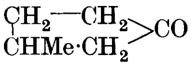
CLXII.—*The Chemistry of Alkyl*cyclo*pentanones. Part I. Derivatives of 3-Methyl*cyclo*pentanone.*

By Ranchhodji Dajibhai Desai.

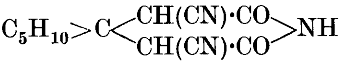
The work of Ingold, Thorpe, and their collaborators on the influence of rings and groups on the carbon tetrahedral angle has shown that the *cyclo*hexane ring is strained, and the *cyclo*pentane ring strainless (Beesley, Ingold, and Thorpe, J., 1915, **107**, 1081; Becker and Thorpe, J., 1920, **117**, 1580; Lanfear and Thorpe, J., 1923, **123**, 1683, etc.). The methyl*cyclo*pentane ring has now been examined in this respect in order to find how far it resembles the *cyclo*pentane ring.

This communication deals with the preparation of some of the derivatives of 3-methyl*cyclo*pentanone: the formation and stability of its *spiro*-compounds will be discussed in a later paper.

The ketone (I) condenses very readily with ethyl cyanoacetate, and ammonia in ethyl-alcoholic solution (compare Kon and Thorpe, J., 1919, **115**, 686), giving a 45% yield of the *dicyano-imide* (II). If the mixture is resaturated with ammonia after removal of the ammonium salt of the imide and kept for 2 weeks, a considerable quantity of the *di-iminodi-imide* of 3-methyl*cyclo*pentane-1 : 1-dimalonic acid (III) is precipitated on dilution with water, together with a small amount of *3-methyl*cyclo*pentylidenecyanoacetamide* (IV). Acidification of the mother-liquor produces some dicyano-imide (II), and the *di-imide* of 3-methyl*cyclo*pentane-1 : 1-dimalonic acid (V) after some time.

(I.)


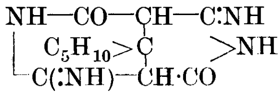
$$\begin{array}{l}\mathrm{CH_2{-}CH_2}\\ \mathrm{CHMe{\cdot}CH_2}\end{array}\!\!>\mathrm{CO}$$



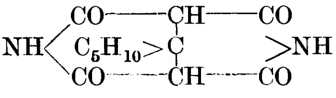
$$\mathrm{C_5H_{10}}>\mathrm{C}<\begin{array}{l}\mathrm{CH(CN){\cdot}CO}\\ \mathrm{CH(CN){\cdot}CO}\end{array}\!\!>\mathrm{NH}$$

(II.)

(IV.) $C_5H_{10}>C{:}C(CN){\cdot}CO{\cdot}NH_2$

(III.)


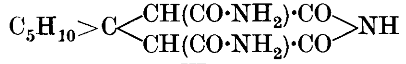
$$\begin{array}{l}\mathrm{NH{-}CO{-}CH{-}C{:}NH}\\ \quad\mathrm{C_5H_{10}>C}\qquad\quad >\mathrm{NH}\\ \mathrm{C({:}NH){-}CH{\cdot}CO}\end{array}$$



$$\mathrm{NH}<\begin{array}{l}\mathrm{CO{-}{-}CH{-}{-}CO}\\ \mathrm{C_5H_{10}>C}\qquad\quad >\mathrm{NH}\\ \mathrm{CO{-}{-}CH{-}{-}CO}\end{array}$$

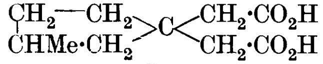
(V.)

