683. *Investigations on the Synthesis of 2-Acetylcyclohex-2-enone. Part II.*[1] *Some Related Experiments, and the Constitution of the Dimeric Product,* $C_{16}H_{20}O_4$.

By C. W. T. Hussey and A. R. Pinder.

Dehydrochlorination of 2-acetyl-2-chlorocycloheptanone yields an enolic product formulated as (XIII). The properties of this product, and that derived similarly from 2-acetyl-2-chlorocyclohexanone,[1] and the comparative stability of 2-acetyl-2-chloro-4,4-dimethylcyclohexanone towards base, suggest that 2-acylcycloalk-2-enones are unstable, and stabilise themselves by enolisation.

The structure (XXII), derived from tricyclo[6,2,2,$0^{2,7}$]dodecane, is advanced for the dimeric product $C_{16}H_{20}O_4$ described in Part I.[1]

Experiments described in Part I [1] of this series were concerned with the dehydrochlorination of 2-acetyl-2-chlorocyclohexanone (I; R = H), which led to an enolic compound formulated, not as the expected (II; R = H), but as (III), existing chiefly as its enolic

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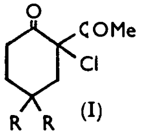
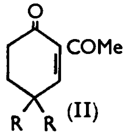
[1] Part I, McEntee and Pinder, *J.*, 1957, 4419.

form (IV). A dimeric product $C_{16}H_{20}O_4$, believed to be the dimer of (II; R = H), was formed simultaneously.

Because of the restricted manner in which dehydrochlorination may occur, it was of interest to study the behaviour of 2-acetyl-2-chloro-4,4-dimethylcyclohexanone (I; R = Me) on treatment with base. The chloro-ketone was obtained from 4,4-dimethylcyclohexanone by acetylation followed by treatment with sulphuryl chloride. It proved to be remarkably stable to the action of collidine. Even after prolonged treatment more than half was recovered, and the amount of collidine hydrochloride formed was less than half that expected; the main product was tar. A trace of alkali-soluble material was obtained when the reaction was conducted on a large scale, but this, on spectral and chemical evidence, was 2-acetyl-4,4-dimethylcyclohexanone. The reductive elimination of halogen atoms during treatment with collidine has been reported in the steroid field.[2] This unsuccessful attempt to force the dehydrochlorination (I $\longrightarrow$ II; R = Me) suggests that in a cycloalkenone system a double bond in the 2,3-position in cross-conjugation with two carbonyl groups is unstable. A similar instability has been noted with certain acyclic model compounds.[1]


(I)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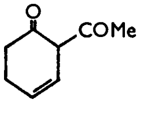
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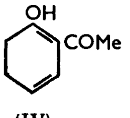
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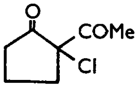
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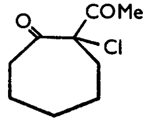
(VI)

Similar dehydrochlorinations of 2-acetyl-2-chlorocyclopentanone (V) and 2-acetyl-2-chlorocycloheptanone (VI) have been examined. Neither chloro-compound showed enolic properties; the chlorine atoms are therefore correctly placed at position 2. On treatment with collidine and other basic reagents the former yielded tar accompanied by unchanged chloro-ketone; the latter afforded approximately one mol. of collidine hydrochloride and a volatile product $C_9H_{12}O_2$, which on catalytic hydrogenation gave 2-acetylcycloheptanone, with uptake of one mol. of hydrogen. This product is therefore an acetylcycloheptenone, and formulæ (VII)—(XI) have to be considered.

The product $C_9H_{12}O_2$ is enolic in its behaviour, being readily soluble in aqueous alkali, giving a deep purple ferric test, forming a copper complex, and having a typical conjugate chelate infrared absorption curve. On careful oxidation with permanganate it yielded only glutaric acid. This observation eliminates structures (IX) and (X), and their respective enolic forms (XIV) and (XV). We feel also that the structure (XI), with its enol (XVI), can be eliminated by analogy with the behaviour of 2-acetyl-2-chlorocyclohexanone (I; R = H), which we showed gave a product different from 2-acetylcyclohex-5-enone.[1] Further, it is unlikely that a double bond would appear in the 6,7-position as a result of the elimination of a chlorine atom at position 2.

