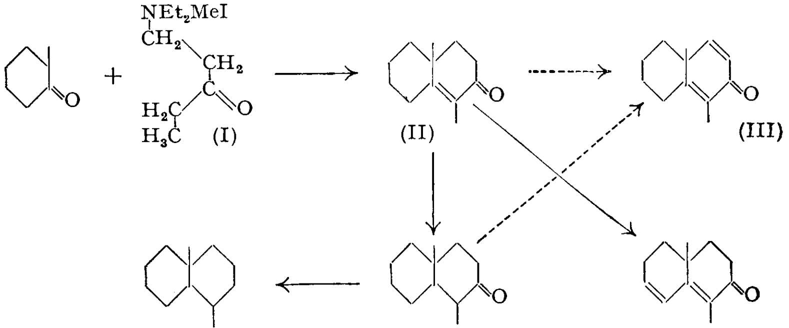
263. *Experiments on the Synthesis of Santonin. Part II.* The Preparation of Compounds containing the Dienone System present in Santonin.*

By F. D. Gunstone and R. M. Heggie.

Attempts to prepare 2 : 5 : 6 : 7 : 8 : 10-hexahydro-2-keto-1 : 10-dimethylnaphthalene (III) from the 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-octahydro-ketone (II) or the decahydro-ketone (V) have failed although the hexahydro-10-monomethyl-ketone (VII) was prepared by the methods attempted for the conversion of (V) into (III). Condensation of 2-methyl*cyclo*hexanone with ethyl ethynyl ketone has given (III) in small yield.

Having prepared the lactone of α-(2-hydroxy-3-keto*cyclo*hexyl)propionic acid [formula (IV) of Part I *] we turned our attention to the dienone system present in santonin, and this paper describes the attempts to prepare 2 : 5 : 6 : 7 : 8 : 10-hexahydro-2-keto-1 : 10-dimethylnaphthalene (III).

Propionyl chloride condense with ethylene in presence of aluminium chloride in chloroform, giving 1-chloropentan-3-one (McMahon, Roper, Untermohlen, Hasek, Harris, and Brant, *J. Amer. Chem. Soc.*, 1948, **70**, 2971), which with diethylamine (Adamson, McQuillin, Robinson, and Simonsen, *J.*, 1937, 1576) and then methyl iodide (Wilds and Shunk, *J. Amer. Chem. Soc.*, 1943, **65**, 469) gave 1-diethylaminopentan-3-one methiodide (I). Condensation of this with 2-methyl*cyclo*hexanone by the method of du Feu, McQuillin, and Robinson (*J.*, 1937, 53) yielded 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-octahydro-2-keto-1 : 10-dimethylnaphthalene (II).



It was hoped that the mono-unsaturated product (II) would yield the required dienone (III) by reaction with *N*-bromosuccinimide and subsequent dehydrobromination. The carbonyl derivatives thus obtained had the required molecular formulæ but their spectra showed the ketone to be (IV) rather than (III); this was not without precedent since similar reactions in the steroid series yield this extended dienone system (cf. Djerassi, *Chem. Reviews*, 1948, **43**, 271). Attempts were then made to add bromine to (II) in the hope that the dibromide would react with *N*-bromosuccinimide and then yield (III) by subsequent loss of one molecule each of hydrogen bromide and bromine (cf. Plattner, Heusser, and Segre, *Helv. Chim. Acta*, 1948, **31**, 249): however, spontaneous dehydrobromination occurred during the initial addition and the product was again (IV). Compounds containing the crossed conjugated dienone system present in (III) absorb at *ca.* 240 mμ (log ε *ca.* 4·1) (Ruzicka, Cohen, Furter, and van der Sluys-Veer, *Helv. Chim. Acta*, 1938, **21**, 1735; Woodward and Singh, *J. Amer. Chem. Soc.*, 1950, **72**, 494; Woodward, *ibid.*, 1940, **62**, 1208; Djerassi and Ryan, *ibid.*, 1949, **71**, 1000) whilst compounds in which the extended dienone system (IV) occurs absorb at *ca.* 280 mμ (log ε *ca.* 4·1) (Evans and Gillam, *J.*, 1945, 432; Djerassi and Ryan, *loc. cit.*, Birch, Murray, and Smith, *J.*, 1951, 1945). The product from these reactions had a high absorption

