13. *Synthetical Studies of Terpenoids. Part III.*[1] *Syntheses of Azulene Derivatives.*

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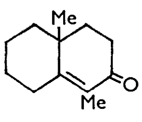
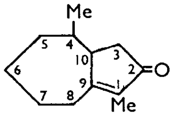
Isomeric dimethylbicyclo[5,3,0]decen-2-ones, expected to be useful intermediates in the synthesis of guaianolides, have been prepared.

THE present communication records preliminary steps towards the synthesis of guaianolides.[2] For the synthesis of santonin and its isomers, the octalone (I) has been used;[1,3] it was hoped that the isomeric ketone (II) would be suitable for the synthesis of related azulenic lactones, and a few methods have been successfully developed.

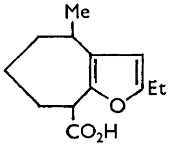
The first approach gave only a minute yield. The unsaturated cyano-ester (III), prepared[5] from ethyl 6-oxoheptanoate[4] and ethyl cyanoacetate, was catalytically reduced and the sodio-derivative of the product (IV) was condensed with bromomethyl ethyl ketone,[6] yielding diethyl 6-cyano-5-methyl-8-oxodecane-1,6-dicarboxylate (V). Refluxing this with hydrochloric and acetic acid and subsequent esterification gave cyano-free diester (VI). The derived ketal ester (VII) was subjected to ring-closure in the presence of potassium t-butoxide in xylene, by a modified high-dilution technique.[7] The cyclised product could not be purified and was, therefore, treated directly with methanolic hydrochloric acid followed by potassium hydroxide. A crystalline acid was obtained, but the expected neutral product (II) could not be isolated. Elementary analyses of the acid, its methylation with diazomethane, ultraviolet absorption maximum at 227 mμ (log ε 3·9), no loss of carbon dioxide in refluxing collidine in the presence of copper powder, failure to respond to carbonyl tests, and recovery after attempted reduction with sodium borohydride, together with analogy from the cyclopentenone series,[8] indicate that the acid is the furan derivative (VIII). In another attempt the crude cyclised material was first subjected to ketonic hydrolysis by alkali; the neutral product, on removal of the ketal group and ring-closure, afforded a ketone [$\lambda_{max.}$ 242 mμ (log ε 4·0)] in a very poor yield. This gave a mixture of 2,4-dinitrophenylhydrazones from which a minute quantity of one component corresponding to that of ketone (II) was isolated by laborious fractional crystallisation. The structure of ketone (II) was established by an independent synthesis (see below).



(I)



(II)



(VIII)

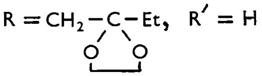
$EtO_2C\cdot[CH_2]_4\cdot CMe{=}C(CN)\cdot CO_2Et$ (III)

$EtO_2C\cdot[CH_2]_4\cdot CHMe\cdot CRR'\cdot CO_2Et$

(IV) $R = H,\ R' = CN$

(V) $R = CH_2\cdot COEt,\ R' = CN$

(VI) $R = CH_2\cdot COEt,\ R' = H$



(VII) $R = CH_2-\underset{O\quad O}{C}-Et,\ R' = H$

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[1] The papers by Chakrabarti, Dutt, and Dutta, *J.*, 1956, 4978, and Mahajan, Dutt, and Dutta, *J.*, 1957, 5069, are held to constitute Parts I and II respectively.

[2] Cf. Barton and de Mayo, *Quart. Rev.*, 1957, **11**, 207.

[3] Abe, Harukawa, Ishikawa, Miki, Sumi, and Toga, *J. Amer. Chem. Soc.*, 1956, **78**, 1416.

[4] Ruzicka, Siedel, Schinz, and Pfeiffer, *Helv. Chim. Acta*, 1948, **31**, 422.

