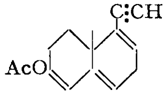
656. *Some Reactions of 3-Methyl*cyclo*pent-2-enone.*

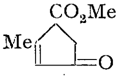
By R. M. Acheson.

Neither 3-methyl*cyclo*pent-2-enone nor methyl 4-keto-2-methyl*cyclo*pent-2-ene-1-carboxylate appears to undergo the Diels–Alder reaction. 3-Methyl*cyclo*pent-2-enone reacts with benzaldehyde to give a mixture of α-(4-keto-2-methyl*cyclo*pent-2-enyl)benzyl alcohol and 3-styryl*cyclo*pent-2-enone.

A number of *cyclo*pent-2-enone derivatives, including *cyclo*pent-2-enone itself, 5 : 5-dibromo*cyclo*pent-2-ene-1 : 4-dione, and 2-methyl*cyclo*pent-2-ene-1 : 5-dione (Dane *et al.*, *Annalen*, 1939, **537**, 246 and earlier papers), 2-methyl- (Bockemüller, U.S.P. 2,179,809; Gaddis and Butz, *J. Amer. Chem. Soc.*, 1947, **69**, 1203), and 2 : 4-dimethyl*cyclo*pent-2-enone (Nazarov and Bergel'son, *Zhur. Obschei Chim.*, 1950, **20**, 648) have been successfully used in the Diels–Alder synthesis of sterol derivatives containing the intact D ring. It was therefore hoped to build up the sterol ring system by this reaction from 3-methyl*cyclo*pent-2-enone derivatives (*e.g.*, II) by reaction with dienes of the 3 : 7 : 8 : 9-tetrahydro-1-vinyl- or 3 : 7 : 8 : 9-tetrahydro-1-ethynyl-naphthalene type (*e.g.*, I) (Acheson and Robinson, *J.*, 1952, 1127).

(I)



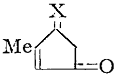


(II)

Towards this end 3-methyl*cyclo*pent-2-enone (Acheson and Robinson, *loc. cit.*) was heated with 2-methoxybutadiene and a trace of pyrogallol at 200° for 24 hours; the addition of a little diethylamine or diethylaniline did not alter the course of the reaction which yielded small quantities of a colourless solid, and an oil which gave a yellow derivative with 2 : 4-dinitrophenylhydrazine in methanolic sulphuric acid.

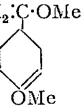
The solid did not react with 2 : 4-dinitrophenylhydrazine or semicarbazide although its infra-red absorption spectrum indicated the presence of a highly conjugated carbonyl group. It is almost certainly 3-methyl-4-(3-methyl*cyclo*pent-2-enylidene)*cyclo*pent-2-enone (IV) formed by the self-condensation of the 3-methyl*cyclo*pent-2-enone. Its ultra violet absorption [max. at 2550 (ε 8900) and 3250 Å (ε 19,050) in methanol] is more in accord with (IV) than with the isomeric (III), and (IV) is analogous to one of the products

(III)



(IV)

(V)



(VI)

obtained from 3-methyl*cyclo*pent-2-enone and benzaldehyde (see below). The third possibility, (V), is excluded as Kuhn–Röth determination indicated the presence of more than one *C*-methyl group in the molecule. A similar self-condensation product, 2-*cyclo*pentylidene*cyclo*pentanone, has been obtained from *cyclo*pentanone and sodium ethoxide (Wallach, *Ber.*, 1896, **29**, 2955).

The oily product is almost certainly 1-methoxy-4-1'-methoxyvinyl*cyclo*hexene (VI), which has been prepared by heating 2-methoxybutadiene with pyrogallol at 180—190° (Nazarov, Verkholetova, and Bergel'son, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk.*, 1948, 511) and is easily hydrolysed by dilute acid to 4-acetyl*cyclo*hexanone. The yellow 2 : 4-dinitrophenylhydrazone appears to be the bis-derivative of this diketone.