The second stage of the Guareschi condensation resembles the action of the ketone on cyanoacetamide (Thole and Thorpe, J., 1912, **99**, 422; Kon and Thorpe, *loc. cit.*), as compounds (III), (IV), and (V) are also produced if cyanoacetamide and the ketone are condensed in presence of piperidine in aqueous-alcoholic solution. The formation of (IV) precedes that of (III), as the latter is formed if the unsaturated amide (IV) is condensed with one molecule of cyanoacetamide in presence of piperidine in alcoholic solution at 40°; the formation of (V) is due to the hydrolysis of the imino-groups. The dicyano-imide (II) gives the *dicarbamyl* derivative (VI) on treatment with cold concentrated sulphuric acid, and complete hydrolysis with 60% sulphuric acid converts it into 3-*methyl*cyclo*pentane*-1 : 1-*diacetic acid* (VII). As the same acid is also formed by the hydrolysis of (III) and (V) with 60% sulphuric acid, the yield of the diacetic acid from the ketone is fairly good (65—70%). In the solubility of its salts, the diacetic acid resembles its analogue from 4-methyl*cyclo*hexanone rather than those from *cyclo*pentanone and *cyclo*hexanone (Thorpe and Wood, J., 1913, **103**, 1598). The bromination and dibromination of the diacetic acid and the hydrolysis of the products are under investigation.



$$C_5H_{10}{>}C{<}\begin{matrix}CH(CO{\cdot}NH_2){\cdot}CO\\CH(CO{\cdot}NH_2){\cdot}CO\end{matrix}{>}NH$$

(VI.)

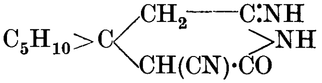


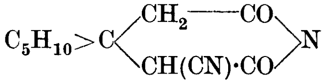
$$\begin{matrix}CH_2—CH_2\\CHMe{\cdot}CH_2\end{matrix}{>}C{<}\begin{matrix}CH_2{\cdot}CO_2H\\CH_2{\cdot}CO_2H\end{matrix}$$

(VII.)

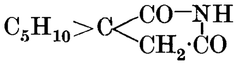
Ethyl 3-*methyl*cyclo*pentylidenecyanoacetate*, required for the synthesis of 1-carboxy-3-methyl*cyclo*pentane-1-acetic acid to be used in further synthetical work, was readily obtained by condensing ethyl cyanoacetate with 3-methyl*cyclo*pentanone in presence of piperidine. It resembles other αβ-unsaturated esters in condensing readily with potassium cyanide and with ethyl cyanoacetate and is identical with the ester prepared by Harding, Haworth, and Perkin's method (compare J., 1908, **93**, 1947; Kandiah and Linstead, J., 1929, 2142). It is smoothly reduced by aluminium amalgam to *ethyl* 3-*methyl*cyclo*pentylcyanoacetate* and a bimolecular compound, which was not further investigated: the yield of the bimolecular compound (12%) is the same as in the case of the *cyclo*pentane compound (Vogel, J., 1928, 2010). However, the ester contains the βγ-form also, as it is readily methylated, and the methylated *ester* (VIII) gives the usual reactions of βγ-unsaturated esters. The pyrogenic decomposition of 3-*methyl*cyclo*pentylidenecyanoacetic acid* gave 3-*methyl*cyclo*pentenylacetonitrile*. This reacted in the βγ-form in giving the *piperonylidene* derivative (IX) (Kandiah and Linstead, *loc. cit.*), and in the αβ-form when it was condensed with sodiocyanoacetamide, giving the imino-derivative (X), which was hydrolysed to the *imide* (XI) with hydrochloric acid and to 3-methyl*cyclo*pentane-1 : 1-diacetic acid (VII) with 60% sulphuric acid. By removal of a carbethoxy-group from (VIII), the methylated *nitrile* was obtained. This is probably the αβ-form, as it shows exaltation in molecular refraction (Birch and Kon, *loc. cit.*); attempts to condense it with sodiocyanoacetamide, however, resulted in a very poor yield of the product. No attempt was made to prove whether the double bond in the methylated ester and the acetonitrile is in position 1 : 2 or 1 : 5. The condensation of ethyl 3-methyl*cyclo*pentylidenecyanoacetate with potassium cyanide proceeds smoothly in alcoholic solution, and a good yield of the *dicyano*-ester (XII) is formed, but in the process of removing the excess of alcohol on the water-bath a considerable quantity is decomposed into the *dinitrile* (XIII). The constitution of the dinitrile is proved by the fact that it gives the *imide* (XIV) on treatment with cold concentrated sulphuric acid, and 1-*carboxy*-3-*methyl*cyclo*pentane*-1-*acetic acid* on hydrolysis with 50% hydrochloric acid. The dicyanoester yields the same acid on acid hydrolysis. The acid thus obtained is a mixture, the constituents of which are tedious to separate by fractional crystallisation. The main constituent, m. p. 125°, gives its own *anhydride*, *anilic acid*, and anil. Another acid, m. p. 105—110°, was obtained, but in amount too small for purification.