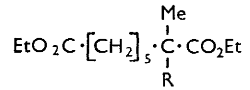
[5] Cope, Hofmann, Wyckopp, and Hardenbergh, *J. Amer. Chem. Soc.*, 1941, **63**, 3452.

[6] Catch, Elliott, Hey, and Jones, *J.*, 1948, 272.

[7] Leonard and Sentz, *J. Amer. Chem. Soc.*, 1952, **74**, 1704; Leonard and Schimelpfenig, *J. Org. Chem.*, 1958, **23**, 1708.

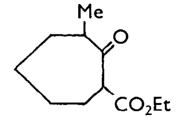
[8] Wilds and Close, *J. Amer. Chem. Soc.*, 1946, **68**, 83; Baumgarten, Creger, and Villars, *ibid.*, 1958, **80**, 6609.

In the ketone (II) the double bond is in 1,9-position. It will be difficult to introduce a suitable side-chain at position 2 of 3-methylcycloheptanone in order to have the double bond in the desired position. For this reason, a side-chain was introduced before ring-closure in the preceding scheme. It may, however, be noted that owing to the high mobility of the double bond in a cyclopentenone system, the 3,10-double bond, even if first formed, would be expected to shift to the more substituted 1,9-position under the experimental conditions.[9] This has now been experimentally realised and the ketone (II) synthesised, as follows: The tri-ester (IX), obtained from ethyl 6-bromohexanoate [10] and diethyl methylmalonate in the presence of sodium ethoxide, was converted by acid or alkaline hydrolysis and subsequent esterification into diethyl α-methylsuberate (X). On ring-closure as mentioned above, this gave the cycloheptanone (XI). Condensation with 1-bromoethyl methyl ketone was then disappointing but subsequent hydrolysis gave some of the ketone (II), characterised by its absorption maximum at 242 mμ (log ε 4·0) and a red 2,4-dinitrophenylhydrazone. As expected, condensation with bromomethyl ethyl ketone gave a very good yield of the isomeric ketone (XIII), which also was characterised by absorption at 242 mμ (log ε 4·1) and a red 2,4-dinitrophenylhydrazone. The two dinitrophenylhydrazones were not identical and this ruled out the possibility of isomeric change in 1-bromoethyl methyl ketone during condensation. However, owing to the extremely poor yield of the ketone (II), this route had also to be abandoned.

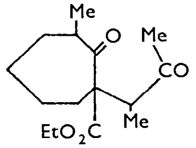


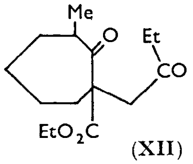
$\mathrm{EtO_2C{\cdot}[CH_2]_5{\cdot}\overset{Me}{\underset{R}{C}}{\cdot}CO_2Et}$

(IX) R = CO_2Et
(X) R = H

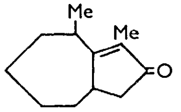


(XI)

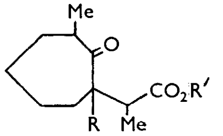




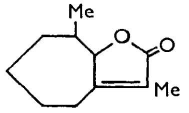
(XII)



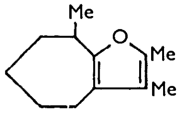
(XIII)



(XIV) R = CO_2Et, R′ = Et
(XV) R = R′ = H

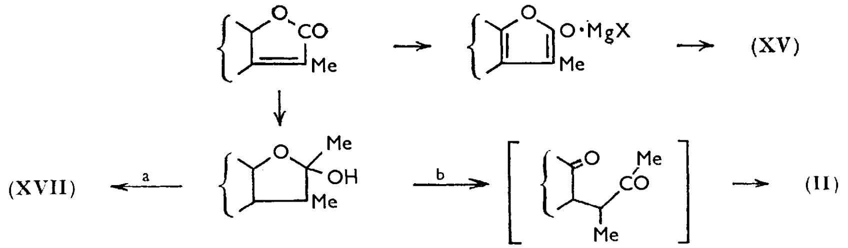


(XVI)