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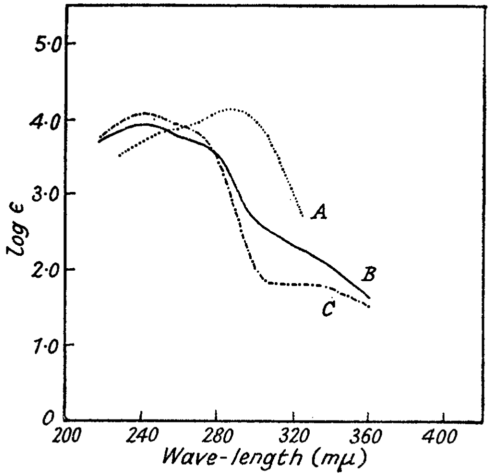
* Part I, *J.*, 1952, 1354.

band (see Fig. 1) at 286 mμ (log ε 4·13) and an inflexion at 249 mμ (log ε 3·83), indicating that the product was mainly (IV) but possibly contained an impurity which gave rise to the inflexion.

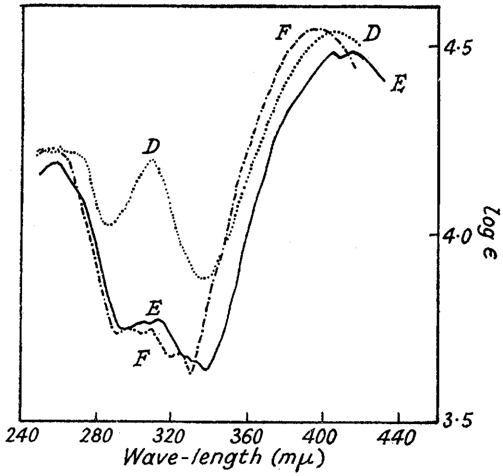
Catalytic hydrogenation of santonin gives dihydrosantonin (Bargellini, *Atti R. Accad. Lincei*, 1912, **22**, 443) which is an analogue of (II). Efforts to repeat this result with palladium–charcoal or Raney nickel, however, yielded almost entirely tetra- and hexahydrosantonin respectively.

FIG. 1.



A, 2 : 3 : 4 : 5 : 6 : 10-*Hexahydro-2-keto-1* : 10-*dimethylnaphthalene* (IV).
B, 2 : 5 : 6 : 7 : 8 : 10-*Hexahydro-2-keto-1* : 10-*dimethylnaphthalene* (III).
C, *Santonin.*

FIG. 2.



2 : 4-*Dinitrophenylhydrazones of*:
D, (IV); *E*, (III); *F*, *Santonin.*

The condensation product (II) was highly coloured and its reduction with palladium–charcoal was extremely slow. After various failures, treatment with Raney nickel was found to give a colourless ketone, the absorption spectrum showing that no reduction had occurred. The purified product readily absorbed hydrogen in the presence of palladium–charcoal yielding 2-keto-1 : 10-dimethyldecalin (V). The ultra-violet absorption spectrum showed that this contained only a very small quantity (<1%) of unsaturated ketone, most of which was removed by treatment with dilute potassium permanganate. This ketone was reduced by the Clemmensen procedure to *cis*-1 : 10-dimethyldecalin (VI) (Linstead, Millidge, and Walpole, *J.*, 1937, 1140; Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1151, 1171).

It was hoped that bromination-dehydrobromination of (V) might result in the introduction of double bonds first into the 3 : 4-position and only then into the 1 : 9-position, yielding (III). The experiments and results are shown in the Table. The products from reaction of *N*-bromosuccinimide (1 mol.) and subsequent dehydro-

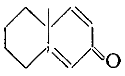
Products obtained by bromination-dehydrobromination (*pyridine or collidine*) *of* (V).