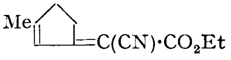
Attempts to effect a Diels–Alder condensation between methyl 4-keto-2-methyl*cyclo*pent-2-ene-1-carboxylate, prepared from the corresponding acid (Acheson and Robinson, *loc. cit.*) with diazomethane, and *cyclo*pentadiene in the presence of a trace of pyrogallol, with or without trimethylamine or trichloroacetic acid, at room temperature or at 40° were unsuccessful. *cyclo*Pentadiene similarly failed to react with 3-methyl*cyclo*pent-2-enone.

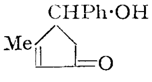
An attempt to condense 6-acetoxy-1-ethynyl-3 : 7 : 8 : 9-tetrahydro-9-methylnaphthalene (I) (Friedmann and Robinson, unpublished) with methyl 4-keto-2-methyl*cyclo*pent-2-ene-1-carboxylate (II) in the presence of a trace of pyrogallol at 155—165° for 7 hours under nitrogen gave unchanged material and small quantities of yellow gums which had no appreciable ultra-violet absorption in the region of 2750 Å. Thus little, if any, material was present containing the *cyclo*hexa-1 : 3-diene system which must be formed in a normal Diels–Alder reaction. The infra-red absorption spectra indicated that the gums were complex mixtures.

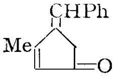
It is of interest that none of the *cyclo*pent-2-enones which undergo the Diels–Alder reaction have a methyl group in position 3, and that the introduction of a methyl group in the β-position of an αβ-unsaturated ketone which undergoes the reaction almost always reduces the yield (cf. Table V, listing Diels–Alder reactions, in "Organic Reactions," Vol. IV, p. 96).

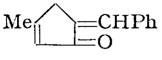
In order to see whether any cationoid activity was exhibited at position 3 in 3-methyl*cyclo*pent-2-enone this compound was treated with cold ethyl sodiocyanoacetate. None of the Michael addition product could be isolated, but ethyl α-cyano-3-methyl*cyclo*pent-2-enylideneacetate (VII) was obtained in good yield. This was stable to boiling concentrated hydrochloric acid (3 hours), and reacted slowly with bromine in hot carbon tetrachloride.

Benzaldehyde and 3-methyl*cyclo*pent-2-enone in the presence of aqueous sodium hydroxide (cf. *Org. Synth.*, Coll. Vol. 1, 1932, p. 69) gave α-(4-keto-2-methyl*cyclo*pent-2-enyl)benzyl alcohol (VIII) and a small proportion of 3-styryl*cyclo*pent-2-enone (characterised as its bright red 2 : 4-dinitrophenylhydrazone) which were separated on alumina.


(VII)


(VIII)


(IX)


(X)

The alcohol (VIII) was dehydrated to 4-benzylidene-3-methyl*cyclo*pent-2-enone (IX) by acidic reagents, and also lost water in the presence of 2 : 4-dinitrophenylhydrazine in methanolic sulphuric acid to give the dull red 2 : 4-dinitrophenylhydrazone of (IX) which was also prepared directly therefrom. The second condensation product contained no *C*-methyl group and must therefore have the structure stated, which is confirmed by the similarity of its absorption spectrum [max. at 2400 (ε 8600) and 3200 Å (ε 39,000) in methanol] with that of 6-phenylhexa-3 : 5-dien-2-one [max. at 2340 (ε 6760) and 3190 Å (ε 36,300); Wilds, Beck, Close, Djerassi, Johnson, Johnson, and Shunk, *J. Amer. Chem. Soc.*, 1947, **69**, 1993). The absorption spectrum of its 2 : 4-dinitrophenylhydrazone is also consistent with this structure [max. at 4200 Å (ε 38,700) in chloroform; octatrienal 2 : 4-dinitrophenylhydrazone, 4100 Å (ε 36,500) (Braude and Jones, *J.*, 1945, 498)].