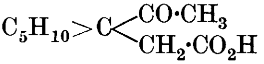
(VIII.) $C_5H_9{\gg}C{\cdot}CMe(CN){\cdot}CO_2Et$ $C_5H_9{\gg}C{\cdot}C(CN){:}CH{\cdot}C_7H_5O_2$ (IX.)

(X.)

$C_5H_{10}{>}C{<}\begin{matrix}CH_2\text{——}C{:}NH\\ CH(CN){\cdot}CO\end{matrix}{>}NH$


$C_5H_{10}{>}C{<}\begin{matrix}CH_2\text{——}CO\\ CH(CN){\cdot}CO\end{matrix}{>}NH$
(XI.)

(XII.) $C_5H_{10}{>}C(CN){\cdot}CH(CN){\cdot}CO_2Et$ $C_5H_{10}{>}C(CN){\cdot}CH_2{\cdot}CN$ (XIII.)

(XIV.)

$C_5H_{10}{>}C{<}\begin{matrix}CO-NH\\ CH_2{\cdot}CO\end{matrix}$


$C_5H_{10}{>}C{<}\begin{matrix}CO{\cdot}CH_3\\ CH_2{\cdot}CO_2H\end{matrix}$
(XV.)

The formation of two lævulic acids (XV) from 1-carboxy-3-methyl*cyclo*pentane-1-acetic acid by the Blaise–Maire method shows that at least two acids are present. This portion of the work, however, and the synthesis of the carboxy-acetic acid by Higson and Thorpe's method (J., 1906, **89**, 1455) are reserved for the later paper.

EXPERIMENTAL.

β-*Methyladipic Acid.*—4-Methyl*cyclo*hexanone (500 g.) was slowly added to boiling concentrated nitric acid (1·5 litres) (compare D.R.-P. 221,849). A vigorous reaction ensued, and the external heating was stopped when the mixture remained in a boiling condition. The solid obtained after complete removal of the nitric acid on the water-bath was triturated with concentrated hydrochloric acid and collected (400 g.). After one crystallisation from benzene, the acid melted at 90—91° (Found for the silver salt: Ag, 57·4. Calc. for $C_7H_{10}O_4Ag_2$: Ag, 57·7%).

3-*Methyl*cyclo*pentanone* (I).—A mixture of the above acid (400 g.) and powdered baryta (40 g.) was heated to 270—275°, the distillate of water and the ketone extracted with ether, and the extract washed with a dilute solution of sodium carbonate, dried, and distilled. The ketone (175 g.) boiled at 142°/758 mm. and had $d_{4°}^{19°}$ 0·9146, $n_{D}^{19°}$ 1·43507; the semicarbazone melted at 183—184° (Zelinsky, *Ber.*, 1902, **35**, 2489, gives b. p. 141—143°/760 mm., $d_{4°}^{19°}$ 0·9140, $n_{D}^{19°}$ 1·4340, m. p. of semicarbazone 184°).

Condensation of 3-*Methyl*cyclo*pentanone with Ethyl Cyanoacetate. ω-Imide of* 3-*Methyl*cyclo*pentane*-1 : 1-*dicyanoacetic Acid* (II).—An ice-cold mixture of 3-methyl*cyclo*pentanone (147 g.) and ethyl cyanoacetate (339 g.) was added to absolute ethyl alcohol (500 c.c.) which was cooled in a freezing mixture and saturated with ammonia. After the mixture had been kept in a stoppered bottle for 2 weeks, the ammonium salt which had been precipitated was collected and decomposed with hot dilute hydrochloric acid. The *imide* obtained was washed with hot water, dried (yield, 180 g.), and crystallised from dilute alcohol, forming silvery scales, m. p. 194° (Found : C, 62·0; H, 5·9. $C_{12}H_{13}O_2N_3$ requires C, 62·3; H, 5·6%).

