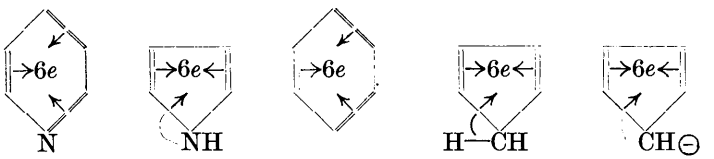
CLXVI.—*The Tautomerism of* cyclo*Pentadienes. Part I. Some Derivatives of Methyl*cyclo*pentadiene.*

By FRANK ROBERT GOSS and CHRISTOPHER KELK INGOLD.

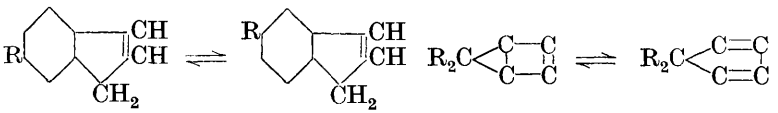
THE theory that aromatic systems owe their stability to a sextuple valency group is expressed in one form by the centric structure, and in another by Thiele's partial-valency formula, for benzene, and these may be regarded as the classical representatives of the two views that the association is central and peripheral respectively. The principal evidence in favour of the general conception is, however, that given by Bamberger (*Ber.*, 1891, **24**, 1758; 1893, **26**, 1946; *Annalen*, 1893, **273**, 373), whose arguments are simple and conclusive: pyrroles are exceptionally weak bases, and this is because the salt-forming valencies of the nitrogen atom (in modern terminology, its unshared electrons) are required to form the sextuple group; pyridines, on the other hand, are relatively strong bases, because the sextuple group can be formed without calling on the latent valencies of the nitrogen atom, which therefore remain available for salt-formation. Without assumption as to the precise location of the stable group, the conception may be expressed by (I) and (II), where each arrow denotes a contributing duplet. An interesting application has been made by Armit and Robinson (J., 1925, **127**, 1605), who have shown that the existence of the stable group is consistent with the properties of anhydronium bases, and yet another illustration forms the subject of this paper.



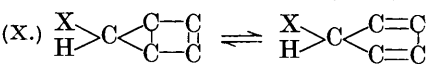
In a recent communication (Baker, Cooper and Ingold, this vol., p. 426), a valency-group of a different type was considered, and it was shown that the non-basicity of nitriles and the power of acetylenes to yield metallic derivatives are phenomena of identical origin. Excluding the triarylmethyls, which require separate discussion (see this vol., p. 905, footnote), the only other group of hydrocarbons characterised by their ability to form highly stable metallic compounds are the *cyclo*pentadienes, including their polynuclear derivatives, indene and fluorene. It will be evident that the reasoning by which the properties of acetylenes were correlated with those of nitriles also enables the chemistry of the

above-mentioned cyclic hydrocarbons to be correlated with that of the very weak bases considered by Bamberger. Benzene (III) is obviously in the same case as pyridine in regard to its ability to provide the electrons for the stable sextet, but *cyclo*pentadiene can do so only by the appropriation of the electrons of one of its hydrogen atoms; it is this circumstance which gives to the hydrocarbon and its derivatives properties analogous to those of an acid (IV), and confers stability on the corresponding anion (V).

The same circumstance should also confer tautomeric (prototropic) mobility on *cyclo*pentadiene and indene, but probably not on fluorene, since the lateral rings will tend to fix the structure of the central ring in this hydrocarbon. The case of indene has already been examined by Ingold and Piggott (J., 1923, **123**, 1469), who found that it exhibited prototropy; derivatives of types (VI) and (VII) were identical and they also responded to the "fission" and "substitution" tests (*loc. cit.*) for tautomeric mobility in symmetrical systems. This series of papers has originated in an attempt to test the matter for the simple *cyclo*pentadiene nucleus. Many simple *cyclo*pentadienes have been studied by Perkin, Thorpe, Farmer, Seeley, and others, who have shown that they exhibit valency-tautomerism of the intra-annular type; that is to say, they are not only *cyclo*pentadienes, but also *dicyclo*pentenes (VIII, IX). These compounds, however, were unsuitable for our purpose, since they contain the *gem*-grouping indicated in the formulæ (or an equivalent spiran ring), and thus do not contain a hydrogen atom which might be induced to ionise by the tendency to form a nuclear electron-group. We have therefore undertaken the study of analogous compounds (X, XI) which do not suffer from the disability mentioned, and in this paper derivatives are described in which the *gem*-dialkyl group of the previous work is replaced (i) by $\overset{CH_3}{H}\!>\!C$, and (ii) by $\overset{CO_2Me}{H}\!>\!C$ and $\overset{CO_2Et}{H}\!>\!C$. It may be stated here that the results obtained, although, perhaps, not wholly conclusive, tend strongly in the direction indicated above.



