25. *The Modes of Addition to Conjugated Unsaturated Systems. Part VII. The Addition of Hydrogen Cyanide and Methyl Malonate to Methyl Cinnamylidenemalonate.*

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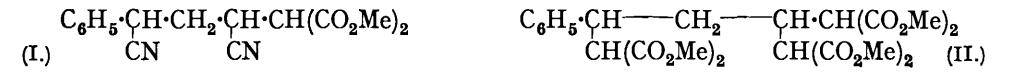
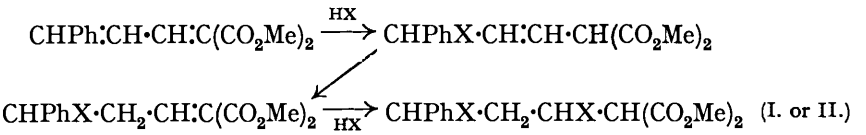
The preceding paper completes the general survey, commenced in 1928, of conjugative addition reactions from the viewpoint of the orientation theory of additions proposed in that year by Burton and one of us. It now remains to deal with the very few examples in which a reported experimental result appears to present a difficulty. Actually, prior to 1928, there were only two recorded cases of this kind, and these are considered in the present paper. The instances which have since arisen will be dealt with in due course.

The cases with which we are now concerned are at first sight related to each other. First, Thiele and Meisenheimer (*Annalen*, 1899, **306**, 247) prepared the product of addition of two molecules of hydrogen cyanide to one of methyl cinnamylidenemalonate, and regarded it as having formula (I). Secondly, Meerwein (*Annalen*, 1908, **360**, 336) obtained the addition product of two molecules of methyl malonate and one molecule of methyl cinnamylidenemalonate, and, by analogy with the previous example, ascribed to this adduct the corresponding formula (II).



(I.) (II.)

Our difficulty with these reactions was that, if they are really analogous, then the first step must consist in the formation of a 1 : 4-addition product, the prototropy of which will permit the further addition reaction required for the formation of the product obtained [(I), X = CN; (II), X = $CH(CO_2Me)_2$]:



From a theoretical point of view the important point about these additions is that they are additions of very weak acids (ψ-acids in fact) to a butadiene ester which contains a δ- but no β-aryl substituent. The theoretical argument against the view that such a reaction can lead to a stable αδ-addition product has already been given (Bloom and Ingold, J., 1931, 2765), and there is a practical argument in the same sense which cannot be disregarded. First, Thiele and Meisenheimer, in spite of their assumption of an αδ-intermediate in the formation of the double-addition product to which they gave formula (I), succeeded in isolating only the αβ-addition product when they treated methyl cinnamylidenemalonate with one molecular proportion of hydrogen cyanide. Furthermore, it has been shown by Hinrichsen and Triepel (*Annalen*, 1904, **336**, 202) that methyl cinnamylidenemalonate can be caused to add on ethyl alcohol through the agency of sodium ethoxide, and that the addition product is the αβ-derivative. Again, Kohler and Engelbrecht (*J. Amer. Chem. Soc.*, 1919, **41**, 764) have found that the addition of nitromethane to the same unsaturated ester yields essentially the αβ-product. Considerations such as these do not of course necessarily indicate any fallacy in the proposed structures (I) and (II), for reversible reactions can sometimes be canalised in the direction of a relatively unstable intermediate by some subsequent reaction of the latter; on the other hand, the whole matter seemed sufficiently curious to warrant further attention.

A perusal of Thiele and Meisenheimer's paper reveals no reason, apart from a tacitly admitted predisposition to assume 1 : 4-addition when possible, for their adoption of formula (I) to represent the double-addition product of hydrogen cyanide to methyl cinnamylidenemalonate. Employing the alternative hypothesis that the real inter-

mediate is the αβ-isomeride, which is expected to be the more stable and is known to be formed, it follows that the product of the second stage of the addition must have the structure (III). This result could arise simply from the circumstance that the αβ-intermediate product is expected to be prototropic under the conditions of the reaction [(III), X = CN; (IV), X = $CH(CO_2Me)_2$]:

$$CHPh{:}CH{\cdot}CH{:}C(CO_2Me)_2 \xrightarrow{HX} CHPh{:}CH{\cdot}CHX{\cdot}CH(CO_2Me)_2$$

$$CH_2Ph{\cdot}CH{:}CX{\cdot}CH(CO_2Me)_2 \xrightarrow[HX]{} CH_2Ph{\cdot}CHX{\cdot}CHX{\cdot}CH(CO_2Me)_2 \quad \text{(III. or IV.)}$$