(XVII)

Next it was planned to fuse the cyclopentenone moiety to the cycloheptane system by the action of methylmagnesium iodide on the lactone (XVI), derived from the keto-acid (XV), because conversion of the carboxyl group into acetyl through the acid chloride has been found inapplicable in a closely related system.[11] The Grignard procedure has been successfully developed for building up the cyclohexenone system,[12] but it failed when applied to cyclopentenones.[13] The β-keto-ester (XI) and ethyl α-bromopropionate



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[9] Barton and de Mayo, *J.*, 1956, 142.
[10] Brown and Partridge, *J. Amer. Chem. Soc.*, 1944, **66**, 839.
[11] Dutta, *J. Indian Chem. Soc.*, 1957, **34**, 761.
[12] Fujimoto, *J. Amer. Chem. Soc.*, 1951, **73**, 1856.
[13] Jacob and Takahashi, *ibid.*, 1958, **80**, 4865.

readily gave the diester (XIV) which yielded the keto-acid (XV) on hydrolysis with barium hydroxide and this in refluxing acetic anhydride containing a catalytic amount of fused sodium acetate afforded the lactone (XVI) in good yield,[14] the double bond being conjugated with the carbonyl group since the absorption maximum is at 220 mμ (log ε 4·05).[15] This lactone was allowed to react with methylmagnesium iodide but gave a mixture, whose components (XV), (XVII), and (II), may be accounted for as follows. Regeneration of the acid (XV) may arise by enolisation of the lactone (XVI) under the influence of the Grignard reagent, leading to the formation of the hydroxyfuran and eventually to the acid (XV). Dehydration of the intermediate hydroxy-compound may proceed by paths (a) and (b). The yields of the products, which are easily separated by distillation, depend on the conditions used in decomposing the Grignard complex. An excess of mineral acid and higher temperatures increased the yield of the furan (XVII), and use of ammonium chloride solution brought about no noticeable improvement in the yield of desired ketone (II). Use of dilute acetic acid was found to be the best. The product (XVII) has been characterised as a tetrasubstituted furan derivative by its absorption maximum at 223 mμ (log ε 3·8),[16] its colour reactions, and its tendency to polymerise in contact with mineral acids or on storage. The ketone (II) had an absorption maximum at 242 mμ (log ε 4·1) and afforded a red 2,4-dinitrophenylhydrazone identical with that mentioned above.

With the ultimate object of attaching the lactonic group, characteristic of guaianolides, preliminary attempts were made to introduce the dienone system into the ketone (II) by use of *N*-bromosuccinimide and collidine. About a third of the ketone (II) was recovered, coloured blue by an azulene: the rest was tar. The other alternative route was through the action of per-acids on the enol-acetate and subsequent dehydration; but acetic anhydride and acetyl chloride resinified the ketone (II).

EXPERIMENTAL

Ultraviolet spectra were measured for ethanolic solutions.

Diethyl 2-*Cyano*-3-*methyloct*-2-*enedioate* (III).—Ethyl 6-oxoheptanoate (224 g.), ethyl cyanoacetate (147 g.), acetic acid (24 c.c.), ammonium acetate (15 g.), and benzene (350 c.c.) were refluxed under a water-separator for 8 hr. The cooled mixture was washed with water, the low-boiling products were removed, and the residue was finally distilled, affording the *product* (262 g.), b. p. 175—180°/0·6 mm. (Found: C, 63·0; H, 8·0. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·9%).

Diethyl α-*Cyano*-β-*methylsuberate* (IV).—The ester (III) (70 g.) in ethanol (70 c.c.) was hydrogenated in the presence of 10% palladium–carbon (300 mg.). The *suberate* (69 g.) had b. p. 163—165°/0·7 mm. (Found: C, 62·6; H, 8·6. $C_{14}H_{23}O_4N$ requires C, 62·5; H, 8·6%).