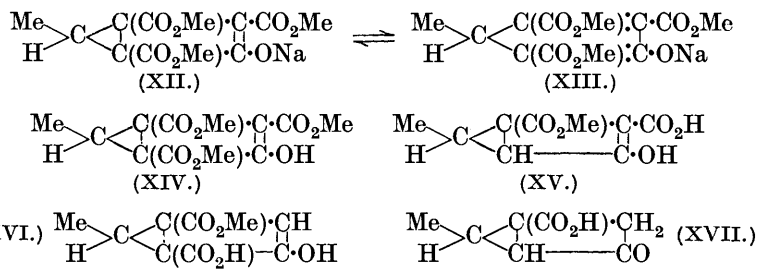
(VI.) (VII.) (VIII.) (IX.)



(X.) (XI.)

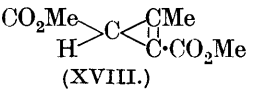
For the preparation of the first series of compounds we employed the method whereby Perkin and Thorpe originally synthesised the

sodio-derivative of ethyl 5 : 5-dimethyl*cyclo*pentadien-3-ol-1 : 2 : 4-tricarboxylate (dimethyl*dicyclo*pentenoltricarboxylate) from ethyl αα′-dibromo-ββ-dimethylglutarate, ethyl sodiomalonate, and sodium ethoxide. Using ethyl dibromo-β-methylglutarate, we obtained the corresponding yellow sodium compound of the 5-methyl-5-hydrogen series, which resembled its analogue, but was unfortunately much more soluble and hence difficult to isolate and purify. This obstacle was, however, largely overcome by the use of methyl in place of ethyl esters, and it is therefore the yellow sodium compound (XII, XIII) which has been examined in the greatest detail. Its hydrolysis was followed through the stages represented, as to one tautomeric form, by (XIV) and (XV or XVI), the final product being (XVII).

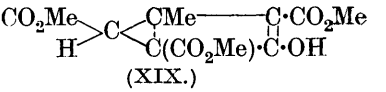


The starting point of the second series of preparations was the methyl*cyclo*propenedicarboxylic ester (XVIII), the constitution of which rests on results described in several former communications (Goss, Ingold, and Thorpe, J., 1923, **123**, 327, 3342; 1924, **125**, 1927; 1925, **127**, 460), in which it is shown, *inter alia*, that the additive reactions of the corresponding acid definitely determine that the double linking is in the position indicated, and not in the symmetrical endocyclic position or the semicyclic position. By the interaction of this ester with methyl sodiomalonate and sodium methoxide, the compound (XIX) might obviously be produced, and there is evidence that this is the case, although extensive side-reactions also occur which render difficult the purification of the dicyclic product. The condensation of the *cyclo*propene ester with methyl sodiocyanoacetate, however, pursues a smoother course, and a *cyclo*propane-cyanoacetic ester (XX) is formed, which on ring-closure produces an amino-ester, apparently analogous to the hydroxy-esters which are formed when the corresponding *cyclo*propane-malonic esters undergo ring formation. The amino-compound is a weak base, and it also behaves as a weak acid, since a solid sodio-derivative is obtainable. By analogy with the hydroxy-esters it may be represented by (XXI) and (XXII), possibly together

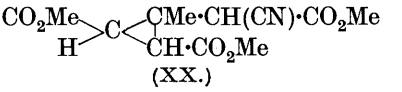
with the corresponding imino-phases. Partial hydrolysis to a compound represented, as to one phase, by (XXIII) or (XXIV) can be effected without loss of the amino-group, and the final hydrolysis product is the nitrogen-free acid (XXV). Closely similar results were obtained when the ethyl ester corresponding to (XVIII) was used, the final product being the same acid (XXV).