Of the remaining structures, (VIII) would enolise to (XIII). Theoretically, (VII) could enolise to (XII), *via* the reactive methylene group at position 7, but such an enolisation usually requires additional activation of the hydrogen atoms concerned. Further, the enol (XII) cannot be stabilised by resonance between zwitterionic forms.[3] Enolisation might, however, involve the allylic methylene group at position 4, and this would lead to (XIII), so that (VII) and (VIII) would have a common enolic form. The most satisfactory explanation of the properties of the compound $C_9H_{12}O_2$ seems to be that it is 2-acetylcyclohept-2-enone (VII), but that owing to the instability of the doubly conjugated 2,3-double bond, as shown by the behaviour of the analogue (I; R = Me) on dehydrochlorination, the compound stabilises itself by enolisation, its structure being therefore (XIII).

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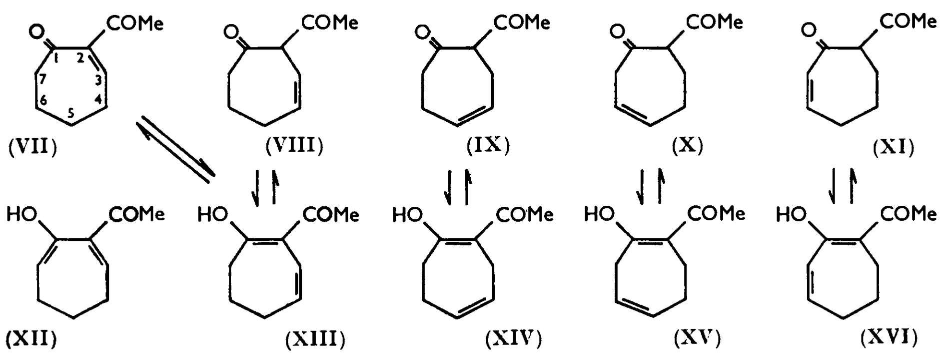
[2] Cf. Schwenk and Whitman, *J. Amer. Chem. Soc.*, 1937, **59**, 949; Jacobsen, *ibid.*, 1940, **62**, 1620.

[3] Cf. Smith, *J.*, 1953, 803.

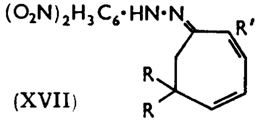
The corresponding compound in the cyclohexane series [1] we regard as (IV), derived from (II; R = H) by a similar stabilisation.

Alkaline hydrolysis of the compound $C_9H_{12}O_2$ gave a neutral product, as well as acetic acid and a syrupy unsaturated keto-acid which could not be purified. The keto-acid resulted from ring scission; analogous hydrolyses of 2-acylcyclopentanones and 2-acylcyclohexanones yield keto-acids.[4] The neutral hydrolysis product was treated with 2,4-dinitrophenylhydrazine and the resulting derivative subjected to chromatography, whereby it was separated into cycloheptanone 2,4-dinitrophenylhydrazone and a deep red derivative, m. p. 201—202°. The latter showed a depression in m. p. on admixture with cyclohept-2-enone 2,4-dinitrophenylhydrazone, m. p. 122°, $\lambda_{max.}$ 377 mμ, prepared by the dehydrobromination of 2-bromocycloheptanone.[5] The analysis and ultraviolet absorption [max. at 385 mμ; ε = 29,600 (in chloroform); compare eucarvone 2,4-dinitrophenylhydrazone (XVII; R = R′ = Me), $\lambda_{max.}$ 388 mμ, ε = 27,450 (in chloroform) [6]] suggest that it is cyclohepta-2,4-dienone 2,4-dinitrophenylhydrazone (XVII; R = R′ = H). This functional derivative of cyclohepta-2,4-dienone has been described by Dewar and Pettit,[7] who have recorded its m. p. as 149—150°. We feel that the difference here may be accounted for either by dimorphism or, more probably, by *cis–trans*-isomerism. Cyclohepta-2,4-dienone and cycloheptanone have presumably arisen by disproportionation of cyclohept-2-enone, the true hydrolysis product.