*ω-Imide of αα'-Dicarbamyl-*3-*methyl*cyclo*pentane*-1 : 1-*diacetic Acid* (VI).—A solution of the dicyano-imide in concentrated sulphuric acid (10 parts) was kept for 24 hours and poured into water. The solid obtained crystallised from absolute alcohol in small prisms, m. p. 235—236° (decomp.) (Found : C, 53·8; H, 6·7. $C_{12}H_{17}O_4N_3$ requires C, 53·9; H, 6·4%).

ω-Di-iminodi-imide of 3-*Methyl*cyclo*pentane*-1 : 1-*dimalonic Acid* (III).—(a) The alcoholic mother-liquor from which the ammonium salt of the dicyano-imide had been removed was resaturated with ammonia and kept for 2 weeks. The ammonia was then removed, water added, and the precipitated solid collected and digested with alcohol. The microcrystalline residue was dissolved in dilute hydrochloric acid, reprecipitated by aqueous sodium acetate, and dried; recrystallisation was not possible owing to partial hydrolysis of the imino-groups; m. p. 285° (decomp.) (Found : C, 57·9; H, 6·6. $C_{12}H_{16}O_2N_4$ requires C, 58·1; H, 6·4%). (b) The *di-iminodi-imide* was also formed when 3-methyl*cyclo*pentanone (1 mol.) and cyanoacetamide (2 mols.) were condensed in dilute alcoholic solution in presence of a few drops of piperidine at 40°; it separated as a microcrystalline powder in poor yield.

ω-Di-imide of 3-*Methyl*cyclo*pentane*-1 : 1-*dimalonic Acid* (V).—This *compound* was isolated from the mother-liquor in (a) above as stated in the introduction, and freed from the dicyano-imide (II), which was readily soluble in dilute alcohol. It was also obtained by acidifying the mother-liquor in (b), and by boiling the di-iminodi-imide with dilute hydrochloric acid for 10 minutes. It crystallised from alcohol in small plates, unmelted below 300°, and dissolved in hot sodium carbonate solution (Found : C, 57·9; H, 5·5. $C_{12}H_{14}O_4N_2$ requires C, 57·6; H, 5·6%). The combined yield of di-iminodi-imide and di-imide was 25%.

3-*Methyl*cyclo*pentylidenecyanoacetamide* (IV).—The alcoholic solution obtained in the purification of the di-iminodi-imide was concentrated, the solid removed, and the filtrate kept; it deposited the *amide* (IV), which, after several crystallisations from dilute alcohol, was obtained in silvery scales, m. p. 151—152°. The amide was also formed by condensing the ketone (1 mol.) and cyanoacetamide (1 mol.) in dilute alcoholic solution in presence of piperidine at 20° (Found : C, 65·9; H, 7·1. $C_9H_{12}ON_2$ requires C, 65·8; H, 7·3%). It was very soluble in almost all solvents. When treated in ice-cold concentrated sulphuric acid with 20% sodium nitrite solution, it gave 3-methyl*cyclo*pentylidenecyanoacetic acid, which is described later.

3-*Methyl*cyclo*pentane*-1 : 1-*diacetic Acid* (VII).—The dicyanoimide (100 g.) was dissolved in concentrated sulphuric acid (300 c.c.), after 24 hours water (400 c.c.) was added, and the mixture was heated for 24 hours and then diluted with water. The *diacetic acid*, which crystallised on cooling, was dissolved in dilute sodium carbonate solution, reprecipitated with concentrated hydrochloric acid (yield, 75 g.), and crystallised from water, forming prismatic needles, m. p. 135°, easily soluble in the usual solvents, but insoluble in light petroleum (b. p. 40—60°) (Found: C, 59·7; H, 7·9. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%).

