. p. 40—60°). Distillation yielded n-*pentadecanal diethyl acetal* as a colourless mobile oil, b. p. 138—140°/0·6 mm., n_D^{20} 1·4384 (4·3 g., 90%) (Found: C, 75·9; H, 13·2. $C_{19}H_{40}O_2$ requires C, 76·0; H, 13·3%). Hydrolysis with dilute acid gave the free aldehyde characterised as its oxime, needles (from ethanol), m. p. 85° (lit., m. p. 86°), and by oxidation as previously to *n*-pentadecanoic acid, plates (from moist ethanol), m. p. 51° (lit., m. p. 51° and 53°).

4-*Ketopentadecanoic Acid.*—The keto-ester from decanoyl chloride (21·5 g., 0·098 mol.) and tribenzyl sodioethanetricarboxylate (0·1 mol.) was hydrogenated in ethyl acetate (200 ml.) in the presence of 10% palladised strontium carbonate (4 g.) in the usual manner. The catalyst was filtered off and exhaustively extracted with boiling dry benzene (200 ml. in all). The combined organic extracts were then boiled under reflux for 30 minutes, the solvent was removed, and the residue refluxed with acetic acid (50 ml.)–sulphuric acid (20 ml.; 20N.) for 0·5 hour. After removal of acetic acid in steam, the residue was made alkaline by sodium hydroxide, and the resulting clear solution acidified while hot with hydrochloric acid. The keto-acid was removed from the cooled solution by filtration, dried (24 g., 94%; m. p. 86—89°), and crystallised from benzene as prisms, m. p. 92·5° (Found: C, 70·3; H, 10·5%; equiv., 255. Calc. for $C_{15}H_{28}O_3$: C, 70·3; H, 10·9%; equiv., 256) Asano and Kameda (*J. Pharm. Soc. Japan*, 1941, **60**, 80) reported m. p. 91·5—92·5°. It formed an *oxime*, plates [from light petroleum (b. p. 60—80°)], m. p. 67° (Found: N, 5·37. $C_{15}H_{29}O_3N$ requires N, 5·2%), and a p-*bromophenacyl* ester, needles [from light petroleum (b. p. 40—60°)], m. p. 90° (Found: C, 60·9; H, 7·2. $C_{23}H_{33}O_4Br$. requires C, 60·9; H, 7·5%).

4-*Hydroxypentadecanoic Lactone.*—The foregoing keto-acid (8 g.) and aluminium *iso*propoxide (5 g.) in *iso*propanol (150 ml.) was submitted to slow distillation through a Fenske column fitted with a variable take-off head until no more acetone distilled off (acetone removed, 2·0 g., estimated as oxime; theory, 1·8 g.). The bulk of the solvent was then removed under reduced pressure and the residue decomposed with dilute sulphuric acid. Isolated with benzene and distilled, the *lactone* was an oil, b. p. 155—157°/0·8 mm., n_D^{20} 1·4590 (7 g.; 93%) which slowly solidified and then separated from light petroleum (b. p. 40—60°) in plates, m. p. 25° (Found: C, 74·9; H, 11·6. $C_{15}H_{28}O_2$ requires C, 75·0; H, 11·7%).

Attempts to Employ Ethyl Phenylmalonate.—(1) *By using* m-*anisoyl chloride.* The acid chloride (17 g., 0·098 mol.) was treated with dibenzyl sodiophenylmalonate (0·1 mol.), and the resulting product hydrogenated according to the general procedure. Absorption of hydrogen, although rapid at first, continued slowly (4 ml./min.) after the theoretical volume (0·2 mol.) had been absorbed. The hydrogenation was stopped and the product worked up as usual. The residue, in benzene, was freed from acids by dilute aqueous sodium hydroxide, and was distilled, giving m-*anisyl phenyl ketone*, a pale yellow oil, b. p. 160—162°/1 mm., n_D^{20} 1·6038 (5·5 g., 24%), which solidified and then separated from ethanol at −20° in colourless needles, m. p. 38·5° (Found: C, 79·6; H, 6·3. $C_{15}H_{14}O_2$ requires C, 79·6; H, 6·2%). It formed an *oxime*, plates [from acetone–light petroleum (b. p. 40—60°)], m. p. 117—118° (Found: C, 74·3; H, 6·4; N, 5·8. $C_{15}H_{15}O_2N$ requires C, 74·7; H, 6·2; N, 5·8%).