Brominating agent	Yield (g.)[1]	$\lambda_{max.}$ (mμ) (log ε) in ethanol	
$(CH_2{\cdot}CO)_2NBr$ (1 mol.) (*a*)	0·51	245 (3·74)	285 (3·12)
(*b*)	0·55	238 (3·64)	285 (3·06)
„ (2 mols.) (*a*)	0·50	232·5 (3·86)	280 (3·59)
(*b*)	0·30	231 (3·89)	289 (3·63)
Br–AcOH (2 mols.)	0·38	222 (3·93)[2]	293 (3·89)
Br–CCl_4 (2 mols.)	0·34	230 (3·90)	300 (3·47)
Br–AcOH (3 mols.)	0·13	226 (3·59)	287 (3·82)
$(CH_2{\cdot}CO)_2NBr$ (2 mols.)[3]	0·06	230 (3·77)	288 (4·05)

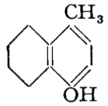
[1] Yield from 1 g. of starting material. [2] Inflexion at 245 mμ (log ε 3·83). [3] Experiment carried out on (II).

bromination had absorption bands at 245 and 285 mμ. The former is close to the value expected from the dienone (V) or the monounsaturated ketone (II), but repetition of the experiment gave a lower value (238 mμ). This suggested that the product was actually a variable mixture [probably of the Δ^3- (225 ± 5 mμ; cf. Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123) and the $\Delta^{1(9)}$-compound (248 mμ)]. The absorption band at 285 mμ indicated the presence of more unsaturated compounds. 3-Keto-steroids with the *cis*-configuration about rings A and B are known to brominate in the 4-position [1-position in (V)] (Djerassi and Scholtz, *Experientia*, 1947, **3**, 107), and since (V) has been shown to have the *cis*-configuration it is possible that bromination has taken place partly at the 1- and partly at the 3-position. Bromination with 2 mols. of *N*-bromosuccinimide might yield the 1 : 3-dibromo-compound as precursor of the required dienone. In fact bromination with 2 mols. of *N*-bromosuccinimide or of bromine in acetic acid or carbon tetrachloride solution again gave mixtures. The absorption band of high wave-length (280—300 mμ) is characteristic of the system CH:CH·CH:CH·CO and may be due to the presence of the dienone (IV) or the 1(9) : 3 : 7-trienone, which could result if the 1-bromo-compound suffered spontaneous dehydrobromination. The absorption at lower wave-length (222—232 mμ) is probably due to one or more of the $\Delta^{1(9)}$ and Δ^3-monounsaturated ketones and the 1(9) : 3-dienone. Finally an effort was made to prepare the 1(9) : 3 : 7-trienone from (II) and from (V) but whilst the absorption band at higher wave-lengths was augmented the product, obtained in low yield, was probably still a mixture.

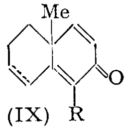
Some of these methods, which have failed to yield the required dienone, are known to yield the system when applied to analogous systems in the sterol series (see Fieser and Fieser, "Natural Products related to Phenanthrene," 3rd edn., 1949, New York). This difference may be due to some peculiarity in the chemistry of the steroids or to the presence of the 1-methyl group (4-methyl in the sterol molecule). Whilst this work was in progress the monomethyl compound (VII) was prepared by Woodward and Singh (*J. Amer. Chem. Soc.*, 1950, **72**, 494) by other methods. We have now prepared (VII) by methods analogous to those already described. It appears then that failure of these methods when applied to (V) is connected with the presence of the 1-methyl group. 2-Keto-10-methyldecalin (du Feu *et al.*, *loc. cit.*), when brominated in acetic acid solution, and subsequently dehydrobrominated (collidine), gave (VII). Similar results were obtained in carbon tetrachloride solution and less satisfactory results with *N*-bromosuccinimide.