The isomeric ketone, obtained by dehydration of the alcohol, contained one *C*-methyl group and must therefore be (IX) or (X). According to its absorption spectrum [max. at 2300 (ε 11,300) and 3000 Å (ε 18,400) in methanol] it is much less conjugated than 3-styryl*cyclo*pent-2-enone. Unfortunately the absorption spectrum of 5-methyl-1-phenylhexa-1 : 4-dien-3-one, an open-chain analogue (Esafov and Raikher, *J. Gen. Chem., U.S.S.R.*, 1943, **13**, 809), is not available for comparison. The ketone (IX or X) and 3-styryl*cyclo*pent-2-enone exhibit a higher degree of conjugation than benzylideneacetone, which has a maximum at 2860 Å (ε 23,400) (Wilds *et al., loc. cit.*). The absorption of the 2 : 4-dinitrophenylhydrazone of the ketone (IX or X) [max. at 4200 (ε 28,000) in chloroform] is very similar to that of the 3-styryl*cyclo*pentenone derivative which suggests that the conjugation in both ketones is similar and that the ketone in question is therefore (IX). There is however no recorded spectrum for a reference compound similarly conjugated to the 2 : 4-dinitrophenylhydrazone of (IX), and the less conjugated phorone 2 : 4-dinitrophenylhydrazone shows a maximum at 3950 Å (ε 24,500) (Braude and Jones, *loc. cit.*). The ketone is therefore provisionally considered to have structure (IX) which is analogous to that of the 3-methyl*cyclo*pent-2-enone self-condensation product (IV). The parent alcohol is therefore (VIII), but the alternative structures for this and its dehydration product are not excluded. The infra-red absorption spectrum of the alcohol shows that there is no appreciable interaction between the keto- and the hydroxy-group; this might take place if it had the isomeric structure. The rather short wave-length of the absorption maxima of (IX) in comparison with that of 3-styryl*cyclo*pent-2-enone may be due to stereochemical factors, and a comparison with the absorption of the *cis*- and the *trans*-form of 1-phenylbutadiene [max. at 2650—2690 (ε 18,400) and 2800 Å (ε 29,800) respectively (Grumitt and Christoph, *J. Amer. Chem. Soc.*, 1949, **71**, 4157)] is of interest in this connexion.

3-Methyl*cyclo*pent-2-enone reacted vigorously with selenium dioxide in dioxan or glacial acetic acid, to give a product containing selenium. Very little distillable material was formed, and the reaction was not further investigated.

EXPERIMENTAL

*Methyl 4-Keto-2-methyl*cyclo*pent-2-ene-1-carboxylate* (II).—4-Keto-2-methyl*cyclo*pent-2-ene-1-carboxylic acid (Acheson and Robinson, *loc. cit.*) in methanol on treatment with the theoretical quantity of ethereal diazomethane gave the *methyl* ester, b. p. 112—116°/0·5 mm., n_D^{18} 1·5030 (Found: C, 62·6; H, 6·6. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in long orange-red prisms, m. p. 195° (Found: C, 50·6; H, 4·3; N, 16·7. $C_{14}H_{14}O_6N_4$ requires C, 50·3; H, 4·2; N, 16·8%). The *semicarbazone* separated from aqueous methanol in prisms, m. p. 227—228° (decomp.; darkening from *ca.* 200°) (Found: C, 51·3; H, 6·2; N, 19·6. $C_9H_{13}O_3N_3$ requires C, 51·2; H, 6·2; N, 19·9%).

*3-Methyl*cyclo*pent-2-enone and 2-Methoxybutadiene.*—3-Methyl*cyclo*pent-2-enone (15·0 g.; purified *via* its semicarbazone), 2-methoxybutadiene (3·3 g.), and pyrogallol (0·07 g.) were kept at 200—215° for 24 hours. Very little methoxybutadiene remained (smell) when the tube was opened. The residual brown liquid on distillation gave unchanged 3-methyl*cyclo*pent-2-enone (12·7 g.; n_D^{17} 1·4908), b. p. 69—73°/14 mm., and yellow oils; A, b. p. 120—70°/0·08 mm. (1·0 g.), and B, b. p. 170—200°/0·08 mm (0·75 g.).