Its normal ammonium salt gave white precipitates with solutions of calcium chloride, lead acetate, and silver nitrate, and a bluish-green precipitate with copper sulphate solution either in the cold or on heating. The barium salt was soluble in cold water, but a slight turbidity was produced on warming and this did not disappear on cooling (Found for the *silver* salt : Ag, 51·8. $C_{10}H_{14}O_4Ag_2$ requires Ag, 52·1%).

The *imide* crystallised from water in lustrous scales, m. p. 133—134° (Found : C, 66·1; H, 8·5. $C_{10}H_{15}O_2N$ requires C, 66·2; H, 8·3%). The *ethyl* ester boiled at 156°/15 mm. and had $d_{4^\circ}^{20^\circ}$ 1·009, $n_D^{20^\circ}$ 1·44933, whence $[R_L]_D$ 68·04 (calc., 67·96) (Found : C, 65·3; H, 9·3. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%). The *dianilide*, prepared by heating the acid with excess of aniline for 2 hours at 180°, crystallised from alcohol in prismatic needles, m. p. 174° (Found : C, 75·0; H, 7·7. $C_{22}H_{26}O_2N_2$ requires C, 75·4; H, 7·4%). The *di*-p-*toluidide* crystallised from dilute alcohol in plates, m. p. 192° (Found : C, 75·8; H, 8·1. $C_{24}H_{30}O_2N_2$ requires C, 76·3;

H, 7·9%). The *anhydride*, prepared by heating the acid with excess of acetic anhydride, was a clear liquid, b. p. 177°/10 mm. (Found: C, 65·6; H, 8·1. $C_{10}H_{14}O_3$ requires C, 65·9; H, 7·7%). It was fairly stable to boiling water, but was converted into the acid by hot dilute alkali solutions. The *anilic acid*, obtained from the anhydride and aniline (1 mol. each) in benzene solution, crystallised from dilute alcohol in tiny needles, m. p. 115—116° (Found: C, 69·6; H, 7·8. $C_{16}H_{21}O_3N$ requires C, 69·8; H, 7·6%). The *anil*, prepared by heating the anilic acid at 140° for 2 hours, crystallised in lustrous scales, m. p. 125° (sintering at 112°) (Found: C, 74·9; H, 7·0. $C_{16}H_{19}O_2N$ requires C, 74·7; H, 7·4%).

*Condensation of 3-Methyl*cyclo*pentanone with Ethyl Cyanoacetate. Ethyl 3-Methyl*cyclo*pentylidenecyanoacetate.*—A mixture of methyl*cyclo*pentanone (98 g.), ethyl cyanoacetate (113 g.), and piperidine (2 c.c.) was kept at room temperature for 3 days and then heated on the water-bath for 10 hours. The product, extracted in ethereal solution, washed with dilute hydrochloric acid, dried, and recovered, distilled at 150—165°/20 mm. On redistillation (b. p. 160—161°/20 mm.) it solidified (yield, 135 g.). The *ester* was soluble in almost all solvents, and crystallised from light petroleum (b. p. 40—60°) in thick plates or cubes, m. p. 66° (Found: C, 68·0; H, 8·1. $C_{11}H_{15}O_2N$ requires C, 68·4; H, 7·8%). It absorbed bromine very slowly and gave 3-methyl*cyclo*pentanone on oxidation with dilute potassium permanganate solution.

*3-Methyl*cyclo*pentylidenecyanoacetic acid*, which could not be prepared by hydrolysing the above ester with alcoholic sodium ethoxide, was obtained by Harding, Haworth, and Perkin's method (*loc. cit.*). 3-Methyl*cyclo*pentanone (25 g.) was added to a suspension of ethyl sodiocyanoacetate (ethyl cyanoacetate 28 g., sodium 5·5 g., alcohol 75 c.c.), the mixture heated for 3 hours, the excess of alcohol distilled off, water added, the precipitated oil removed in ether, and the aqueous solution acidified. The oil thus produced was extracted and dried in ether and recovered; it partly solidified in a vacuum. The solid was crystallised several times from benzene, and the required acid obtained in flattened needles, m. p. 145—146° (Found: C, 65·2; H, 6·9. $C_9H_{11}O_2N$ requires C, 65·5; H, 6·7%); the mother-liquor contained an acid, m. p. 90—100°, in amount insufficient for further investigation. The acid did not combine with bromine readily, and was oxidised to 3-methyl*cyclo*pentanone by a dilute solution of potassium permanganate.