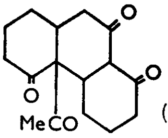


(VII) (VIII) (IX) (X) (XI)

(XII) (XIII) (XIV) (XV) (XVI)



(XVII)



(XVIII)

Some preliminary studies on the structure of the dimeric product $C_{16}H_{20}O_4$ were described in Part I [1]. It was assumed that the product resulted from the dimerisation of 2-acetylcyclohex-2-enone (II; R = H), but the structure (XVIII), analogous to that of the dimer of 1-acetylcyclohexene,[8] was rejected because the dimer contains no non-enolisable carbonyl group, and two *C*-methyl groups. The dimerisation is therefore apparently

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[4] Hauser, Swamer, and Ringler, *J. Amer. Chem. Soc.*, 1948, **70**, 4023; Manyik, Frostick, Sanderson, and Hauser, *ibid.*, 1953, **75**, 5030.

[5] Braude and Evans, *J.*, 1954, 607.

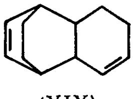
[6] Campbell, Islam, and Raphael, *J.*, 1956, 4096.

[7] Dewar and Pettit, *J.*, 1956, 2021.

[8] Jones and Koch, *J.*, 1942, 393.

of a cyclohex-2-enone rather than of an acetylcyclohexene. Examples of the base-catalysed dimerisation of cyclohex-2-enones have been described frequently in the literature; they invariably involve Michael addition reactions,[9] and small rings are not usually formed under these conditions.[10]

The dimer yielded on hydrolysis acetic acid, a syrupy keto-acid which could not be characterised, and a diketone $C_{12}H_{16}O_2$, containing no *C*-methyl groups. This diketone afforded a tripiperonylidene derivative, the formation of which proved the presence of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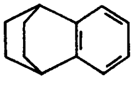
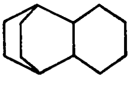

(XX)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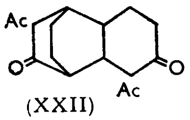
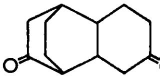

(XXII)

three reactive methylene groups. Wolff–Kishner reduction of the diketone yielded a saturated hydrocarbon $C_{12}H_{20}$, which must be tricyclic. Reduction of the diketone with lithium aluminium hydride gave a diol $C_{12}H_{20}O_2$, which when heated with palladised carbon was dehydrated and dehydrogenated to a mixture of hydrocarbons with an odour strongly reminiscent of tetralin. On infrared evidence this product was a mixture containing a high proportion of an *ortho*-disubstituted benzenoid hydrocarbon, probably tetralin itself. A similar product resulted from dehydrogenation of the hydrocarbon $C_{12}H_{20}$.

The behaviour on dehydrogenation resembles that of the tricyclic hydrocarbon (XIX), the dimer of cyclohexa-1,3-diene,[11] and one of its dihydro-derivatives, which yield naphthalene [12] and 1,4-ethylene-1,2,3,4-tetrahydronaphthalene (XX).[13] It seemed likely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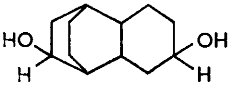
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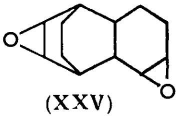
(XXV)

therefore that our $C_{12}H_{20}$ hydrocarbon was tricyclo[6,2,2,0^{2,7}]dodecane (XXI); this hydrocarbon was prepared by catalytic hydrogenation of the cyclohexadiene dimer (XIX).[14] It proved to be identical in b. p. and refractive index with the $C_{12}H_{20}$ hydrocarbon, and the two infrared absorption curves were superimposable. The carbon framework of the $C_{12}H_{20}$ hydrocarbon, the diol $C_{12}H_{20}O_2$, and the diketone $C_{12}H_{16}O_2$ is therefore established. If it is assumed that dimerisation of 2-acetylcyclohex-2-enone, by the mutual Michael addition of two molecules, is involved, the only possible structure for the dimer $C_{16}H_{20}O_4$ consistent with the established constitution for the $C_{12}H_{20}$ hydrocarbon is (XXII). The diketone and the diol are then formulated as (XXIII) and (XXIV) respectively.