Fraction A was chromatographed in light petroleum (b. p. 40—60°; 20 c.c.) on alumina (20 g.). Elution with light petroleum (b. p. 40—60°; 140 c.c.) gave a pale yellow oil C (0·33 g.); pure benzene gave a colourless oil D which partly solidified (0·1 g.); and ethyl acetate gave a thick yellow oil E (0·1 g.). The oil C gave a deep red solid derivative with 2 : 4-dinitrophenylhydrazine in methanolic sulphuric acid. Repeated crystallisation of this derivative from dioxan gave yellow needles of *4-acetyl*cyclo*hexanone bis-2 : 4-dinitrophenylhydrazone*, m. p. 205—207° (decomp.) (Found: C, 48·1; H, 4·4; N, 22·0. $C_{20}H_{20}O_8N_8$ requires C, 48·0; H, 4·0; N, 22·4%). No other crystalline material could be isolated from the (first) deep red mother-liquor. The oil D crystallised from water containing a little ethanol, giving colourless prisms of *3-methyl-4-(3-methyl*cyclo*pent-2-enylidine)*cyclo*pent-2-enone* (IV), m. p. 126—127° (Found: C, 82·6; H, 8·1; *C*-Me, 14·5. $C_{12}H_{14}O$ requires C, 82·8; H, 8·0; 2*C*-Me, 17·2%). The oil E gave a non-crystalline derivative with 2 : 4-dinitrophenylhydrazine in methanolic sulphuric acid. The oil B was chromatographed in light petroleum (b. p. 60—80°) containing 5% (v/v) of benzene on alumina. The benzene eluate (0·25 g.) was the only one which could be identified. It was largely 3-methyl-4-(3-methyl*cyclo*pent-2-enylidene)*cyclo*pent-2-enone which after crystallisation had m. p. 124—127° alone or mixed with a specimen obtained from the first chromatogram.

*Ethyl α-Cyano-3-methyl*cyclo*pent-2-enylideneacetate.*—3-Methyl*cyclo*pent-2-enone (9·6 g.) was added to a solution of sodium (4·5 g.) in ethyl cyanoacetate (45·0 g.). After 1 day at room temperature the mixture changed from a yellow sludge in much liquid to an apparently solid red-yellow mass. After 4 days in all the mixture was treated with ether (200 c.c.) and water (75 c.c.) containing concentrated hydrochloric acid (11 c.c.). After filtration from some of the product (2·8 g.), which was later combined with the main portion, the ethereal solution, which was red and had a green fluorescence, was washed with water and dried. The ether and excess of ethyl cyanoacetate were removed *in vacuo*. The residual oil solidified, to give *ethyl α-cyano-3-methyl*cyclo*pent-2-enylideneacetate* (11·1 g.; total, 73% crude yield), which crystallised from ethanol in colourless prisms, m. p. 123° (Found: C, 69·1; H, 6·8; N, 7·4. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·8; N, 7·3%). Its infra-red absorption spectrum in paraffin paste showed maxima at 4·51 (CN), 5·84 (αβ-unsaturated ester), 6·21 and 6·39 (double bond), 7·83 (ester), and at 11·85 mμ.

*3-Methyl*cyclo*pent-2-enone and Benzaldehyde.*—A mixture of 3-methyl*cyclo*pent-2-enone (10·0 g.), benzaldehyde (5·3 g.), and 10% aqueous sodium hydroxide (1·0 c.c.) was vigorously stirred at room temperature for 18 hours. The mixture became dark brown and was neutralised with dilute hydrochloric acid and extracted with ether, followed by benzene. The mixed extracts were washed with water, filtered from a yellow solid (A; 1·05 g.), and dried. On distillation the solution gave 3-methyl*cyclo*pent-2-enone (3·8 g.), n_D^{17} 1·4830, b. p. 60—75°/15 mm., and a thick yellow oil (B; 4·0 g.), n_D^{17} 1·6032, b. p. 160—175°/0·3 mm.