*Reduction of Ethyl 3-Methyl*cyclo*pentylidenecyanoacetate with Aluminium Amalgam. Ethyl 3-Methyl*cyclo*pentylcyanoacetate.*—The unsaturated ester (25 g.) was kept in contact with aluminium amalgam (25 g.) covered with moist ether (500 c.c.) for 24 hours, the filtered solution was then dried, and the ether removed. The product distilled at 146—150°/20 mm., leaving a resinous residue (12%), m. p. 75—80°, which was probably the bimolecular compound. After redistillation *ethyl* 3-*methyl*cyclo*pentylcyanoacetate* had b. p. 148°/20 mm., and $d_{4°}^{20°}$ 1·002, $n_{D}^{20°}$ 1·45033, whence $[R_L]_D$ 52·4 (calc., 52·3) (Found : C, 67·5; H, 8·9. $C_{11}H_{17}O_2N$ requires C, 67·7 ; H, 8·7%).

3-*Methyl*cyclo*pentylmalonic Acid.*—The reduced ester (15 g.) was heated with caustic potash (20 g.) in water (40 c.c.) and rectified spirit (30 c.c.) until the evolution of ammonia ceased. After removal of alcohol, the aqueous solution was extracted with ether to remove the unchanged ester and acidified ; the precipitated *acid* crystallised from chloroform–light petroleum (b. p. 40—60°) in soft white needles, m. p. 155° (decomp.) (Found : C, 57·8 ; H, 7·7 ; equiv., by titration with baryta, 92. $C_9H_{14}O_4$ requires C, 58·1 ; H, 7·5% ; equiv., 93).

The *ethyl* ester boiled at 146°/20 mm. and had $d_{4°}^{19°}$ 1·016, $n_{D}^{19°}$ 1·44622, whence $[R_L]_D$ 63·6 (calc., 63·3) (Found : C, 64·2; H, 9·3. $C_{13}H_{22}O_4$ requires C, 64·5 ; H, 9·1%). The *dianilide*, prepared by heating the ester with excess of aniline at 180° for 6 hours, crystallised from alcohol in needles, m. p. 238° (Found : C, 74·9 ; H, 6·8. $C_{21}H_{24}O_2N_2$ requires C, 75·0 ; H, 7·1%).

3-*Methyl*cyclo*pentylacetic acid*, prepared by heating the malonic acid at 160° for 4 hours, was a liquid, b. p. 141°/25 mm., $d_{4°}^{21°}$ 0·9811, $n_{D}^{20°}$ 1·44633, whence $[R_L]_D$ 38·6 (calc., 38·5) (Found : C, 67·3 ; H, 10·2. $C_8H_{14}O_2$ requires C, 67·6 ; H, 9·9%). The *ethyl* ester boiled at 94°/15 mm. and had $d_{4°}^{20}$ 0·9258, $n_{D}^{20°}$ 1·43487, whence $[R_L]_D$ 47·90 (calc., 47·83) (Found : C, 70·2 ; H, 10·8. $C_{10}H_{18}O_2$ requires C, 70·6 ; H, 10·6%).

3 - *Methyl* - $\Delta^{1:2\ (\mathrm{or}\ 1:5)}$ - cyclo*pentenylacetonitrile.*—3 - Methyl - *cyclo*pentylidenecyanoacetic acid decomposed when heated slowly under reduced pressure, and the *nitrile* passed over at 105—115°/29 mm. After redistillation, it had b. p. 82°/10 mm., and $d_{4°}^{19°}$ 0·9145, $n_{D}^{19°}$ 1·45972, whence $[R_L]_D$ 36·2 (calc., 36·3) (Found : C, 78·9 ; H, 8·9. $C_8H_{11}N$ requires C, 79·4 ; H, 9·1%).