(VII)



(VIII)



(IX)

Paranjape, Phalnikar, Bhide, and Nargund (*Rasayanam*, 1943, **1**, 233; *Chem. Abstr.*, 1944, **38**, 4266) also claim to have prepared (VII). The structure of their product depended on the characterisation of the acid-rearrangement product as 5 : 6 : 7 : 8-tetrahydro-4-methyl-2-naphthol. Woodward and Singh (*loc. cit.*), however, have shown that (VII) yields (VIII) on rearrangement and we have confirmed this. It appears from the work of Woodward and Singh (*loc. cit.*) and also of Djerassi *et al.* (*J. Amer. Chem. Soc.*, 1951, **73**, 990) that the nature of the dienone–phenol rearrangement product of compounds containing the structure (IX) depends (*a*) on whether R is H or alkyl and (*b*) on the presence or absence of an additional conjugated double bond in the adjacent ring as shown in (IX). It is not clear what happens when there is no angular methyl group or additional double bond and when R = H. Galinovsky (*Ber.*, 1943, **76**, 230) however has shown that bromination and subsequent dehydrobromination of β-tetralone afford directly β-tetralol. We have confirmed Galinovsky's observation, thus showing that the Woodward–Singh type of rearrangement, which would yield α-tetralol, does not apply in this case.

The methods used by Woodward and Singh (*loc. cit.*) to prepare 2 : 5 : 6 : 7 : 8 : 10-hexahydro-2-keto-10-methylnaphthalene involved (*a*) condensation of 2-formyl-2-methyl-*cyclo*hexanone with acetone in the presence of piperidine acetate (cf. Paranjape *et al.*, *loc. cit.*, and Wilds and Djerassi, *J. Amer. Chem. Soc.*, 1946, **68**, 1715) and (*b*) condensation of 2-methyl*cyclo*hexanone with ethynyl methyl ketone in the presence of sodium hydride. Condensation of 2-formyl-2-methyl*cyclo*hexanone with ethyl methyl ketone gave a fraction which may have contained (III). This was obtained, however, in very small yield and was possibly a mixture of position isomers. Paranjape *et al.* (*loc. cit.*) claim to have obtained (III) by this method but in view of other criticisms made concerning this work (see p. 1439 and especially Wilds and Djerassi, *loc. cit.*) little reliance can be placed on this.

By the use of previously described methods (Heilbron, Jones, and Weedon, *J.*, 1945, 81; Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39) the hitherto unknown ethyl ethynyl ketone has been prepared. It condensed with 2-methyl*cyclo*hexanone in the presence of sodamide to give a liquid, albeit in low yield, having the properties expected of the desired dienone (III). Hydrogenation of the product afforded a liquid ketone, which gave the 2 : 4-dinitrophenylhydrazone of (V), thus proving that the compound has the correct skeletal structure. Two ethylenic linkages are indicated by the quantitative hydrogenation and by analysis of the 2 : 4-dinitrophenylhydrazone. The position of these double bonds is clearly shown to be as in (III) from the absorption spectra (see Figs. 1 and 2) of the ketone and of its 2 : 4-dinitrophenylhydrazone. The dinitrophenylhydrazone obviously differs from that of (IV). We have not yet been able to obtain any solid tetralol from the alkali-soluble liquid resulting from the acid rearrangement of (III).

This work is being continued.

EXPERIMENTAL

M. p.s are uncorrected. Absorption spectra were determined with a Unicam quartz spectrophotometer, ethanol or chloroform being used as solvent.

1-*Diethylaminopentan*-3-*one Methiodide* (I).—Propionyl chloride and ethylene reacted in the presence of aluminium chloride in chloroform solution (McMahon *et al.*, *loc. cit.*) to give 1-chloropentan-3-one (48%), b. p. 43—47°/3 mm., n_D^{15} 1·4461 (lit., n_D^{20} 1·4361), and thence 1-carbamyl-3-ethylpyrazoline, m. p. 94° (picrate, m. p. 132—134°) (Maire, *Bull. Soc. chim.*, 1908, **3**, 272, gives 96° and 137° respectively). The chloro-ketone and diethylamine (Adamson *et al.*, *loc. cit.*) yielded 1-diethylaminopentan-3-one (80%), b. p. 85—89°/17 mm., n_D^{16} 1·4441 (semicarbazone, m. p. 97—99°; picrate, m. p. 76—78°; Blaise and Maire, *Bull. Soc. chim.*, 1908, **3**, 543, report 100° and 78° respectively), with an equal weight of methyl iodide (cf. Wilds and Shunk, *loc. cit.*), this afforded the methiodide (I) (92%), which was used without further purification.