It is also just possible that the anion of the αβ-intermediate might undergo a rearrangement thus:

$$C_6H_5{\cdot}CH{=}CH{\cdot}\overset{X}{\underset{|}{C}}H{-}\overset{\ominus}{C}(CO_2Me)_2 \longrightarrow C_6H_5{\cdot}\overset{\ominus}{C}H{-}\overset{X}{\underset{|}{C}}H{\cdot}CH{=}C(CO_2Me)_2$$

For, although mobility in such a system is expected to be slight, the structure does conform to the general scheme for the Wagner rearrangement given by Ingold and Shoppee (J., 1928, 371). The product of such a change is seen to be the anion of a substance which, on union with a further molecule HX, would yield compound (III).

Thiele and Meisenheimer hydrolysed the dinitrile-ester, to which they assigned formula (I), to a tricarboxylic acid. We therefore synthesised the *tricarboxylic acid* (V), which a compound of formula (I) would yield on hydrolysis. The starting materials were ethyl atropate and ethyl ethanetricarboxylate, and the synthesis is unambiguous:

$$C_6H_5{\cdot}C(CO_2Et){:}CH_2 + (CO_2Et)_2CH{\cdot}CH_2{\cdot}CO_2Et \xrightarrow{NaOEt} C_6H_5{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}C(CO_2Et)_2{\cdot}CH_2{\cdot}CO_2Et \longrightarrow C_6H_5{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H \quad \text{(V.)}$$

The acid was not identical with that of Thiele and Meisenheimer. This in itself does not prove the incorrectness of Thiele and Meisenheimer's formulation, because formula (V) contains two asymmetric carbon atoms and thus represents two optically inactive stereoisomerides. We therefore synthesised the *tricarboxylic acid* (VI), corresponding to a dinitrile-ester of formula (III). For this purpose ethyl benzylmalonate was condensed with either ethyl fumarate or ethyl bromosuccinate, and the *tetracarboxylic ester* thus obtained was hydrolysed:

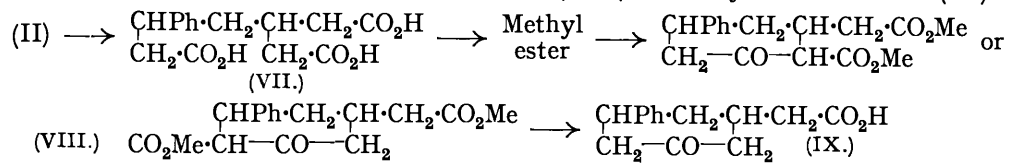
$$CH_2Ph{\cdot}CH(CO_2Et)_2 + CO_2Et{\cdot}CH{:}CH{\cdot}CO_2Et \text{ or } CO_2Et{\cdot}CHBr{\cdot}CH_2{\cdot}CO_2Et \xrightarrow{NaOEt}$$

$$\underset{\text{(two forms)}}{CH_2Ph{\cdot}C(CO_2Et)_2{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CO_2Et} \longrightarrow \underset{\text{(two forms)}}{CH_2Ph{\cdot}CH(CO_2H){\cdot}CH(CO_2H)}{\cdot}\underset{\text{(VI.)}}{CH_2{\cdot}CO_2H}$$

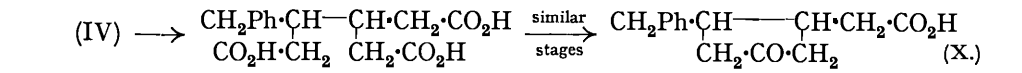
Thus the tricarboxylic acid (VI) was obtained in both the possible optically inactive stereoisomeric forms, one being produced when fumaric ester was used, and the other when bromosuccinic ester was employed. The second of these acids was identical with the acid of Thiele and Meisenheimer. Evidently, therefore, the double addition product of hydrogen cyanide with methyl cinnamylidenemalonate is a βγ-dinitrile of formula (III), and not a βδ-dinitrile of formula (I), as Thiele and Meisenheimer supposed. Equally plainly, the intermediate in the reaction is the αβ-adduct, which theory requires to possess greater thermodynamic stability than its αδ-isomeride. The remaining question as to whether the second stage of addition depends on a Wagner change, or merely on a prototropic change, of the αβ-intermediate is dealt with later.