The nitrile added on bromine readily and condensed with piperonal and with cyanoacetamide in presence of sodium ethoxide. The *piperonylidene* derivative (IX) crystallised from alcohol in pale yellow needles, m. p. 95°. Its solution in concentrated sulphuric acid had a deep red colour (Found : C, 75·6 ; H, 6·2. $C_{16}H_{15}O_2N$ requires C, 75·9 ; H, 5·9%).

ω-*Imide of* α-*Cyano*-3-*methyl*cyclo*pentane*-1 : 1-*diacetic Acid* (XI).—The imino-derivative (X) resulting from the condensation of equimolecular quantities of the nitrile and sodiocyanoacetamide was boiled with dilute hydrochloric acid. The *imide* (XI), which separated on cooling, crystallised from alcohol in white needles, m. p. 167—168° (Found : C, 64·3; H, 6·7. $C_{11}H_{14}O_2N_2$ requires C, 64·1; H, 6·8%). When hydrolysed with 60% sulphuric acid, it gave 3-methyl*cyclo*pentane-1 : 1-diacetic acid, m. p. 135°.

Ethyl α-*Cyano*-α-3-*methyl*-$\Delta^{1:2\ (\text{or}\ 1:5)}$-cyclo*pentenylpropionate* (VIII).—Ethyl 3-methyl*cyclo*pentylidenecyanoacetate (16 g.) was added to a solution of sodium (2 g.) in alcohol (40 c.c.), a deep red colour being produced, and, after cooling, methyl iodide (20 g.) was slowly added. The mixture was kept at room temperature for 1 hour, heated on the water-bath for 1 hour, and diluted with water. The oil precipitated was extracted with ether, dried, and distilled. On redistillation the pure *ester* boiled at 140°/30 mm.; it had $d_{4^\circ}^{27^\circ}$ 0·9614, $n_D^{27^\circ}$ 1·43801, whence $[R_L]_D$ 56·50 (calc., 56·42) (Found : C, 69·2; H, 8·5. $C_{12}H_{17}O_2N$ requires C, 69·6; H, 8·2%) In chloroform solution it combined rapidly with bromine.

α-3-*Methyl*cyclo*pentylidene*-1-*propionitrile*.—The above ester (8 g.) was added to a solution of sodium (1·5 g.) in methyl alcohol (30 c.c.), the mixture kept at 35° for 5 hours, and water added. The precipitated oil, extracted and dried in ether, distilled at 130—135°/50 mm. After redistillation, the pure *nitrile* had b. p. 132°/50 mm. and $d_{4^\circ}^{25^\circ}$ 0·8950, $n_D^{25^\circ}$ 1·47429, whence $[R_L]_D$ 42·4 (calc., 40·9) (Found : C, 79·5; H, 9·4. $C_9H_{13}N$ requires C, 80·0; H, 9·6%). It did not add on bromine readily and was oxidised by potassium permanganate solution to 3-methyl*cyclo*pentanone.

Condensation of Ethyl 3-*Methyl*cyclo*pentylidenecyanoacetate with Potassium Cyanide. Ethyl* 1-*Cyano*-3-*methyl*cyclo*pentylcyanoacetate* (XII) *and* 1-*Cyano*-3-*methyl*cyclo*pentylacetonitrile* (XIII).—When a solution of potassium cyanide (20 g.) in water (45 c.c.) was added to ethyl 3-methyl*cyclo*pentylidenecyanoacetate (30 g.) dissolved in rectified spirit (150 c.c.) there was an evolution of heat, and a little solid separated. After 3 days, the alcohol was removed on the water-bath; on dilution of the residue with water, a considerable quantity of an oil separated. This was extracted with ether, dried, and distilled. On redistillation, 1-*cyano*-3-*methyl*cyclo*pentylacetonitrile* was obtained as a clear mobile liquid, b. p. 146°/10 mm.; $d_{4^\circ}^{19^\circ}$ 0·9877, $n_D^{19^\circ}$ 1·4622, whence $[R_L]_D$ 41·2 (calc., 41·2) (Found : C, 72·7; H, 8·2. $C_9H_{12}N_2$ requires C, 73·0; H, 8·1%). Yield, 40%.