The initial condensation, effected in excess of propionyl chloride as solvent, gave ethyl vinyl ketone (69%).

2 : 3 : 4 : 5 : 6 : 8 : 10-*Octahydro*-2-*keto*-1 : 10-*dimethylnaphthalene* (II).—2-Methyl*cyclo*hexanone (99 g.), sodamide (18·4 g.), and ether (150 ml.) were stirred for 4 hours at room temperature in a stream of dry nitrogen. 1-Diethylaminopentan-3-one methiodide (135 g.) in ethanol (60 ml.) was added gradually and stirring continued for 4 hours at room temperature and for 2 hours at the b. p. After addition of dilute hydrochloric acid the solution was extracted (ether), dried, and distilled. The octahydroketonaphthalene (II) 37 g. (46%), b p. 99—100°/1 mm., thus obtained was purified by stirring it with Raney nickel in ethanol for 30 minutes and then redistilling it; n_D^{20} 1·5260 and an absorption max. at 248 mμ (log ε 4·14), inflexion at 290 mμ (log ε 2·27) in ethanol, were then observed. The 2 : 4-*dinitrophenylhydrazone* had m. p. 198—199°, scarlet plates from ethanol (Found : C, 60·2; H, 6·1; N, 15·9. $C_{18}H_{22}O_4N_4$ requires C, 60·3; H, 6·2; N, 15·6%), absorption max. at 260 (log ε 4·28) and 394 mμ (log ε 4·47) and inflexion at 296 mμ (log ε 4·06) in chloroform. The *semicarbazone* had m. p. 203—204°, colourless prisms from ethanol [Found : C, 66·3; H, 9·1; N, 17·9. $C_{13}H_{21}ON_3$ requires C, 66·4; H, 9·0; N, 17·9%], absorption max. at 271 mμ (log ε 4·47) in ethanol.

Bromination of (II).—(a) N-*Bromosuccinimide*. *N*-Bromosuccinimide (4·45 g.) was added to a solution of the octahydro-ketone (4·45 g.) in carbon tetrachloride (25 ml.) and the mixture refluxed for 30 minutes. Succinimide (2·41 g.) was removed from the cold solution, as was the solvent, and the residue refluxed with pyridine (10 ml.) for 2 hours. The product was 2 : 3 : 4 : 5 : 6 : 10-hexahydro-2-keto-1 : 10-dimethylnaphthalene (2·53 g., 58%), b. p. 106—108°/1 mm., n_D^{20} 1·5590 [2 : 4-*dinitrophenylhydrazone*, m. p. 216°, dark red plates from acetic acid (Found : C, 60·3; H, 5·9; N, 15·6. $C_{18}H_{20}O_4N_4$ requires C, 60·7; H, 5·7; N, 15·7%), absorption max. at 251, 261, 311, and 407 mμ (log ε 4·22, 4·22, 4·19, and 4·53 respectively) and inflexion at 272 mμ (log ε 4·20) in chloroform; semicarbazone, m. p. 216—217°, absorption max. at 300 mμ (log ε 4·54) in ethanol].

(b) *Bromine.* Bromine (1 ml.) in carbon tetrachloride (10 ml.) was added to a cooled, stirred solution of the octahydro-ketone (3·56 g.) in the same solvent (50 ml.). The temperature slowly rose to room temperature (5—6 hours), the solvent was removed and the residue on distillation afforded the above hexahydro-ketone (2 g., 55%), b. p. 118—126°/1·5 mm. [2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 214°; *semicarbazone,* m. p. and mixed m. p. 212—213° (Found: C, 67·1; H, 8·2; N, 18·0. $C_{13}H_{19}ON_3$ requires C, 66·9; H, 8·2; N, 18·0%)].