Turning now to Meerwein's investigation of the double addition of methyl malonate to methyl cinnamylidenemalonate, there appear to have been two reasons which led this author to assign to his product the constitution of a βδ-dimalonic ester (II). In the first place Thiele and Meisenheimer had already advanced an analogous formula (I) for their double addition product. Secondly, formula (II) provided an adequate interpretation

of a series of reactions by means of which Meerwein converted his addition product into a tricarboxylic acid (VII), a cyclic ketonic ester (VIII), and a cyclic ketonic acid (IX):

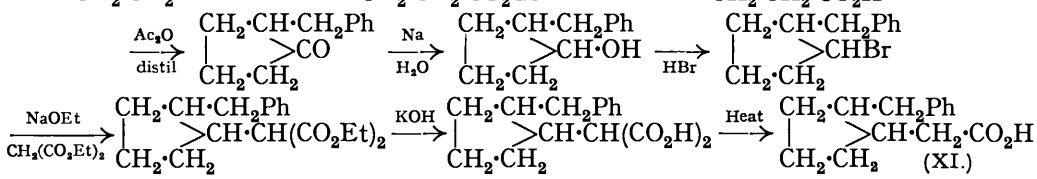


It follows, however, from the investigation already described, that the analogy on which Meisenheimer relied leads, not to the βδ-dimalonic ester structure (II), but to the isomeric βγ-structure (IV). Moreover, it is equally possible, on this basis, to account for Meerwein's reactions, the main difference being that the compounds which he regarded as phenyl-*cyclo*hexanones become formulated as benzyl*cyclo*pentanones:

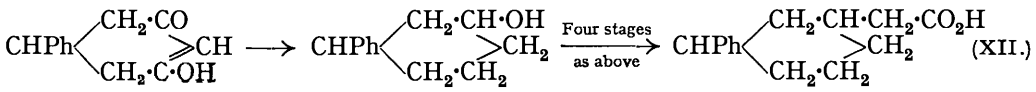


There is, however, a distinction between the hydrogen cyanide and the methyl malonate additions, which, *prima facie*, is of sufficient importance to render their analogy doubtful: it is that, whereas the βδ-double addition products (I) and (II) might have been formed by identical mechanisms, since the respective αδ-intermediates contain similar prototropic systems, the βγ-double-addition products (III) and (IV) could not arise analogously merely through the incursion of prototropic change, but could *only* do so through the intervention of the Wagner rearrangement. The reason for this is that, whilst in the hydrogen cyanide case the intermediate αβ-addition product, being a βγ-unsaturated nitrile, has great prototropic mobility, in the malonic ester addition the αβ-intermediate is a γδ-unsaturated ester, and therefore would not possess prototropic mobility permitting the second stage of the addition. Thus the existence or not of an analogy can be decided only by experiment.

First, assuming analogy with the hydrogen cyanide addition, it follows that Meerwein's cyclic ketonic acid, which in this event receives formula (X), should on reduction by Clemmensen's method yield 2-benzyl*cyclo*pentane-1-acetic acid. Meerwein's cyclic ketonic acid was therefore reduced in the manner indicated and 2-*benzyl*cyclo*pentane*-1-*acetic acid* (XI) was synthesised from ethyl *cyclo*pentanone-2-carboxylate, *via* α-*benzyl*-*adipic acid* and 2-*benzyl*cyclo*pentanone*, as indicated in the following scheme of formulæ:



The acid thus synthesised was not identical with the reduction product of Meerwein's cyclic ketonic acid. On the other hand, formula (XI) represents two optically inactive stereoisomerides, and therefore the observed non-identity does not prove that the acid obtained by Clemmensen's reduction has not formula (XI). The alternative is that there is no analogy between this addition and the hydrogen cyanide addition, and that Meerwein's formulæ are correct. In this case his cyclic ketonic acid has formula (IX), and its reduction product must be 3-phenyl*cyclo*hexane-1-acetic acid. Therefore we synthesised an acid of this constitution (XII) from phenyldihydroresorcinol, *via* the already known 3-phenyl*cyclo*hexanol (Boyd, Clifford, and Probert, J., 1920, **117**, 1383), the later steps being analogous to those of the previous synthesis:



The acid thus obtained was identical with the product of the Clemmensen reduction of Meerwein's cyclic ketonic acid. It follows that Meerwein's formulæ are correct, and, in particular, that his addition product is a βδ-dimalonic ester of formula (II).

This result proves that the suggested Wagner change has nothing to do with the malonic ester addition, and we may assume, with great probability of being correct, that it also is not concerned in the hydrogen cyanide addition. This being admitted, the reason why the two double additions take the particular directions that they do becomes clear. Each reaction may yield two products of single addition, an αβ-derivative and an αδ-isomeride, and the former of these is in each case thermodynamically the more stable. In the case of the hydrogen cyanide addition, *both* intermediates are capable of further change in the presence of excess of the reagent, and, accordingly, reaction proceeds mainly through that intermediate which is formed in greater amount. In the malonic ester addition, on the other hand, only one of the intermediates is capable of further reaction, and although that happens to be the one which is thermodynamically the less stable, every stage in the whole system of reactions is reversible, and the presence of excess of the reagent will therefore direct the change through the only channel by which that excess can be consumed. Consistent with this interpretation is the circumstance that, although in the hydrogen cyanide addition the presence of the intermediate single adduct can readily be shown, it has hitherto been found impossible to arrest the malonic ester reaction at the stage corresponding to the single addition compound: in the one case the intermediate is thermodynamically stable, in the other thermodynamically unstable.

Experimental.

Section 1. *Constitution of the Product of Addition of Two Molecules of Hydrogen Cyanide to Methyl Cinnamylidenemalonate.*

Preparation of the Addition Product and Certain of its Derivatives.—The addition product was prepared by the following modification of Thiele and Meisenheimer's method. A solution of potassium cyanide (30 g.) in water (50 g.) was added to one of the ester (40 g.) in ethyl alcohol (650 c.c.) during 75 minutes; the bulk of the alcohol was then removed by distillation, and the residue was diluted with water, extracted with ether, acidified, and again extracted. The crude nitrile-ester obtained from the second extract was hydrolysed by boiling for 100 hours with 25% aqueous potassium hydroxide, and the acid products were isolated by evaporating the acidified solution to dryness, washing the residue with a small amount of chloroform in order to remove some dark coloured impurities, and then extracting the organic acids by means of acetone. The product, after decolorisation by means of charcoal, consisted of the phenylbutanetricarboxylic acid, together with cinnamylsuccinic acid. Under the conditions described, however, the latter was not formed in an amount sufficient to necessitate separation by the fractional precipitation of barium salts, and the phenylbutanetricarboxylic acid could be directly purified by crystallisation from acetic acid. It had m. p. 187—190° (decomp.) (Found: C, 58·6; H, 5·3. Calc.: C, 58·8; H, 5·3%).

The *trimethyl* ester, prepared from the well-dried silver salt and excess of methyl iodide in boiling methyl alcohol, separated from methyl alcohol in colourless needles, m. p. 60° (Found: C, 62·4; H, 6·5. $C_{16}H_{20}O_6$ requires C, 62·4; H, 6·6%). During one of the preparations of the tricarboxylic acid the attempt was made to isolate and purify this by converting the crude acid product into silver salts and then into methyl esters, the intention being to isolate from these the trimethyl ester by crystallisation. Possibly the silver salt used in this experiment was not entirely neutral, for the esters, on crystallisation from methyl alcohol, yielded the *dimethyl* ester, which separated from chloroform–ligroin in colourless prisms, m. p. 112° (Found: C, 61·4; H, 6·1. $C_{15}H_{18}O_6$ requires C, 61·2; H, 6·2%). A useful derivative for identification of the tricarboxylic acid is its anhydro-acid, which Thiele and Meisenheimer prepared by heating the tribasic acid. Our preparation, crystallised from chloroform–ligroin, had m. p. 114°, and rapidly reverted to the tribasic acid when left in contact with moist air.