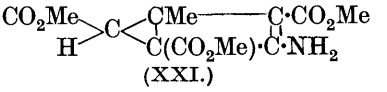
(XVIII.)



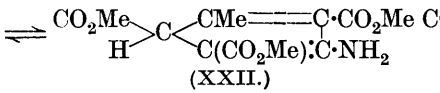
(XIX.)



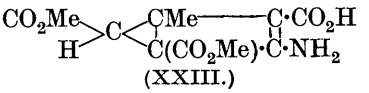
(XX.)



(XXI.)



(XXII.)



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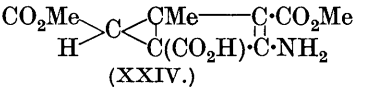
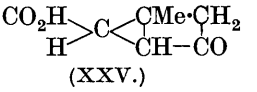


(XXIV.)

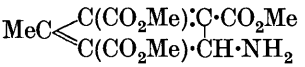


(XXV.)

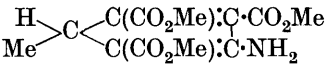
This acid is identical with that represented by formula (XVII). Intra-annular tautomerism is insufficient to account for this result, and it follows that in either or both the series examined nuclear prototropy must be present.

In following up the matter we were necessarily bound by practical considerations, but are able to include in this paper an account of a detailed study of the mild oxidation of the amino-ester (XXI, XXII). Of the six products isolated and recognised, the most significant from the structural point of view are β-methylglutaconic acid, β-acetylacrylic acid and α-methylglutaconic acid. The production of β-methylglutaconic acid may be regarded as normal, since it corresponds to the isolation of αα-dialkyl aconitic acid derivatives by oxidative degradation of 5 : 5-dialkyl*cyclo*pentadiene compounds. β-Acetylacrylic acid, however, is a substance which would have been expected to arise more readily from compounds of the series prepared from β-methylglutaric acid, and we suggest that the form (XXVI) is an intermediate in its production. The formation of α-methylglutaconic acid is difficult to explain in any complete way, but the most probable view seems to be that it is produced through form (XXVII), or a valency tautomeride. The formation of the tautomeric modifications (XXVI) and (XXVII) from (XXI) or (XXII) involves a mobile-hydrogen change of precisely the type required to effect the conversion of an acid of formula (XVII) into its isomeride (XXV), and *vice versa*. At this

stage in the research our stock of material, which had taken long to accumulate, became exhausted, but the work is being continued and it is hoped later to obtain further evidence regarding the structural and other conditions required to produce the nuclear transformations, the existence of which has been indicated.



(XXVI.)



(XXVII.)

EXPERIMENTAL.

(A) *Syntheses starting from β-Methylglutaric Acid.*

Methyl 5-*Methyl*dicyclo*penten*-3-*ol*-1 : 2 : 4-*tricarboxylate* (*Methyl* 5-*Methyl*cyclo*pentadien*-3-*ol*-1 : 2 : 4-*tricarboxylate*) (XIV).—Methyl malonate (16 g.) and methyl dibromo-β-methylglutarate (Ingold, J., 1922, **121**, 2685) (20 g.) were successively added to a solution of sodium methoxide prepared from sodium (5 g.) and methyl alcohol (60 g.). After being kept at the ordinary temperature for 15 hours, the mixture was heated just below the boiling point for 3 hours, cooled, poured on 50 g. of ice, and evaporated at room temperature until separation of the sodium compound was complete. The solid was collected (12 g.) and crystallised from methyl alcohol. *Methyl sodio-5-methyl*dicyclo*penten*-3-*ol*-1 : 2 : 4-*tricarboxylate* (XII, XIII) separated in bright yellow needles, m. p. 270° (decomp.), which gave a deep violet colour with ferric chloride (Found : Na, 8·0. $C_{12}H_{13}O_7Na$ requires Na, 7·9%). For the preparation of the free *hydroxy-ester*, the sodium compound was covered with ether and shaken with dilute hydrochloric acid until the yellow colour disappeared. The colourless oil obtained when the ethereal extract was dried and evaporated had b. p. 180°/1 mm. (Found : C, 53·6; H, 5·1. $C_{12}H_{14}O_7$ requires C, 53·3; H, 5·2%).