An attempt was made to synthesise the diketone (XXIII) from the diene (XIX), which was converted by perbenzoic acid into the diepoxide (XXV). The latter, however, was not rearranged by treatment with lithium diethylamide in ether.[15]

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[9] See, for example, Knoevenagel and Reinecke, *Ber.*, 1899, **32**, 418; Treibs, *Ber.*, 1930, **63**, 2738; *J. prakt. Chem.*, 1933, **138**, 299; Briggs, Harland, Ralph, and Simmonds, *J.*, 1953, 3788; Taylor, *Chem. and Ind.*, 1954, 252; Ayer and Taylor, *J.*, 1955, 2227; Büchi, Hansen, Knutson, and Koller, *J. Amer. Chem. Soc.*, 1958, **80**, 5517.

[10] Mustafa, *Chem. Rev.*, 1952, **51**, 1; de Mayo, *Adv. Org. Chem.*, 1960, **2**, 387.

[11] Alder and Stein, *Annalen*, 1932, **496**, 197.

[12] Hofmann, *Chem.-Ztg.*, 1933, **57**, 5.

[13] Kazanskii and Vol'fson, *J. Gen. Chem.* (*U.S.S.R.*), 1938, **8**, 1685.

[14] Alekseevskii, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 1586.

[15] Cope, Trumbull, and Trumbull, *J. Amer. Chem. Soc.*, 1958, **80**, 2844.

EXPERIMENTAL

2-*Acetyl*-2-*chlorocyclopentanone* (V).—2-Acetylcyclopentanone [16] (18·7 g., 0·15 mol.) in carbon tetrachloride (84 c.c.) was stirred at room temperature during the gradual (1 hr.) addition of sulphuryl chloride (22·0 g., 0·16 mol.) in carbon tetrachloride (30 c.c.). After being stirred for a further 12 hr. the solution was shaken with water and aqueous sodium hydrogen carbonate and dried. The solvent was removed under reduced pressure through a short Vigreux column, and the residual 2-*acetyl*-2-*chlorocyclopentanone* distilled; it had b. p. 92—94°/13 mm. (17·2 g.) (Found: C, 51·6; H, 5·85; Cl, 22·6. $C_7H_9ClO_2$ requires C, 52·3; H, 5·6; Cl, 22·1%), and, as liquid film, carbonyl bands at 1714 and 1754, and a C–Cl band at 766 cm.$^{-1}$. The compound gave no colour with alcoholic ferric chloride.

Attempts to dehydrochlorinate the product by heating it with collidine, pyridine, methanolic sodium methoxide, or methanolic potassium acetate afforded tar and unchanged chloro-ketone.

2-*Acetyl*-2-*chlorocycloheptanone* (VI).—A similar chlorination of 2-acetylcycloheptanone [17] (20 g.) in carbon tetrachloride (90 c.c.) with sulphuryl chloride (19·3 g.) in carbon tetrachloride (35 c.c.) yielded 2-*acetyl*-2-*chlorocycloheptanone* (21·6 g.), b. p. 112—114°/10 mm. (Found: C, 56·7; H, 6·9. $C_9H_{13}ClO_2$ requires C, 57·3; H, 6·9%), $\nu_{max.}$ (liquid film) at 1707 and 1723 (C=O), and 767 cm.$^{-1}$ (C–Cl). The product gave no colour with alcoholic ferric chloride. The 2,4-*dinitrophenylhydrazone*, prepared in cold, alcoholic solution, crystallised from ethanol in golden-yellow needles, m. p. 165° (decomp.) (Found: C, 49·0; H, 4·65. $C_{15}H_{17}ClN_4O_5$ requires C, 48·8; H, 4·65%).