*Synthesis of δ-Phenyl-*n*-butane-αβδ-tricarboxylic Acid* (V).—Atropic acid, prepared from tropic acid by boiling with 50% aqueous potassium hydroxide, was crystallised from aqueous alcohol and esterified by treatment of its silver salt with ethyl iodide. The ester had b. p. 118—122°/12 mm. Ethyl ethanetricarboxylate, prepared from ethyl malonate and ethyl bromoacetate, had b. p. 146—148°/10 mm. A mixture of ethyl atropate (10·8 g.), ethyl ethane-

tricarboxylate (15·1 g.), and alcoholic sodium ethoxide, prepared from sodium (1·4 g.) and ethyl alcohol (18·4 g.), was kept at room temperature for 1 week, and then poured into water and extracted with ether. The extract, after washing with water and sodium hydrogen carbonate solution, yielded *ethyl δ-phenyl*-n-*butane-αββδ-tetracarboxylate* as a viscous oil, b. p. 165°/0·03 mm. (Found: C, 61·6; H, 7·0. $C_{22}H_{30}O_8$ requires C, 62·6; H, 7·1%).

The tetracarboxylic ester (1 vol.) was boiled for 16 hours with a mixture of sulphuric acid (1 vol.), water (1 vol.), and formic acid (3 vols.). The cooled solution on keeping yielded crystals of *δ-phenyl*-n-*butane-αβδ-tricarboxylic acid*, which separated from water in small prisms, m. p. 210—212° (Found: C, 58·1; H, 5·4. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%). This acid yields a liquid trimethyl ester.

Synthesis of δ-Phenyl-n-*butane-αβγ-tricarboxylic Acid* (VI) *in Two Stereoisomeric Forms.*—A solution of ethyl benzylmalonate, b. p. 163—165°/10—11 mm. (50 g.), ethyl fumarate, b. p. 118—122°/11 mm. (45 g.), and sodium ethoxide, prepared from sodium (4·6 g.) and ethyl alcohol (60 g.), was heated for a short time on the water-bath, and then kept at room temperature for 1 week. The solution was poured into water and extracted with ether; the extract, washed with water and sodium hydrogen carbonate solution and dried, yielded ethyl δ-phenyl-*n*-butane-αβγγ-tetracarboxylate as a viscous oil, b. p. 204—208°/0·09 mm. On hydrolysis by boiling with a mixture of aqueous formic and sulphuric acids the ester yielded *δ-phenyl*-n-*butane-αβγ-tricarboxylic acid*, which, crystallised from acetic acid, had m. p. 168° (Found: C, 58·2; H, 5·3. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%).

Ethyl α-bromosuccinate, prepared by directly brominating succinic acid or succinic anhydride by Volhard's method (*Annalen*, 1899, **252**, 150, 156) and decomposing the bromo-acid halide with ethyl alcohol, had b. p. 121—124°/10 mm. This ester (35 g.) was cautiously added to an ethyl-alcoholic solution of ethyl benzylmalonate (45 g.) and sodium ethoxide prepared from sodium (4·1 g.) and alcohol (64 g.). The mixture was warmed until neutral, poured into water, and extracted with ether, and the extract was washed with water and sodium hydrogen carbonate solution. *Ethyl δ-phenyl*-n-*butane-αβγγ-tetracarboxylate* was thus obtained as a colourless oil, b. p. 184—186°/0·6 mm. (Found: C, 62·9; H, 7·1. $C_{22}H_{30}O_8$ requires C, 62·6; H, 7·1%). Hydrolysis of this ester by the method used in the case of its stereoisomeride yielded a *δ-phenyl*-n-*butane-αβγ-tricarboxylic acid* which, crystallised from acetic acid, had m. p. 187—190° (decomp.) (Found: C, 58·4; H, 5·4. $C_{13}H_{14}O_6$ requires C, 58·6; H, 5·3%). This acid was identified by mixed m. p. and direct comparison with the acid prepared from Thiele and Meisenheimer's dinitrile. Its identity was further confirmed by the preparation of its trimethyl ester (Found: C, 62·3; H, 6·5. Calc.: C, 62·3; H, 6·5%), and anhydro-acid (Found: C, 62·2; H, 4·8. Calc.: C, 62·9; H, 4·8%), which were likewise identified with the corresponding derivatives prepared from the addition product of Thiele and Meisenheimer.