Ethyl 5-*Methyl*dicyclo*penten*-3-*ol*-1 : 2 : 4-*tricarboxylate* (*Ethyl* 5-*Methyl*cyclo*pentadien*-3-*ol*-1 : 2 : 4-*tricarboxylate*).—This was prepared in a similar manner from ethyl malonate, ethyl dibromo-β-methylglutarate (Ingold, *loc. cit.*), and ethyl-alcoholic sodium ethoxide, with the exception that, after being kept over-night in the cold, the mixture was heated just short of the b. p. for 24 hours. The mixture was poured into water and extracted twice with ether; the aqueous solution was then saturated with carbon dioxide and thoroughly extracted with much ether. The second extract on evaporation yielded a residue which, after drying in a desiccator, set to a yellow solid, m. p. about 70°; this contained sodium and gave a violet colour with ferric chloride. The free *hydroxy-ester*, which was obtained as in the preceding example, behaved similarly

towards ferric chloride (Found: C, 57·2; H, 6·1. $C_{15}H_{20}O_7$ requires C, 57·7; H, 6·5%).

Methyl Hydrogen 5-*Methyl*dicyclo*penten*-3-*ol*-1 : 2(or 1 : 4)-*dicarboxylate* (*Methyl*cyclo*pentadienoldicarboxylate*) (XV or XVI).—The sodio-methyl ester was digested at the ordinary temperature for 72 hours with 30% methyl-alcoholic potassium hydroxide. During this period the sodio-compound dissolved, and a yellow precipitate, consisting of *dimethyl potassium potassio*-5-*methyl*dicyclo*pentenol-tricarboxylate* (Found: K, 23·1. $C_{11}H_{10}O_7K_2$ requires K, 23·5%), appeared, which was collected and washed with methyl alcohol. On decomposing this with acid and extracting the solution with ether the *methyl hydrogen* ester was obtained as a viscous liquid which gave a deep violet colour with ferric chloride (Found: C, 54·1; H, 5·4. $C_9H_{10}O_5$ requires C, 54·5; H, 5·1%).

Ethylation of the Yellow Methyl Sodio-compound (XII, XIII).—The sodio-compound was boiled with an excess of ethyl iodide in ethyl-alcoholic solution for 24 hours. The excess of alcohol was removed by evaporation, and the residue poured into water and extracted with ether. The extract was washed with much water, dried, and distilled; *methyl* 5-*methyl*-2(or 4)-*ethyl*dicyclo*pentan* (or cyclo*penten*)-3-*one*-1 : 2 : 4-*tricarboxylate* was then obtained as a colourless neutral oil, b. p. 210°/6 mm. (Found: C, 56·2; H, 6·1. $C_{14}H_{18}O_7$ requires C, 56·3; H, 6·1%).

5-*Methyl*dicyclo*pentan*-3-*one*-1-*carboxylic Acid* (5-*Methyl*cyclo*penten*-3-*one*-1-*carboxylic Acid*) (XVII, XXV).—This acid was obtained when any of the above ring compounds (except the ethylation product) was boiled for 2 hours with hydrochloric acid. The cooled solution was extracted with much ether, and the residue obtained on evaporation of the extract crystallised from ligroin (b. p. 80—100°), needle clusters being obtained, m. p. 60° (Found: C, 59·9; H, 5·7. $C_7H_8O_3$ requires C, 60·0; H, 5·8%). The acid gives no colour with ferric chloride, and on oxidation with alkaline permanganate yields only oxalic acid. The *oxime*, which was prepared by using the theoretical quantity of hydroxylamine hydrochloride and one equivalent of sodium carbonate, crystallised when the solution was warmed for a few minutes, and separated from ethyl acetate in needles, m. p. 216° (decomp.) (Found: C, 53·8; H, 5·7. $C_7H_9O_3N$ requires C, 54·2; H, 5·9%).