2-*Acetylcyclohepta*-1,3-*dien*-1-*ol* (XIII).—A mixture of 2-acetyl-2-chlorocycloheptanone (5 g.) and collidine (15 c.c.) was heated at 180° for 2½ hr. The cooled mixture was diluted with ether, and the collidine hydrochloride removed. The ethereal filtrate was shaken in turn with dilute hydrochloric acid, dilute sodium hydroxide, and water, and dried. Evaporation of the ether yielded only tar. The alkaline extract was cooled, acidified with 5N-hydrochloric acid, and extracted with ether. Evaporation of the dried extract afforded 2-*acetylcyclohepta*-1,3-*dien*-1-*ol*, b. p. 97—98°/8 mm., 102°/10 mm. (1·8 g.) (Found: C, 71·8; H, 8·4. $C_9H_{12}O_2$ requires C, 71·1; H, 7·9%). Infrared absorption (liquid film) showed a typical conjugate chelate spectrum, with bands at 3020 (OH), 1590 (C=O), and 701 cm.$^{-1}$ (*cis*-CH=CH). The compound was soluble in aqueous sodium hydroxide, gave a deep purple ferric test, and formed a *copper complex*, which separated from benzene–light petroleum (b. p. 60—80°) in green needles, m. p. 180—181° (Found: C, 59·2; H, 6·4. $C_{18}H_{22}CuO_4$ requires C, 59·1; H, 6·0%). On catalytic hydrogenation in ethanol at room temperature and pressure in the presence of 5% palladised charcoal, the compound absorbed one mol. of hydrogen with the formation of 2-acetylcycloheptanone, identified as its *copper complex*, grey needles [from benzene–light petroleum (b. p. 60—80°)], m. p. and mixed m. p. 210—211° (Found: C, 58·65; H, 6·8. $C_{18}H_{26}CuO_4$ requires C, 58·3; H, 7·0%).

Oxidation of 2-*Acetylcyclohepta*-1,3-*dien*-1-*ol*.—A solution of the foregoing enol (2·5 g.) in dry, permanganate-stable acetone (75 c.c.) was stirred at 0—5° whilst finely powdered potassium permanganate was added gradually, until a permanent pink colour was observed. After a further hour's stirring the solution was filtered and the residue dried at room temperature. It was mixed with water (150 c.c.) and the mixture filtered from manganese dioxide. Excess of permanganate was destroyed by the addition of a little solid sodium hydrogen sulphite, and the solution acidified with 5N-hydrochloric acid and subjected to continuous ether-extraction overnight. Evaporation of the dried extract yielded glutaric acid (0·7 g.), m. p. and mixed m. p. 97—98°.

Action of Aqueous Alkali on 2-*Acetylcyclohepta*-1,3-*dien*-1-*ol*.—The enol (2·0 g.) was refluxed for 2 hr. with 5% aqueous sodium hydroxide (15 c.c.). The cooled solution was extracted several times with ether, and the extracts were dried and evaporated through a short Vigreux column. The residual oil distilled at 56—57°/9 mm. (0·24 g.); it was mixed with alcoholic 2,4-dinitrophenylhydrazine sulphate and the orange-red precipitate collected and purified by chromatography in chloroform solution on bentonite–kieselguhr. Elution with chloroform gave, after evaporation, cycloheptanone 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 147°. Further elution with chloroform–ethanol afforded, after evaporation, a *product* which

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[16] *Org. Synth.*, Coll. Vol. II, 1943, p. 531.

[17] Buchta and Kranz, *Angew. Chem.*, 1955, **67**, 77.

crystallised from ethyl acetate in deep red needles, m. p. 201—202° (Found: C, 54·3; H, 4·6; N, 19·4. $C_{13}H_{12}N_4O_4$ requires C, 54·2; H, 4·2; N, 19·4%), $\lambda_{max.}$ (in chloroform) 385 mμ (ε 29,600). Dewar and Pettit [7] give cyclohepta-2,4-dienone 2,4-dinitrophenylhydrazone, m. p. 149—150°.

Acidification of the original alkaline solution gave acetic acid (*S*-benzylthiouronium salt, m. p. and mixed m. p. 136°), and a gummy acid, isolated with ether. The latter was unsaturated and ketonic, but could not be converted into a crystalline derivative.