Section 2. Constitution of the Addition Product of Two Molecules of Methyl Malonate to Methyl Cinnamylidenemalonate.

Preparation of the Addition Product and Some of its Derivatives.—The addition product was prepared as Meerwein has described by union of the factors in the presence of methyl-alcoholic sodium methoxide, extracted with ether after addition of excess of dilute hydrochloric acid, and crystallised first from this solvent and then from methyl alcohol containing a little acetic acid. It had m. p. 81° (Found: C, 56·4; H, 5·9. Calc.: C, 56·5; H, 5·9%). Following Meerwein's general method, β-phenyl*iso*hexane-αεε-tricarboxylic acid was prepared from the addition compound by hydrolysis with constant-boiling aqueous hydrobromic acid. The acid, m. p. 140° (Found: C, 61·2; H, 6·2. Calc.: C, 61·2; H, 6·1%), was esterified with methyl alcohol by the method of Fischer and Speier, and the trimethyl ester, b. p. 250°/0·2 mm. (Found: C, 64·0; H, 7·1. Calc.: C, 64·3; H, 7·1%), was subjected to the Dieckmann reaction. It was found advantageous to employ 1 mol. of sodium in place of the 2 mols. recommended by Meerwein, but under all the conditions investigated we obtained not only the cyclic ketonic ester, m. p. 139° (Found: C, 67·0; H, 6·5. Calc.: C, 67·1; H, 6·6%), described by Meerwein, but also an *isomeride* having m. p. 64°, which was considerably more soluble in methyl alcohol (Found: C, 67·1; H, 6·6. $C_{17}H_{20}O_5$ requires C, 67·1; H, 6·6%). Two formulæ are available for these substances: they might be either methyl 6-carboxy-3-phenyl*cyclo*hexanone-5-acetate or methyl 2-carboxy-3-phenyl*cyclo*hexanone-5-acetate. Whichever may be correct, the two compounds are evidently stereoisomerides possessing the same formula, because the more fusible isomeride changes into the other on keeping for several months, or very rapidly on treatment with a small amount of hydrogen chloride in cold methyl alcohol. These facts

clearly suggest that the isomerides differ only in the configuration of the 6- or 2-carbomethoxy-group relative to the other substituents in the *cyclo*hexane ring. Owing to the tendency of the more fusible isomeride to spontaneous change, we cannot be sure that any of our specimens was completely free from the less fusible compound. The ester having m. p. 139°, on hydrolysis by boiling with a mixture of concentrated hydrochloric and formic acids, yielded 3-phenyl-*cyclo*hexanone-5-acetic acid, m. p. 118—119° (Found : C, 72·7; H, 6·9. Calc. : C, 72·4; H, 6·9%).

In order to obtain a derivative which could conveniently be synthesised, the above ketonic acid was reduced to *3-phenyl*cyclo*hexane-1-acetic acid* by boiling for 5 hours with excess of amalgamated zinc and 20% hydrochloric acid; the product, obtained as an oil which solidified on the surface of the cooled solution, crystallised from light petroleum in needles or plates, m. p. 52—54° (Found : C, 76·9; H, 8·2. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·2%).