Diethyl 6-*Cyano*-5-*methyl*-8-*oxodecane*-1,6-*dicarboxylate* (V).—The cyano-ester (IV) (124 g.) was allowed to react overnight with sodium dust (11·5 g.) under benzene (250 c.c.). Next, bromomethyl ethyl ketone (83 g.) in dry benzene (100 c.c.) was added to the ice-cold mixture, and the whole set aside for 4 hr., then refluxed on a water-bath for 8 hr. The cooled mixture was washed with water, the low-boiling products were removed, and the residue was distilled in a vacuum. A fraction (106 g.) was collected up to 200°/0·5 mm. Extensive decomposition ensued on further heating and distillation was abandoned at this stage. The above distillate was fractionated to separate unchanged cyano-compound (28 g.) from the condensation *product* (76 g.), which redistilled as a pale yellow liquid, b. p. 194—198°/0·5 mm. (Found: C, 63·6; H, 8·5. $C_{18}H_{29}O_5N$ requires C, 63·7; H, 8·5%).

Diethyl 5-*Methyl*-8-*oxodecane*-1,6-*dicarboxylate* (VI).—The ester (V) (75 g.), as well as the residue (*ca.* 40 g.) from the first distillation, were refluxed for 20 hr. with hydrochloric (600 c.c.) and acetic acid (120 c.c.), and the dried residue left after removal of the low-boiling products under reduced pressure was esterified with alcohol and sulphuric acid), to afford the *keto-diester*

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[14] Woodward, Sondheimer, Taub, Heusler, and McLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223.

[15] Ames, Bowman, and Grey, *J.*, 1954, 375.

[16] Cocker, Cross, Duff, Edward, and Holley, *J.*, 1953, 2540.

(64 g.) as a pale yellow liquid, b. p. 160—165°/0·5 mm. (Found: C, 65·1; H, 9·5. $C_{17}H_{30}O_5$ requires C, 65·0; H, 9·5%). In later batches only the unchanged cyano-ester in the preceding experiment was distilled off and the residue was directly hydrolysed and esterified as above, thereby improving the yield slightly.

Ethylene Ketal of the Ester (VI).—The ester (VI) (20 g.), freshly distilled ethylene glycol (6 c.c.), dry benzene (100 c.c.), and toluene-*p*-sulphonic acid (100 mg.) were refluxed under a water-separator for 8 hr. The cooled mixture was washed with 10% sodium carbonate solution and water, the solvent removed, and the residual *ketal* (VII) distilled as a pale yellow liquid (16 g.), b. p. 175—177°/0·5 mm. with a forerun (8 g.) up to 170°/0·5 mm. (Found: C, 63·9; H, 9·2. $C_{19}H_{34}O_6$ requires C, 63·7; H, 9·5%).