2-*Acetyl*-4,4-*dimethylcyclohexanone*.—4,4-Dimethylcyclohexanone was synthesised from *p*-cresol, through 4-dichloromethyl-4-methylcyclohexa-2,5-dienone [18] and 4,4-dimethylcyclohexanol.[19, 20] The 2,4-*dinitrophenylhydrazone* crystallised from ethanol in orange-yellow needles, m. p. 148—149° (Found: C, 54·4; H, 6·0; N, 18·7. $C_{14}H_{18}N_4O_4$ requires C, 54·9; H, 5·9; N, 18·3%). The ketone (10·6 g.) was mixed with acetic anhydride (17·1 g.), and the solution was saturated with boron trifluoride at 0°. Working up in the usual manner [21] gave 2-*acetyl*-4,4-*dimethylcyclohexanone*, b. p. 120—125°/20—21 mm. (10·0 g.) (Found: C, 71·0; H, 9·5. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%). The *copper complex* separated from light petroleum (b. p. 60—80°) in green needles, m. p. 165·5° (Found: C, 59·8; H, 7·7. $C_{20}H_{30}CuO_4$ requires C, 60·4; H, 7·5%). The infrared absorption of the diketone was typically conjugate chelate in type. The diketone was soluble in dilute aqueous alkali and gave a deep purple ferric test.

2-*Acetyl*-2-*chloro*-4,4-*dimethylcyclohexanone* (I; R = Me).—Treatment of the foregoing diketone (4·2 g.) in carbon tetrachloride (12 c.c.) with sulphuryl chloride (3·7 g.) in carbon tetrachloride (8 c.c.), in the usual manner, gave 2-*acetyl*-2-*chloro*-4,4-*dimethylcyclohexanone*, b. p. 138—140°/19 mm. (4·6 g.) (Found: C, 58·9; H, 7·6. $C_{10}H_{15}ClO_2$ requires C, 59·2; H, 7·4%). The product was insoluble in cold, aqueous alkali and gave a negative ferric test. In a liquid film it had CO bands at 1725 and 1745 cm.$^{-1}$, CMe_2 bands at 1393, 1364, 1170, 1142, and 821 cm.$^{-1}$ and a CCl band at 773 cm.$^{-1}$.

Attempts to dehydrochlorinate the product by heating it with collidine gave largely unchanged material. More prolonged treatment at higher temperature gave, at best, 50% of the calculated amount of collidine hydrochloride, accompanied by tar. A trace of alkali-soluble material was obtained; on infrared and chemical evidence this contained some 2-acetyl-4,4-dimethylcyclohexanone.

Dimeric Product,[1] $C_{16}H_{20}O_4$.—The dehydrochlorination of 2-acetyl-2-chlorocyclohexanone has been improved, to yield the crystalline product, $C_{16}H_{20}O_4$, in 20% yield. It crystallised from methanol in rhombic prisms, m. p. 136°.

Hydrolytic Cleavage of the Dimeric Product (XXII).—The crystalline product, $C_{16}H_{20}O_4$ (10 g.), was refluxed with 5% aqueous potassium hydroxide (90 c.c.) for 1½ hr. under nitrogen. The cooled solution was subjected to continuous ether-extraction overnight, and the extract dried and concentrated. The syrupy *tricyclo*[6,2,2,0^{2,7}]*dodecane*-4,10-*dione* distilled at 150—155° (bath)/0·05 mm. (0·6 g.) (Found: C, 74·9; H, 8·5. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%), $\nu_{max.}$ (in CCl_4) 1720 cm.$^{-1}$ (CO) (see above). The *disemicarbazone* separated in needles, m. p. 226°, from a large volume of ethanol (Found: N, 26·9. $C_{14}H_{22}N_6O_2$ requires N, 27·4%). The diketone condensed with piperonaldehyde in ethanol, in the presence of 5N-aqueous sodium hydroxide, to yield a *tripiperonylidene derivative*, which crystallised from ethanol in solvated needles, m. p. 212—213° (Found: C, 71·85, 71·8; H, 5·4, 5·4. $C_{36}H_{28}O_8,C_2H_6O$ requires C, 71·9; H, 5·4%), $\nu_{max.}$ (in $CHCl_3$) 3571 cm.$^{-1}$ (OH). A reaction under similar conditions with benzaldehyde yielded a gummy product which could not be purified.