*Synthesis of 2-Benzyl*cyclo*pentane-1-acetic Acid* (XI).—Ethyl *cyclo*pentanone-2-carboxylate, b. p. 118—120°/18 mm., prepared in the usual way from ethyl adipate, was treated successively with ethyl-alcoholic sodium ethoxide (1 mol.) and benzyl chloride (1 mol.). The mixture was warmed till neutral, poured into water, and extracted with ether, and the extract was washed with water and sodium hydrogen carbonate solution, dried, and distilled. *Ethyl α-benzyladipate* was thus obtained as a viscous oil, b. p. 208°/16 mm., $n_{5461}^{18°}$ 1·5056 (Found : C, 69·8; H, 8·1. $C_{17}H_{22}O_4$ requires C, 69·9; H, 8·2%). The ester, on hydrolysis by boiling for 3 hours with 20% hydrochloric acid containing a small amount of formic acid, yielded *α-benzyladipic acid*, which crystallised in needles, m. p. 116—118° (Found : C, 66·1; H, 6·8. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%). The acid was boiled for 2 hours with acetic anhydride, and the product was distilled under diminished pressure. The crude ketone was collected at 140—150°/20 mm., and this fraction on further distillation gave pure *2-benzyl*cyclo*pentanone* as an oil, b. p. 144—146°/16 mm. (Found : C, 82·5; H, 8·0. $C_{12}H_{14}O$ requires C, 82·7; H, 8·0%). The *semicarbazone* separated from methyl alcohol in small glistening plates, m. p. 198—200° (Found : C, 67·4; H, 7·5; N, 18·2. $C_{13}H_{17}ON_3$ requires C, 67·5; H, 7·4; N, 18·2%).

In our first attempt to introduce the acetic acid side chain, a mixture of benzyl*cyclo*pentanone (8·7 g.), ethyl cyanoacetate (5·6 g.), and piperidine (10 drops) was kept for 5 days at room temperature and then washed with dilute acid to remove the piperidine, dried, and distilled. The less volatile portion of the distillate solidified, and, on crystallisation from methyl alcohol, yielded *ethyl α-cyano-2-benzyl*cyclo*pentylidene-1-acetate* in silky needles, m. p. 81—83° (Found : C, 75·8; H, 7·1; N, 5·4. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1; N, 5·2%). Satisfactory conditions for the hydrolysis of this cyano-ester were not discovered. Boiling with concentrated hydrochloric acid failed to remove the nitrogen, and concentrated hydrobromic acid yielded a nitrogen-free oil with the properties of a lactone. Treatment with cold concentrated sulphuric acid caused sulphonation, and, on dilution with a limited amount of water, *ethyl 2-sulphobenzyl*-cyclo*pentylidene-1-malonamate*, $SO_3H{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH\!\!-\!\!C\!\!=\!\!C{\cdot}CO{\cdot}NH_2$ / $CH_2{\cdot}CH_2{\cdot}CH_2$ / CO_2Et, separated as an oil which subsequently solidified. It crystallised from chloroform–benzene in colourless silky needles, m. p. 120° (Found : C, 55·4; H, 5·6; N, 3·9; S, 8·7. $C_{17}H_{21}O_6NS$ requires C, 55·6; H, 5·7; N, 3·8; S, 8·7%).

2-Benzyl*cyclo*pentanone was reduced by placing its ethereal solution over water to which sodium (4 atoms) was added in small portions. When solution was complete, the ethereal layer was separated and the aqueous layer was extracted with ether. The combined ethereal solutions on distillation yielded *2-benzyl*cyclo*pentanol* as an oil, b. p. 154°/16 mm. (Found : C, 81·6; H, 9·0. $C_{12}H_{16}O$ requires C, 81·9; H, 9·1%). A mixture of the alcohol (10 g.) and a saturated solution of hydrogen bromide in glacial acetic acid (50 c.c.) was kept at room temperature until no further separation into two layers took place. The upper layer was separated and washed with water, and combined with the further small amount of oil which was obtained after evaporation of the acetic acid layer. The total oil on distillation yielded a small fraction, b. p. about 115°/15 mm., which analysis showed to consist of slightly impure benzyl*cyclo*pentene, and a main fraction, b. p. 150—155°/15 mm., which was the required *2-bromo-1-benzyl*cyclo-*pentane* (Found : C, 60·4; H, 6·2; Br, 31·7. $C_{12}H_{15}Br$ requires C, 60·2; H, 6·3; Br, 33·5%). A solution of sodium ethoxide, prepared from sodium (0·42 g.) and ethyl alcohol (6·7 g.), was treated successively with ethyl malonate (3·01 g.) and the above bromide (5·12 g.). The mixture was boiled for 48 hours, and, as it was then neutral, it was poured into water and extracted with ether; the extract, washed with water, dried, and distilled, yielded *ethyl 2-benzyl*cyclo-*pentane-1-malonate* as an oil, b. p. 142—150°/1 mm. (Found : C, 71·3; H, 8·1. $C_{19}H_{26}O_4$