2-*Keto*-1 : 10-*dimethyldecalin* (V).—The octahydro-2-keto-1 : 10-dimethylnaphthalene (II) (20 g.) was hydrogenated (palladium–charcoal–ethanol), 2·42 l. of hydrogen being absorbed at N.T.P. (theory, 2·51 l.). The solvent and catalyst were removed and the residue was distilled. The distillate (19·13 g., 95%), b. p. 90—91°/0·9 mm., n_D^{19} 1·4961, was purified by occasional shaking with 0·1N-potassium permanganate (400 ml.) during 2 hours. After redistillation 2-keto-1 : 10-dimethyldecalin (85%), b. p. 76—78°/0·5 mm., n_D^{19} 1·4945, was obtained; it gave a yellow 2 : 4-*dinitrophenylhydrazone,* m. p. 186°, from ethanol (Found: C, 59·9; H, 6·6. $C_{18}H_{24}O_4N_4$ requires C, 60·0; H, 6·7%), and a *semicarbazone,* m. p. 189—190°, (plates from ethanol (Found: C, 66·0; H, 9·5; N, 17·7. $C_{13}H_{23}ON_3$ requires C, 65·8; H, 9·8; N, 17·7%).

cis-1 : 10-*Dimethyldecalin* (VI).—2-Keto-1 : 10-dimethyldecalin (4 g.) in toluene (10 ml.) was heated under reflux for 30 hours with zinc (12 g.), water (7·5 ml.) and concentrated hydrochloric acid (17·5 ml. plus 5 × 5 ml. added during refluxing). The reaction mixture after dilution and extraction gave *cis*-1 : 10-dimethyldecalin, b. p. 98—99°/15 mm., n_D^{20} 1·4848. These properties were hardly changed after the material had been heated with dilute potassium permanganate solution and distilled over sodium, *viz.,* b. p. 85—90°/12 mm., (bath-temp.) n_D^{16} 1·4849 (Linstead, Millidge, and Walpole, *J.,* 1937, 1140, give b. p. 84—85°/10 mm., n_D^{16} 1·4787, and Ruzicka *et al., Helv. Chim. Acta,* 1931, **14**, 1151, 1171, give b. p. 85°/12 mm., n_D^{20} 1·4812) (Found: C, 86·7; H, 13·0. Calc. for $C_{12}H_{22}$: C, 86·7; H, 13·3%).

trans-1 : 10-*Dimethyldecalin.*—1 G. each of *cis*-1 : 10-dimethyldecalin and aluminium chloride were left together in a desiccator for 2 days. Dilute hydrochloric acid was then added and the *trans*-form extracted and distilled. It (0·63 g.) had b. p. 86—88°/14 mm. and n_D^{22} 1·4691. The treatment with aluminium chloride was repeated and the product, distilled from sodium, then had b. p. 76—78°/11 mm. (bath-temp.), n_D^{18} 1·4690 (Linstead *et al.,* and Ruzicka *et al., loc. cit.,* give 76—78°/10 mm., n_D^{15} 1·4658 and 77—78°/12 mm., n_D^{20} 1·4659 respectively) (Found: C, 86·6; H, 13·1%).

Bromination-Dehydrobromination of 2-*Keto*-1 : 10-*dimethyldecalin* (V). *General Procedure.*—*N*-Bromosuccinimide was added to a solution of 2-keto-1 : 10-dimethyldecalin in carbon tetrachloride and the mixture refluxed until reaction was complete. Succinimide was removed from the cold solution, followed by the solvent, and the residue, after dehydrobromination by refluxing pyridine or quinoline, was extracted and distilled. Alternatively 2-keto-1 : 10-dimethyldecalin, dissolved in carbon tetrachloride, was treated with bromine in the same solvent at −5° to +5°, or the saturated ketone dissolved in acetic acid was treated with bromine in acetic acid (with addition of 3—4 drops of a 4N-solution of hydrogen bromide in acetic acid) at room temperature with subsequent heating to 50°. In the last two cases the solvent was next removed under reduced pressure and the bromo-compound dehydrobrominated as above. The product was finally distilled under reduced pressure (boiling range for all products, 65—95°/<1 mm.), and examined spectroscopically in ethanol. The results are summarised in the Table.