Acidification of the alkaline hydrolysis liquor yielded, after ether-extraction, an acidic syrup which contained acetic acid (*S*-benzylthiouronium salt, m. p. and mixed m. p. 136°). Evaporation of the acetic acid *in vacuo* left a syrupy mixture of keto-acids, which could not be purified or characterised. It gave a positive reaction with Brady's reagent.

Reduction of the Diketone $C_{12}H_{16}O_2$ *to the Diol* $C_{12}H_{20}O_2$.—The diketone (0·52 g.) in dry ether (20 c.c.) was added gradually to a swirled suspension of lithium aluminium hydride (0·4 g.) in dry ether (15 c.c.). The ethereal suspension was refluxed for 1½ hr. and kept at room temperature overnight. After addition of " Celite " and the minimum quantity of water the ether was decanted, dried, and evaporated. The residual 4,10-*diol* distilled at 155—165°

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[18] von Auwers and Keil, *Ber.*, 1902, **35**, 4207.
[19] Miller and Adams, *J. Amer. Chem. Soc.*, 1936, **58**, 787.
[20] von Auwers and Lange, *Annalen*, 1913, **401**, 303.
[21] *Org. Reactions*, Vol. VIII, p. 130.

(bath)/0·03 mm. (0·48 g.) (Found: C, 73·4, 73·5; H, 10·5, 10·3. $C_{12}H_{20}O_2$ requires C, 73·5; H, 10·2%), $\nu_{max.}$ (in CCl_4) 3642 cm.$^{-1}$ (OH) (no carbonyl band). The *di-*p*-nitrobenzoate* separated from a small volume of benzene in needles, m. p. 209° (Found: N, 5·6. $C_{26}H_{26}N_2O_8$ requires N, 5·7%).

Dehydrogenation of the Diol $C_{12}H_{20}O_2$.—The diol (0·37 g.) and 30% palladised charcoal [22] (0·12 g.) were heated at 300° in a slow current of dry nitrogen for 8 hr. After a few minutes water droplets were noted on the cooler parts of the apparatus. The cooled mixture was leached with methanol, and the solution filtered and concentrated through a short column. The residue (0·2 g.) was steam-distilled, yielding, after isolation with ether, a product, b. p. 70—100°/18 mm. (Found: C, 89·3; H, 9·1. Calc. for $C_{10}H_{12}$ requires C, 90·9; H, 9·1%), with a strong tetralin-like odour, which decolorised acid permanganate solution immediately. The infrared spectrum (liquid film) indicated that the product was a mixture of hydrocarbons, but bands characteristic of an *ortho*-disubstituted benzene system were discernible in the 1600—2000 cm.$^{-1}$ region.

Wolff–Kishner Reduction of the Diketone $C_{12}H_{16}O_2$.—The disemicarbazone (0·48 g.; see above) of the diketone was heated in a sealed tube at 200° for 8 hr. with 98—100% hydrazine hydrate (1 c.c.) and sodium ethoxide, obtained by dissolving sodium (0·75 g.) in ethanol (15 c.c.). The tube was cooled and the contents were poured into a large volume of water. The oil which separated was taken up in ether, and the extract washed with dilute hydrochloric acid and water and dried. Evaporation of the solvent under reduced pressure through a column gave tricyclo[6,2,2,0^{2,7}]dodecane, b. p. 107—108°/14 mm., $n_D^{19·5}$ 1·5080 (0·15 g.) (Found: C, 87·6; H, 12·3. Calc. for $C_{12}H_{20}$: C, 87·8; H, 12·2%), identical (infrared comparison) with an authentic specimen (see below).