(B) *Syntheses starting from* 3-*Methyl*-Δ^2-cyclo*propene*-1 : 2-*dicarboxylic Acid.*

Methyl 3-*Methyl*-1 : 2-*dicarbomethoxy*cyclo*propane*-3-*cyanoacetate* (XX).—Methyl 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylate (Goss, Ingold, and Thorpe, *loc. cit.*) was added to a methyl-alcoholic solu-

tion containing one equivalent of methyl sodiocyanoacetate. The mixture was kept for 2 hours at the ordinary temperature, then boiled for 2 hours, cooled, and poured into water. The oil was extracted with ether, and the extract was washed well with water, and once with dilute sodium hydrogen carbonate solution, dried, and evaporated. The residue on distillation yielded a series of volatile fractions consisting of the original *cyclo*propene ester and its methyl alcohol addition-product (*loc. cit.*), together with the *cyano-ester* (XX), b. p. 200°/20 mm. (Found : C, 54·1; H, 5·2. $C_{12}H_{15}O_6N$ requires C, 53·5; H, 5·6%). The yield (15%) could not be increased by prolonging the period of the reaction, and hence probably represents the equilibrium attained by the Michael addition-reaction in the presence of the side-reaction leading to the methoxy-compound.

Methyl 3-*Amino*-1-*methyl*dicyclo*pentene*-2 : 4 : 5-*tricarboxylate* (*Methyl* 3-*Amino*-1-*methyl*cyclo*pentadiene*-2 : 4 : 5-*tricarboxylate*), *Forms A and B* (XXI, XXII).—A solution of the above cyano-ester in an excess of methyl-alcoholic sodium methoxide was kept over-night at the ordinary temperature, then heated just below the b. p. for 4 hours, cooled, and poured into water. The ethereal extract of the solution yielded on evaporation a small residue from which the *amino-ester B*, m. p. 186° (decomp.), was obtained by crystallisation from benzene or ether (Found : C, 53·5; H, 5·5. $C_{12}H_{15}O_6N$ requires C, 53·5; H, 5·6%). This compound is somewhat soluble in cold alkali and readily soluble in hydrochloric acid; on keeping, it becomes converted into the more stable isomeride-A mentioned below, which is present along with B in the residue from the ethereal extract. The aqueous solution remaining from the ether extraction was saturated with carbon dioxide and again extracted with ether. This extract yielded the *amino-ester A*, m. p. 130° (decomp.), which was finally purified by crystallisation from ligroin (Found : C, 53·9; H, 5·8; N, 5·7. $C_{12}H_{15}O_6N$ requires C, 53·6; H, 5·6; N, 5·2%). This isomeride is fairly readily soluble in caustic alkali, and also in mineral acid; it gives a red precipitate with diazotised aniline. Neither isomeride gives any noticeable colour with ferric chloride. Accompanying the A-compound in the residue from the second extract is a small quantity of a by-product, which has m. p. 186° and is not identical with B. We have not yet obtained sufficient for a detailed investigation, but the product appears to be resistant to hydrolysis by hot hydrochloric acid, and we originally isolated it by destroying the A-compound by this means.

The same compounds, together with others mentioned below, were obtained by the following method. Methyl 3-methyl-Δ^2-

*cyclo*propene-1 : 2-dicarboxylate (10 g.) was added to a solution of methyl cyanoacetate (6 g.) in methyl-alcoholic sodium methoxide prepared from 3 g. of sodium and 35 g. of methyl alcohol. After being kept over-night at the ordinary temperature the mixture was heated to just below the b. p. for 8 hours, and when cool poured into water. A yellow precipitate appeared and almost immediately redissolved, and the solution was then extracted with ether, saturated with carbon dioxide, and again extracted, by which means the two isomeric amino-esters were isolated as described above. The aqueous solution remaining was acidified with hydrochloric acid and again extracted with ether. The solid residue obtained on evaporation of this extract, on crystallisation from ether, yielded three compounds which were isolated in the order named: (1) 3-methoxy-3-methyl*cyclo*propane-1 : 2-dicarboxylic acid (Goss, Ingold, and Thorpe, *loc. cit.*), (2) the monomethyl acid-ester of this acid (*loc. cit.*), and (3) dimethyl hydrogen 3-amino-1-methyl*dicyclo*pentene-2 : 4 : 5-tricarboxylate (see below), the last two substances being obtained in small amount only. The yield of the main product, namely, amino-ester-A, was usually about 12%, and the substitution of potassium methoxide for sodium methoxide effected no substantial improvement.