(2) *By using benzoyl chloride.* The reactants were the acid chloride (0·07 mol.) and dibenzyl sodiophenylmalonate (0·07 mol.). Again hydrogenation proceeded further than that required for debenzylation (0·14 mol.) and, when a total of 4·5 l. (*ca.* 0·2 mol.) had been taken up, was proceeding slowly (0·75 ml./min.). The product was then decarboxylated and separated into neutral and acidic material as in the previous experiment. The former distilled mainly at 140—150°/0·5 mm. as a colourless oil containing only 18% of deoxybenzoin (oxime titration) and was not examined further. The acidic material was esterified azeotropically with ethanol, and the resulting ethyl esters were fractionated *in vacuo*, giving fractions (*a*) b. p. 72—100°/3 mm., mainly ethyl phenylacetate (5·5 g.) and (*b*) b. p. 110—170°/3 mm. (mainly 160°), n_D^{20} 1·5720 (3 g.), ethyl α-phenylcinnamate (100% by sap. equiv.), hydrolysed in good yield to α-phenylcinnamic acid, m. p. 170° alone or mixed with authentic material.

Attempted Reduction of Substituted Benzoylmalonic Esters.—(1) Diethyl benzoyl*iso*propylmalonate (Lund, Hansen, and Voigt, *Kgl. Danske Videnskab. Selskab. Maths-fys. Medd.*, 1933, **12**, 93) formed prisms [from light petroleum (b. p. 60—80°)], m. p. 66° (75%).

(2) Triethyl benzoylmethanetricarboxylate was prepared from benzoyl chloride and sodiomethanetricarbethoxylate in ether (Scholl and Egert, *Annalen*, 1913, **397**, 360) as a colourless oil, b. p. 175—177°/1·2 mm., n_D^{20} 1·5042, which just solidified at room temperature.

(3) *Ethyl benzoylphenylmalonate*, prepared from benzoyl chloride (1 mol.) and sodiophenylmalonate (1 mol.) in benzene in the usual manner, was an oil which after removal of material volatile up to

100°/0·5 mm. solidified and then crystallised from benzene–light petroleum (b. p. 60—80°) in elongated prisms, m. p. 79° (Found: C, 70·5; H, 5·9. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9%).

Attempts to hydrogenate esters from (1) and (3) by using palladised strontium carbonate in ethyl acetate were unsuccessful; in the case of the second ester, a very slow uptake of hydrogen occurred but the products were not isolated.

Miscellaneous Experiments.—(1) n-*Tetradecan-6-one*. The product from *n*-nonanyl chloride and dibenzyl sodio-*n*-butylmalonate was hydrogenolysed, decarboxylated, and freed from solvent at 120°. The residual oil, in light petroleum (b. p. 40—60°), was washed with dilute sodium hydroxide solution, dried, and distilled. The *ketone*, b. p. 112—114°/1 mm., solidified (f. p. 24—25°) and then separated from methanol in plates, m. p. 25° (Found: C, 79·0; H, 13·1. $C_{14}H_{28}O$ requires C, 79·2; H, 13·2%); the derived *hydantoin* formed prismatic needles (from methanol), m. p. 111° (Found: N, 10·2. $C_{16}H_{30}O_2N_2$ requires N, 9·9%).

The hydrogenation was carried out at the b. p. of the solvent (150 ml.) by passage of a brisk stream of hydrogen in the presence of 10% palladised strontium carbonate (3 g. per 0·1 mol.) for 15 minutes after evolution of carbon dioxide (lime-water) had ceased. The following solvents were used (yields in parentheses): ethyl acetate (65%), ethyl acetate–10% acetic acid (60%), and ethyl methyl ketone (65%).

(2) *Hexadecan-8-one*. The reaction, as before, of *n*-nonanyl chloride and dibenzyl sodio-*n*-hexylmalonate furnished the *ketone*, b. p. 125—127°/1 mm., which solidified and then separated from methanol in lustrous plates, m. p. 37° (Found: C, 80·3; H, 13·2. $C_{16}H_{32}O$ requires C, 80·0; H, 13·3%), and formed a *hydantoin*, colourless needles (from methanol), m. p. 124° (Found: N, 8·8. $C_{18}H_{34}O_2N_2$ requires N, 9·0%).

(*a*) The hydrogenation was effected in boiling ethyl methyl ketone as before. The addition of acid (chloride was carried out (i) at room temperature, with, later, refluxing for 30 minutes (yield, 65%), (ii) at the b. p. (yield, 60%), and (iii) at 0°, with, later, storage at this temperature for 24 hours yield, 70%).

(*b*) Hydrogenation was effected in boiling ethyl methyl ketone containing (i) 5% of water (yield, 57%) and (ii) 5% of acetic anhydride (yield, 67%).

(*c*) The hydrogenation was carried out in ethyl methyl ketone at room temperature in the usual manner (yield, 65%).

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