5′-*Ethyl*-7-*methylcyclohepteno*(2′,1′ : 2,3)*furan*-3-*carboxylic Acid* (VIII).—Potassium (4·2 g.) was dissolved in t-butyl alcohol, and the excess of the solvent was then distilled off. Dry xylene (500 c.c.) was introduced and a portion of the solvent distilled off to remove last traces of alcohol. A high-dilution apparatus was fitted to the reaction flask and the ketal (VII) (26 g.) in xylene (100 c.c.) was dropped in. The cyclisation period was reduced to about 4 hr., as compared with several days mentioned by previous workers. The critical factors were slow and gradual addition of the diester, continuous removal of the butyl alcohol formed, efficient stirring, and an atmosphere of nitrogen. At the end of experiment, the dark brown mixture was cooled to room temperature and acidified with acetic acid. The xylene layer was separated and washed with water, and the solvent removed under reduced pressure. The dark brown residue decomposed on attempts at distillation in a high vacuum. The first few drops which passed over gave greenish-blue colour with alcoholic ferric chloride. The crude residue (*ca.* 20 g.) was refluxed for 0·5 hr. with methanol (100 c.c.) containing hydrochloric acid (4 c.c.). Next morning, potassium hydroxide (11 g.) in methanol (100 c.c.) was added and the mixture heated on water-bath for 10 hr. under nitrogen. The cooled mixture was acidified with acetic acid, and methanol removed on the water-bath. The residue was diluted with water, rendered alkaline with sodium carbonate solution, and extracted with ether to remove traces of the neutral material. The alkaline solution was acidified with hydrochloric acid and extracted with ether, affording a brown semi-solid mass, which gave crystals on sublimation at 120—130°/0·3 mm. This *acid* crystallised from light petroleum (b. p. 60—80°) as rhombs, m. p. 124° (1·2 g.), $\lambda_{max.}$ 227 mμ (log ε 3·9) (Found: C, 69·9; H, 8·0. $C_{13}H_{18}O_3$ requires C, 70·3; H, 8·1%). With diazomethane it (1·2 g.) gave an *ester* (1 g.), b. p. 130°/5 mm., which polymerised in a few months (Found: C, 70·9; H, 8·4. $C_{14}H_{20}O_3$ requires C, 71·2; H, 8·5%).

2,3,4,5,6,7,8,10-*Octahydro*-1,4-*dimethyl*-2-*oxoazulene* {2,8-*Dimethylbicyclo*[5,3,0]*dec*-7-*en*-9-*one*} (II).—(*a*) The crude cyclised product (*ca.* 5 g.) described in the last paragraph was refluxed under nitrogen for 15 hr. with potassium hydroxide (3·5 g.) in water (35 c.c.). The mixture was diluted with water and extracted with ether to afford a brown mass which was heated with hydrochloric acid (1 c.c.) in water (15 c.c.) for 1 hr. Next, potassium hydroxide (4·5 g.) in water (30 c.c.) was added, and the mixture refluxed under nitrogen for 6 hr., cooled, diluted with water, and extracted with ether. The product was finally distilled [*ca.* 0·3 g.; b. p. 114—116°/3 mm., $\lambda_{max.}$ 242 mμ (log ε 4·0)]. It gave a 2,4-*dinitrophenylhydrazone* from which a small amount of red needles, m. p. 176—177°, was isolated by laborious fractional crystallisation (Found: C, 60·4; H, 6·2; N, 15·9. $C_{18}H_{22}O_4N_4$ requires C, 60·3; H, 6·1; N, 15·6%).

(*b*) See p. 66.

Triethyl Heptane-1,6,6-*tricarboxylate* (IX).—Ethyl 6-bromohexanoate (70 g.) was refluxed for 8 hr. with diethyl methylmalonate in the presence of sodium (7·2 g.) in ethanol (100 c.c.). The *product* (85 g.) had b. p. 165—168°/3 mm. (Found: C, 60·5; H, 8·5. $C_{16}H_{28}O_6$ requires C, 60·7; H, 8·9%).

Diethyl α-Methylsuberate.—(*a*) The above product (IX) (85 g.) was refluxed for 17 hr. with hydrochloric (450 c.c.) and acetic acid (85 c.c.). The low-boiling products were distilled off under reduced pressure and the residue was esterified. Diethyl α-methylsuberate (60 g.) had b. p. 135—140°/6 mm.

(*b*) The product (IX) (72 g.), dissolved in ethanol (100 c.c.), was refluxed for 10 hr. with 20% aqueous solution of potassium hydroxide (66 g.). The substituted malonic acid so obtained [m. p. 141° (decomp.)] was decarboxylated and the residue esterified, to afford *diethyl α-methylsuberate* (50 g.) (Found: C, 63·6; H, 9·5. $C_{13}H_{24}O_4$ requires C, 63·9; H, 9·8%).