Tricyclo[6,2,2,0^{2,7}]*dodeca*-5,9-*diene* (XIX): *Dimerisation of Cyclohexa*-1,3-*diene*.—Cyclohexa-1,3-diene was prepared from cyclohexene by bromination [23] and dehydrobromination.[24] The hydrocarbon was distilled over sodium through a fractionating column packed with a 25 cm. glass spiral, a lower fraction consisting chiefly of a cyclohexa-1,3-diene–ether azeotrope being rejected. The diene had b. p. 80°, $\lambda_{max.}$ (in hexane) 257 mμ (lit.,[25,26] $\lambda_{max.}$ 256 mμ), n_D^{20} 1·4755 (lit.,[25] n_D^{20} 1·4755). Vapour-phase chromatography of the product on "Embacel" moistened with dinonyl phthalate showed it to be substantially free from diethyl ether. Cyclohexa-1,3-diene (3·25 g.) was heated in a sealed tube at 200—220° for 10 hr.[24] The contents of the tube were distilled over sodium, the dimer (1·3 g.) being collected at 100—102°/9 mm., n_D^{22} 1·5260 (lit.,[24] b. p. 86—87°/0·3 mm., n_D^{20} 1·5288). Infrared absorption (liquid film) showed a C=C band at 1656 cm.$^{-1}$ and *cis*-CH=CH– bands at 710 and 3067 cm.$^{-1}$. The dimer gave the reported colour reactions [24] with concentrated sulphuric acid.

Tricyclo[6,2,2,0^{2,7}]*dodecane* (XXI).—The foregoing dimeric product (0·48 g.) was shaken in ethanol solution in hydrogen at room temperature and pressure for 4 hr. with pre-reduced Adams platinum oxide (absorption: 2 mols.).[13,14] The catalyst and solvent were removed; the residual tricyclo[6,2,2,0^{2,7}]dodecane, distilled over sodium, had b. p. 110—111°/16 mm., n_D^{20} 1·5081 (0·3 g.) (lit.,[14] b. p. 102°/7·5 mm.) (Found: C, 87·5; H, 12·4. Calc. for $C_{12}H_{20}$: C, 87·8; H, 12·2%). The product was identical (infrared comparison) with the hydrocarbon obtained by the Wolff–Kishner reduction of the $C_{12}H_{16}O_2$ diketone (see above).

5,6:9,10-*Diepoxytricyclo*[6,2,2,0^{2,7}]*dodecane* (XXV).—A chloroform solution of perbenzoic acid was prepared [27] from benzoyl peroxide (31·1 g. of 70% purity) in dry toluene (300 c.c.) and sodium ethoxide [from sodium (4·6 g.) and absolute ethanol (100 c.c.)] at −15°. Tricyclo-[6,2,2,0^{2,7}]dodeca-5,9-diene (0·8 g.) (0·005 mol.) was added gradually dropwise, with swirling, to this solution (26 c.c.; 0·0105 mol.) at below 0°, and the mixture was kept at 0° for 48 hr. The chloroform solution was washed in turn with saturated sodium hydrogen carbonate solution and water, dried, and concentrated on the water-bath. The residual *diepoxide* distilled at 96°/0·1—0·2 mm., 88°/0·05 mm. (0·42 g.) (Found: C, 74·8; H, 7·9. $C_{12}H_{16}O_2$ requires C, 75·0; H, 8·3%). Its infrared absorption (in CCl_4) showed *cis*-epoxide bands at 829 and 1250 cm.$^{-1}$, but no C=C or hydroxyl bands. The product gave no colour with tetranitromethane.

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[22] Linstead and Thomas, *J.*, 1940, 1127.

[23] *Org. Synth.*, 1934, **12**, 26.

[24] Hofmann and Damm, *Mitt. Schleschischen Kohlensforschungsinst. Kaiser-Wilhem Ges.*, 1925, **2**, 97; *Chem. Zentr.*, 1926, I, 2342.

[25] Allsopp, *Proc. Roy. Soc.*, 1934, **143***A*, 618.

[26] Henri and Pickett, *J. Chem. Phys.*, 1939, **7**, 439.

[27] *Org. Synth.*, Coll. Vol. I, 1941, 431.

An attempt to rearrange the diepoxide to a diketone by using lithium diethylamide [15] was unsuccessful, resinous material and unchanged diepoxide being obtained.

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