2-*Keto*-10-*methyldecalin.*—1-Diethylaminobutan-3-one, prepared by Wilds and Shunk's method (*loc. cit.*), when treated with 2-methyl*cyclo*hexanone in the presence of sodamide, following the directions of du Feu *et al.* (*loc. cit.*), gave 2 : 3 : 4 : 5 : 6 : 7 : 8 : 10-octahydro-2-keto-10-methylnaphthalene (25%) which, when purified by Raney nickel as already described, had b. p. 72—74°/0·2 mm., n_D^{19} 1·5154. This was reduced catalytically (palladium–charcoal) to 2-keto-10-methyldecalin (89%), b. p. 86—90°/1·5 mm., n_D^{15} 1·4922. Some of the solid isomer, m. p. 47—48°, could be crystallised from this liquid mixture of isomers, but the liquid distillate was used in the subsequent experiments. The 2 : 4-dinitrophenylhydrazone had m. p. 113—116°; du Feu *et al.* give 152—152·5° for the derivative obtained from the solid ketone; Woodward and Singh (*loc. cit.*) give 125·5—127° for the derivative obtained from the ketone, itself prepared by an alternative procedure. The latter may be the derivative of another pure isomer or, like ours, the derivative of a mixture of stereoisomers.

2 : 5 : 6 : 7 : 8 : 10-*Hexahydro*-2-*keto*-10-*methylnaphthalene* (VII).—Bromine (5·79 g.) in acetic acid (35 ml.) was added to 2-keto-10-methyldecalin (3 g.) in acetic acid (45 ml.). The colour faded to pale yellow after 15 minutes; the solution was then heated to 50° and left at room temperature for 3 hours. After removal of the solvent under reduced pressure the residue was refluxed with collidine (15 ml.) for 70 minutes and the product extracted.

2 : 5 : 6 : 7 : 8 : 10-Hexahydro-2-keto-10-methylnaphthalene (VII) (1·01 g., 34·5%) was distilled, having b. p. 100—110°/*ca.* 0·9 mm., n_D^{16} 1·5507, absorption max. at 243 mμ (log ε 3·89) in ethanol [Woodward and Singh, *loc. cit.*, give b. p. 123—124°/3 mm., absorption max. at 240 mμ (log ε 4·1)]. Bromination in carbon tetrachloride solution or with *N*-bromosuccinimide gave less pure products but the presence of the required dienone was shown by the isolation of the acid rearrangement product (see below).

Catalytic reduction (palladium–charcoal) afforded 2-keto-10-methyldecalin (82%) (hydrogen uptake, 71 ml. at N.T.P.; theory, 69 ml.) (2 : 4-dinitrophenylhydrazone, m. p. 113—115° alone or mixed with that obtained above).

5 : 6 : 7 : 8-*Tetrahydro*-4-*methyl*-1-*naphthol* (VIII).—The foregoing hexahydroketone was converted by Woodward and Singh's method (*loc. cit.*) into the acetate (36%), m. p. 80—81°, and then the tetralol (VIII), m. p. 87·8—88·5°. Woodward and Singh (*loc. cit.*) gave m. p. 82° and 87·5—88·5° respectively.

2-*Formyl*-2-*methyl*cyclo*hexanone* (cf. Sen and Mondal, *J. Indian Chem. Soc.*, 1928, **5**, 609).—2-Formyl*cyclo*hexanone (30 g.) (Auwers, Buschmann, and Heidenreich, *Annalen*, 1924, **435**, 277) was converted into its sodio-derivative by sodium (5·74 g.) in benzene (225 ml.) during 30 hours. The filtered and washed salt was then heated with methyl iodide (46 ml.) and benzene (120 ml.) at 95—100° for 12 hours in a steel bomb. Distillation of the filtered reaction mixture gave 2-formyl-2-methyl*cyclo*hexanone (11·9 g., 36%), b. p. 29—31°/<1 mm., $n_D^{17.5}$ 1·4728 (Cornforth, Cornforth, and Dewar, *Nature*, 1944, **153**, 317, give b. p. 47°/0·05 mm., n_D^{18} 1·4683).

Condensation of 2-*Formyl*-2-*methyl*cyclo*hexanone with Ethyl Methyl Ketone.*—Condensation of 2-formyl-2-methyl*cyclo*hexanone (12 g.) with ethyl methyl ketone (125 ml.) in presence of piperidine acetate by Woodward and Singh's method (*loc. cit.*) gave only 0·35 g. of possible condensation product.