requires C, 71·7; H, 8·1%). This ester was hydrolysed by boiling for 30 minutes with 33% aqueous potassium hydroxide. The cooled solution was diluted with an equal volume of water and extracted with ether to remove neutral impurities. *2-Benzylcyclopentanemalonic acid*, precipitated on acidification, crystallised from benzene in small white prisms, m. p. 137° (Found : C, 68·6; H, 7·0. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%). *2-Benzylcyclopentaneacetic acid* was obtained from the malonic acid by heating for 30 minutes at 150°; it crystallised from light petroleum in small prisms, m. p. 53—54° (Found : C, 77·0; H, 8·4. $C_{14}H_{18}O_2$ requires C, 77·1; H, 8·3%).

Synthesis of 3-Phenylcyclohexane-1-acetic Acid (XII).—Phenyldihydroresorcinol, m. p. 180°, prepared in the usual way from styryl methyl ketone and ethyl malonate, was converted by means of phosphorus trichloride in chloroform solution, as recommended by Boyd, Clifford, and Probert (*loc. cit.*), into 3-chloro-5-phenyl-Δ^3-*cyclo*hexenone, which, crystallised from ligroin, had m. p. 65—66°. The reduction of this compound (10 g.) by placing its solution in ether (100 c.c.) on water (100 c.c.) to which sodium (25 g.) was added in small portions, did not proceed well in our hands, the best yield of pure 3-phenyl*cyclo*hexanol, m. p. 79—80°, isolated by distilling the ethereal extract and purified by crystallisation from light petroleum, being 13% (Found : C, 81·4; H, 9·1. Calc. : C, 81·8; H, 9·1%). The principal by-product was a resin, but there was also an unsaturated liquid which distilled with the phenyl*cyclo*hexanol and was not a ketone. Phenyl*cyclo*hexanol was also obtained, although in small yield, by reducing the chloro-compound in 90% ethyl-alcoholic solution by means of the theoretical quantity of hydrogen in the presence of Adams's platinum catalyst. The alcohol was converted into 3-bromo-1-phenyl*cyclo*hexane, b. p. 126°/0·5 mm. (Found : C, 61·5; H, 6·3; Br, 31·7. Calc. : C, 60·3; H, 6·3; Br, 33·5%), by the method used in the corresponding experiment with benzyl-*cyclo*pentanol. The bromide was condensed with ethyl sodiomalonate, the method of the previous synthesis again being followed, and *ethyl 3-phenylcyclohexane-1-malonate*, b. p. 160—165°/0·5 mm., was thus prepared (Found : C, 70·2; H, 7·9. $C_{19}H_{26}O_4$ requires C, 71·7; H, 8·1%). As the analysis shows, the sample was contaminated with unchanged bromide, which, however, did not interfere with the preparation of *3-phenylcyclohexane-1-malonic acid*. This was done by boiling the ester with four times the calculated amount of 33% aqueous potassium hydroxide for 7 minutes. The cooled solution was diluted with an equal volume of water, extracted with ether in order to remove neutral impurities, and then acidified. The acid thus precipitated crystallised from aqueous acetic acid in small needles, m. p. 166° (decomp.) (Found : C, 68·9; H, 6·9. $C_{15}H_{18}O_4$ requires C, 68·7; H, 6·9%). On decarboxylation by heating for 30 minutes in a bath at 170°, 3-phenyl*cyclo*hexane-1-acetic acid was obtained, which, on crystallisation from light petroleum, had m. p. 52°, and was identical, as was shown by direct comparison and a mixed m. p. determination, with the acid of this formula which was prepared as a degradation product of Meerwein's addition compound (Found : C, 76·9; H, 8·5. Calc. : C, 77·1; H, 8·3%).

We thank the Chemical Society for a grant.

UNIVERSITY COLLEGE, LONDON. [*Received, November 27th*, 1933.]