Dimethyl Hydrogen 3-*Amino*-1-*methyl*dicyclo*pentene*-2 : 4 : 5-*tricarboxylate* (3-*Amino*-1-*methyl*cyclo*pentadiene*-2 : 4 : 5-*tricarboxylate*) (XXIII or XXIV).—The amino-ester-A was left at the ordinary temperature in contact with 3*N*-methyl-alcoholic potassium hydroxide for 24 hours, during which it dissolved and a yellow precipitate consisting of the *potassium potassio*-salt of the dimethyl hydrogen ester appeared. When the yellow, aqueous solution of this compound was acidified with hydrochloric acid, the free *acid-ester* was precipitated; this after crystallisation from ether had m. p. 226° (decomp.) (Found: C, 51·7; H, 4·7; *M*, 255. $C_{11}H_{13}O_6N$ requires C, 51·7; H, 5·1%; *M*, 255). On working up the alcoholic mother-liquors, a further quantity of the same substance was obtained, together with an unidentified product, m. p. 97°, and some unchanged amino-ester-A. The dimethyl hydrogen ester gives an intense purple colour with ferric chloride, as also does its yellow potassium salt.

1-*Methyl*dicyclo*pentan*-3-*one*-5-*carboxylic Acid* (1-*Methyl*cyclo*penten*-3-*one*-5-*carboxylic Acid*) (XVII, XXV).—The amino-ester-A was boiled for 1 hour with hydrochloric acid, and the cooled and filtered solution extracted 20 times with ether. The solid residue, after crystallisation from ligroin, had m. p. 60° and was identical with the acid described on p. 1273.

Oxidation of the Amino-ester-A.—The use of alkaline permanganate and chromium trioxide in acetic acid, and sodium chlorate

and osmium tetroxide yielded oxalic acid as the only recognisable product, and potassium ferricyanide in the presence of potassium carbonate gave an intractable gum.

The amino-ester (2 g.) was digested with a solution of potassium persulphate (30 g.) and silver oxide (0·25 g.) in 25 c.c. of 2*N*-sulphuric acid, and the mixture was kept with frequent shaking at a temperature varying from 20° to 40° for some weeks. Several experiments were commenced simultaneously, and the products were worked up at intervals by extracting the solution with ether, washing the extract with sodium carbonate, acidifying the alkaline solution, and re-extracting the acid products. These were then boiled with 20% hydrochloric acid to complete the hydrolysis, and the solution was either evaporated to dryness or extracted with ether. Oxalic acid was removed as the calcium salt from the acids thus obtained and the remainder of the acid product was drained from gum and crystallised from dilute alcohol. Oxalic acid was obtained in all cases, and the chief by-product was fumaric acid, which was identified by direct comparison and by conversion into methyl fumarate. In one experiment a small amount of a very soluble acid, which appeared to be maleic acid but could not be wholly purified, was also obtained.