Ethyl 3-*Methyl*-2-*oxocycloheptanecarboxylate* (XI).—Diethyl α-methylsuberate (49 g.) in xylene (100 c.c.) was cyclised with dry potassium t-butoxide [from potassium (9 g.)] in boiling xylene (500 c.c.) during 4 hr. by the high-dilution technique described above. It gave a colourless *ester* (30 g.), b. p. 115—116°/6 mm. (purple colour with alcoholic ferric chloride) (Found: C, 66·8; H, 8·9. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%).

A fraction (3 g.) of this product was hydrolysed with hydrochloric (12 c.c.) and acetic acid (2 c.c.) to afford 2-methylcycloheptanone (1·7 g.), a liquid with a strong peppermint smell, whose semicarbazone, crystallised from dilute alcohol, had m. p. 131—132° (lit., 129—131°).

Ethyl 3-*Methyl*-2-*oxo*-1-2′-*oxobutylcycloheptanecarboxylate* (XII).—The ester (XI) (10 g.) was allowed to react overnight with sodium dust (1 g.) under dry benzene (50 c.c.). Next, bromomethyl ethyl ketone (7·5 g.) was added to the thoroughly chilled mixture, and the whole was kept cold for 2 hr., then refluxed on a water-bath for 4 hr. The *product* (XII) (5·5 g.) had b. p. 155—160°/5 mm. (Found: C, 67·5; H, 9·0. $C_{15}H_{24}O_4$ requires C, 67·2; H, 9·0%).

2,3,4,5,6,7,8,10-*Octahydro*-1,8-*dimethyl*-2-*oxoazulene* {6,8-*Dimethylbicyclo*[5,3,0]*dec*-7-*en*-9-*one*} (XIII).—The ester (XII) (4·5 g.) was refluxed for 20 hr. under nitrogen with potassium hydroxide (4 g.) in methanol (50 c.c.). The cooled mixture was acidified with acetic acid, methanol was removed on the steam-bath, and the residue diluted with water and extracted with ether to afford the product (XIII) (1·7 g.), b. p. 110°/3 mm., $\lambda_{max.}$ 242 mμ (log ε 4·1). The 2,4-*dinitrophenylhydrazone* crystallised from ethyl acetate as rosettes of red needles, m. p. 161° (Found: C, 60·0; H, 6·0; N, 15·9. $C_{18}H_{22}O_4N_4$ requires C, 60·3; H, 6·1; N, 15·6%). The *semicarbazone* had m. p. 212° (from alcohol) (Found: C, 66·4; H, 9·1; N, 17·7. $C_{13}H_{21}ON_3$ requires C, 66·4; H, 8·9; N, 17·9%).

Ethyl α-(1-*Ethoxycarbonyl*-3-*methyl*-2-*oxocycloheptyl*)*propionate* (XIV).—Diethyl α-methylsuberate (50 g.) was cyclised as described above, but at the end of the reaction more xylene was distilled off until the total volume of the distillate amounted to about 300 c.c. The mixture was cooled and ethyl α-bromopropionate (55 g.) added. After 1 hr. at room temperature with occasional shaking, the mixture was heated at 100—110° for 5 hr. On being worked up in the usual manner, it gave the desired *product* (46 g.), b. p. 156—160°/4 mm. (Found: C, 64·2; H, 8·3. $C_{16}H_{26}O_5$ requires C, 64·4; H, 8·7%).

α-(3-*Methyl*-2-*oxocycloheptyl*)*propionic Acid* (XV).—The ester (XIV) (24 g.), barium hydroxide (70 g.), and methanol (280 c.c.) were refluxed for 20 hr. Excess of methanol was then distilled off and the residue acidified with cold dilute sulphuric acid. Extraction wih ether and distillation afforded the *acid* (14 g.), b. p. 141—142°/0·5 mm. (Found: C, 66·8; H, 9·0. $C_{11}H_{18}O_3$ requires C, 66·7; H, 9·1%).