The yellow solid (A) *α-(4-keto-2-methyl*cyclo*pent-2-enyl)benzyl alcohol* (VIII) separated from ethanol in colourless prisms, m. p. 158° (Found : C, 77·6; H, 7·1; *C*-Me, 6·4. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9; 1*C*-Me, 7·4%). Its infra-red absorption spectrum (paraffin paste) showed maxima at 2·97 (OH), 3·26 (very small; possibly associated OH), 5·98 (αβ-unsaturated 5-membered ring ketone), 6·19 (double bond), and at 6·69 mμ (aromatic double bonds).

This alcohol (0·5 g.) was heated under reflux in acetic anhydride (5 c.c.) for 18 hours. [Refluxing in methanol (50 c.c.) containing concentrated sulphuric acid (1 c.c.) for 10 minutes followed by neutralisation by dilute sodium carbonate solution and evaporation of the methanol gave the same result.] After cooling, the solution was decomposed with water, basified, and extracted with chloroform. Evaporation of the dried extract gave 4-benzylidene-3-methyl*cyclo*pent-2-enone (IX) which crystallised from light petroleum (b. p. 60—80°) in colourless prisms, m. p. 122° (Found : C, 84·5; H, 6·3; *C*-Me, 8·0. $C_{13}H_{12}O$ requires C, 84·7; H, 6·5; 1*C*-Me, 8·2%). The 2 : 4-*dinitrophenylhydrazone*, prepared from the alcohol or its dehydration product with 2 : 4-dinitrophenylhydrazine in methanolic sulphuric acid, separated from ethyl acetate in dull red prisms, m. p. 245° (decomp.) (Found : C, 62·5; H, 4·2; N, 15·7. $C_{19}H_{16}O_4N_4$ requires C, 62·6; H, 4·4; N, 15·4%).

The oil, B, on treatment with the 2 : 4-dinitrophenylhydrazine reagent in the cold, gave an immediate deep red precipitate (C); filtration followed by boiling gave a second deep red precipitate (D). The latter separated from ethyl acetate in deep red prisms, m. p. 242° (decomp.), and was identical (mixed m. p. and analysis) with 4-benzylidene-3-methyl*cyclo*pent-2-enone 2 : 4-dinitrophenylhydrazone. The material C crystallised from ethyl acetate in bright red needles, m. p. 274° (decomp.) alone or mixed with 3-styryl*cyclo*pent-2-enone 2 : 4-dinitrophenylhydrazone, described below (Found : C, 62·7; H, 4·7; N, 15·2%).

A second portion (2·1 g.) of B was chromatographed in benzene–light petroleum (b. p. 60—80°) (1 : 1) on alumina (30 g.). Elution with the same solvent (100 c.c.) gave a colourless solid (E; 0·55 g.); little material was eluted with benzene, and the ethyl acetate eluate on evaporation gave a yellow oil (F, 1·3 g.). Material E crystallised from light petroleum (b. p. 60—80°) as needles, being *3-styryl*cyclo*pent-2-enone*, m. p. 101—102° (Found: C, 84·2; H, 6·3; *C*-Me, 0·0, 0·0. $C_{13}H_{12}O$ requires C, 84·7; H, 6·5%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in bright red needles, m. p. 274° (decomp.) (Found : C, 63·1; H, 4·2; N, 15·5. $C_{19}H_{16}O_4N_4$ requires C, 62·6; H, 4·4; H, 15·4%). The oil F was proved to be largely a mixture of the benzyl alcohol and its dehydration product by complete dehydration with boiling acetic anhydride.

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