The oxidation of the amino-ester (2 g.) with hydrogen peroxide (50 c.c. of 6%) and ferrous sulphate (0·25 g.) was carried out in a similar way, excepting that the mixtures were shaken continuously at the ordinary temperature for periods of from 20 to 120 hours. Oxalic acid was formed in all cases, but in much smaller amount than in the previous series of experiments. The remaining acids were drained on porous porcelain, triturated with ether–ligroin, and crystallised from concentrated hydrochloric acid, an acid, m. p. 141—143°, identified by direct comparison as α-methylglutaconic acid (Found : C, 49·9; H, 5·5. Calc. : C, 50·0; H, 5·6%), being obtained. The hydrochloric acid mother-liquors on evaporation gave a stiff gum; this partly solidified and on draining yielded a product which, after crystallisation from ethyl acetate–ligroin, had m. p. 113—115° and was identified as the more fusible form of β-methylglutaconic acid (Found : C, 49·9; H, 5·5%). Extraction of the porcelain on which the original mixed acids had been drained, and combination of the product with the residues from the ether–ligroin solution, gave a dark brown gum in which, after some days, long needles appeared. After some crystals for inoculation had been collected, the whole product was repeatedly digested with charcoal in aqueous alcohol, and the acids were isolated again and seeded. Crystallisation occurred rapidly, and the drained product was crystallised twice from ether–ligroin, from which almost colourless needles, m. p. 125—126°, were obtained. The m. p. and analysis

(Found: C, 52·3; H, 5·7%) indicating β-acetylacrylic acid, a specimen of this substance was prepared by the recorded method and the identity confirmed.

Ethyl 3-*Amino*-1-*methyl*dicyclo*pentane*-2 : 4 : 5-*tricarboxylate* (-cyclo*pentadienetricarboxylate*).—A solution of ethyl methylcyclopropenedicarboxylate (10 g.) and ethyl cyanoacetate (6·5 g.) in sodium ethoxide prepared from sodium (3 g.) and ethyl alcohol (36 g.) was kept over-night at the ordinary temperature, heated short of the b. p. for 6 hours, boiled for 2 hours, cooled, and poured into water. The *sodio*-derivative of the amino-ester, which was precipitated as a yellow solid contaminated with oil, was collected and washed well with ether (Found: Na, 7·1. $C_{15}H_{20}O_6NNa$ requires Na, 6·9%). The derivative is slightly soluble in water, but its yellow solution does not give a coloration with ferric chloride. Treatment with carbon dioxide decolorises the solution and produces an immediate precipitation of the *amino-ester*, which separates from ligroin in needles, m. p. 107° (Found: C, 57·5; H, 7·0. $C_{15}H_{21}O_6N$ requires C, 57·8; H, 6·8%). The compound is a weak base, for it may be precipitated from its solution in acids by large dilution; it is also a weak acid, because the addition of aqueous sodium hydroxide to its solution in alcohol precipitates the yellow sodium derivative which, as indicated above, is decomposed completely by carbonic acid. Only about half the total quantity of amino-ester formed (about 14%) is isolated by the method described above, and the remainder may be obtained as follows. The filtrate from the sodium compound was extracted with ether and saturated with carbon dioxide. The ethereal extract yielded the amino-ester, and a precipitate in the aqueous suspension consisted of the same substance. The filtrate from this yielded no further product when again extracted with ether, and was therefore acidified with hydrochloric acid. The ethereal extract from this solution yielded a gum which on keeping partly crystallised. The drained crystals, on crystallisation from xylene, yielded the *diethyl hydrogen amino-ester*, m. p. 199° (decomp.) (Found: C, 54·6; H, 5·9. $C_{13}H_{17}O_6N$ requires C, 55·1; H, 6·1%). Yield, about 1%.

Methylation of the Amino-ester.—The yellow sodium compound (0·5 g.) was boiled for 24 hours with a solution of methyl iodide (0·5 g.) in ethyl alcohol (6 c.c.). The *product*, isolated by extraction with ether after the mixture had been poured into water, readily solidified, and separated from ligroin in needles, m. p. 113° (Found: C, 58·8; H, 6·5. $C_{16}H_{23}O_6N$ requires C, 59·1; H, 7·1%).

Ethylation of the Amino-ester.—Ethylation was effected by the same method, and also by using the amino-ester, sodium ethoxide, and ethyl iodide. The *product* crystallised from ligroin in needles,

m. p. 118° (Found : C, 60·4; H, 7·7. $C_{17}H_{25}O_6N$ requires C, 60·6; H, 7·4%). These alkylation products were prepared in the hope that their oxidation would yield useful information, but experiments in this direction have so far not met with success.

Hydrolysis of the Amino-ester.—This experiment was carried out like that described on p. 1275, and with identical results.

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