Ethyl Ethynyl Ketone.—Interaction of propaldehyde (116 g.) with sodium acetylide (from 47 g. of sodium) according to the procedure of Heilbron, Jones, and Weedon (*loc. cit.*) gave ethylethynylcarbinol (pent-1-yn-3-ol) (75 g., 45%), b. p. 126—129°/758 mm., n_D^{18} 1·4344 (3 : 5-dinitrobenzoate, m. p. 87°; McGrew and Adams, *J. Amer. Chem. Soc.*, 1937, **59**, 1497, give m. p. 91°). Oxidation (cf. Bowden, Heilbron, Jones, and Weedon, *loc. cit.*) yielded ethyl ethynyl ketone (28 g., 45%), b. p. 105—107°, n_D^{19} 1·4188 [2 : 4-*dinitrophenylhydrazone*, yellow platelets (from ethanol), m. p. 149—150·5° (Found: C, 50·6; H, 4·0; N, 20·6. $C_{11}H_{10}O_4N_4$ requires C, 50·4; H, 3·8; N, 21·4%); p-*nitrophenylhydrazone*, yellow needles (from 50% aqueous methanol), m. p. 97—97·5° (Found: C, 60·8; H, 5·4. $C_{11}H_{11}O_2N_3$ requires C, 60·8; H, 5·1%)].

Catalytic reduction over palladium–charcoal (uptake, 231 ml. at N.T.P.; theor., 273 ml.) gave diethyl ketone, identified as its 2 : 4-dinitrophenylhydrazone.

2 : 5 : 6 : 7 : 8 : 10-*Hexahydro*-2-*keto*-1 : 10-*dimethylnaphthalene* (III).—2-Methyl*cyclo*hexanone (30 g.), sodamide (7·8 g.), and anhydrous ether (200 ml.) were stirred with glass beads in a stream of dry nitrogen for 30 hours, extra ether being added to replace that lost by evaporation. Ethyl ethynyl ketone (16·4 g.) in anhydrous ether (50 ml.) was then added gradually with stirring which was continued for 4 hours at 0° and for 6 hours at room temperature. The reaction mixture, decomposed in the cold with 2N-hydrochloric acid, and extracted with ether, gave on distillation a fraction which redistilled at 108—110°/1 mm. (1·79 g., 5%, equiv. to 7·6% calc. on unrecovered 2-methyl*cyclo*hexanone). This was the desired hexahydro-2-keto-1 : 10-dimethylnaphthalene (III), n_D^{20} 1·5322 [2 : 4-*dinitrophenylhydrazone*, dark red plates (from *n*-butanol), m. p. 238—239° (Found: C, 60·4; H, 5·5; N, 15·9. $C_{18}H_{20}O_4N_4$ requires C, 60·7; H, 5·7; N, 15·7%)]. It (0·5 g.) was reduced catalytically (palladium–charcoal; uptake, 109 ml. at N.T.P.; theor., 127 ml.) to 2-keto-1 : 10-dimethyldecalin, b. p. 75—85°/0·5 mm., n_D^{20} 1·4915 (2 : 4-dinitrophenylhydrazone, m. p. 180—181° raised to 184—186° when mixed with a previous sample of m. p. 183—185°).

[With J. R. Davidson.] ar-2-*Tetralol from* 2-*Decalone* (cf. Galinovsky, *loc. cit.*).—2-Decalone (1·11 g.) (du Feu *et al.*, *loc. cit.*) was treated with bromine in acetic acid as already described and subsequently with collidine. The alkali-soluble portion of the product solidified after distillation [150—160°/8 mm. (bath-temp.)] and after crystallisation from light petroleum (b. p. 60—80°) melted at 59·5—60°; its benzoate had m. p. 93—94°. For β-tetralol and its benzoate m. p.s 61—62° and 96° respectively are recorded.

We are indebted to the D.S.I.R. for a Maintenance Allowance to one of us (R. M. H.) and to Mr. J. M. L. Cameron and Miss R. H. Kennaway for the microanalyses.

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