4,5,6,7,8,8*a*-*Hexahydro*-3,8-*dimethyl*-2H-*cyclohepta*[b]*furan*-2-*one* (XVI).—The keto-acid (XV) (6·5 g.) and acetic anhydride (30 c.c.) were refluxed under nitrogen for 4 hr. with sodium acetate (50 mg.). Acetic anhydride was then distilled off under reduced pressure. The residue afforded the *lactone* (XVI) (5·5 g.), b. p. 125—130°/4 mm. $\lambda_{max.}$ 220 mμ (log ε 4·05) (Found: C, 72·9; H, 8·8. $C_{11}H_{16}O_2$ requires C, 73·3; H, 8·9%).

The Azulene Derivative (II) (cf. p. 65).—(*b*) Methylmagnesium iodide (from magnesium, 600 mg.) in ether (12 c.c.) was added in 45 min. under nitrogen to a chilled solution of the lactone (XVI) (4 g.) in benzene (22 c.c.) and ether (22 c.c.), stirred for a further 20 min., then slowly treated with cold dilute acetic acid. The organic layer was separated and washed with water, 2% sodium carbonate solution, and water, and evaporated. The residue was refluxed under nitrogen with potassium hydroxide (3·5 g.) in methanol (70 c.c.) for 4 hr. The cooled mixture was acidified with acetic acid, methanol was removed, and the residue diluted with water and extracted with ether. The ethereal extract was washed with sodium carbonate solution [whence the original keto-acid (1 g.) was recovered]. The neutral fraction on distillation afforded two fractions: (i) B. p. 85—90°/2·5 mm. (0·7 g.), $\lambda_{max.}$ 223 mμ (log ε 3·8), giving a bluish-green colour with bromine in carbon tetrachloride, and a deep green colour with sulphuric acid in acetic anhydride, and polymerising in contact with acids or on storage, which showed it to be 5,6,7,8-*tetrahydro*-2,3,8-*trimethyl*-4H-*cyclohepta*[b]*furan* (XVII) (Found: C, 80·5; H, 10·1. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%). (ii) The azulene derivative (II), b. p. 115—118°/2·5 mm. (1·4 g.), $\lambda_{max.}$ 242 mμ (log ε 4·1), whose 2,4-dinitrophenylhydrazone crystallised from ethyl acetate as red needles, m. p. 176—177° alone or mixed with the sample described above. The *semicarbazone* had m. p. 166° (from alcohol) (Found: C, 66·5; H, 9·0; N, 17·8. $C_{13}H_{21}ON_3$ requires C, 66·4; H, 8·9; N, 17·9%).

(*c*) α-Bromoethyl methyl ketone (7·5 g.) was added to a chilled solution of the sodio-derivative prepared from ethyl 3-methyl-2-oxocycloheptanecarboxylate (10 g.) and sodium dust (1 g.) under benzene (50 c.c.). After being kept cold for 2 hr. the mixture was refluxed on the water-bath for 4 hr., cooled, and washed with water, the solvent was removed, and the dark-brown residue distilled. The starting ester (4 g.) was recovered and a pale yellow liquid (*ca.* 2 g.), b. p. 145—165°/5 mm. was obtained; a tar (*ca.* 5 g.) was left in the flask. The distilled product was contaminated with bromine, so it was refluxed with zinc dust and acetic acid. The bromine-free product was then cyclised with methanolic potassium hydroxide, as described earlier. The product (II) (500 mg.) had $\lambda_{max.}$ 242 mμ (log ε 4·0). The 2,4-dinitrophenylhydrazone, after repeated crystallisation from ethyl acetate or ethyl acetate–alcohol, melted at 175—176° alone or mixed with the sample described in the previous paragraph.

Analyses were carried out by Mrs. Chhabi Dutta at the Micro-analytical Laboratory of the University College of Science, Calcutta, and by Mr. Akhil Bandhu Dutta at the analytical section of this Institute.

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