Ethyl 1-*cyano*-3-*methyl*cyclo*pentylcyanoacetate* (XII). The aqueous solution from which the dinitrile was extracted with ether was acidified with dilute sulphuric acid, and the precipitated oil was extracted with ether, dried, and distilled. The *dicyano*-ester was a pale yellow, viscous liquid, b. p. 180°/11 mm. (yield, 40%) (Found : C, 65·2; H, 7·4. $C_{12}H_{16}O_2N_2$ requires C, 65·5; H, 7·3%).

1-*Carboxy*-3-*methyl*cyclo*pentane*-1-*acetic acid* was obtained when the preceding dicyano-ester or dinitrile was boiled with 50% hydrochloric acid (10 parts) for 24 hours. (If the acid is desired as the ultimate product in the condensation of ethyl 3-methyl*cyclo*pentylidenecyanoacetate with potassium cyanide, the mixture can be acidified after removal of the alcohol and hydrolysed.) It crystallised, on cooling, in fine needles, and was purified by solution in dilute aqueous sodium carbonate and precipitation with concentrated hydrochloric acid. The crude mixture melted at 115—120°, but repeated crystallisation from ether–light petroleum (b. p. 40—60°) gave the pure acid, m. p. 125°. This was obtained in various forms, *e.g.*, thick plates from benzene–light petroleum (b. p. 40—60°) (Found: C, 58·0; H, 7·2. $C_9H_{14}O_4$ requires C, 58·1; H, 7·5%). Its normal ammonium salt gave white precipitates with cold or warm solutions of calcium chloride, lead acetate, and silver nitrate; the copper salt was obtained as a bluish-green precipitate, insoluble in cold or hot water (Found for the *silver* salt : Ag, 53·5. $C_9H_{12}O_4Ag_2$ requires Ag, 53·9%).

The *ethyl* ester boiled at 142°/15 mm. and had $d_{4^\circ}^{20^\circ}$ 1·014, $n_D^{20^\circ}$ 1·44522, whence $[R_L]_D$ 63·38 (calc., 63·34) (Found : C, 64·5; H, 8·9. $C_{13}H_{22}O_4$ requires C, 64·5; H, 9·1%). The *anhydride*, prepared by heating the acid with an excess of acetic anhydride for 6 hours, was a liquid, b. p. 151°/15 mm. It gave the original acid when heated with a dilute solution of caustic alkali (Found : C, 64·2; H, 7·3. $C_9H_{12}O_3$ requires C, 64·3; H, 7·1%). The *anilic acid* crystallised from dilute alcohol in plates, m. p. 159° (Found : C, 69·3; H, 7·3. $C_{15}H_{19}O_3N$ requires C, 69·0; H, 7·3%). The *anil*, prepared by heating the anilic acid or a mixture of the succinic acid and aniline at 160° for 3 hours, crystallised from dilute alcohol in tiny needles, m. p. 90—91° (Found : C, 74·2; H, 6·9. $C_{15}H_{17}O_2N$ requires C, 74·1; H, 7·0%). The *imide* (XIV) was formed by the incomplete hydrolysis of the dicyano-ester, and was found in the residue after the acid had been extracted by a solution of sodium carbonate. It was also prepared by dissolving the dinitrile in an equal volume of ice-cold concentrated sulphuric acid, pouring the solution into water after 12 hours, neutralising the acid with ammonia, and extracting the dry residue with acetone. No diamide was formed by this method. The imide crystallised in white silky needles from light petroleum (b. p. 40—60°) or lustrous laminæ from dilute alcohol; m. p. 98° (Found : C, 64·6; H, 7·4. $C_9H_{13}O_2N$ requires C, 64·7; H, 7·8%).

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