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*Studies in the Alicyclic Series. Part III.** *Michael Condensation of 1-Acetyl*cyclo*alkenes with* cyclo*Alkanones.*

By W. J. Rosenfelder and David Ginsburg.

[Reprint Order No. 5311.]

Tricyclic αβ-ethylenic ketones may be obtained by Michael condensation of 1-acetyl*cyclo*alkenes with *cyclo*alkanones. These intermediates are of interest in the preparation of non-benzenoid aromatic systems.

When Dr. W. Taub brought to our attention the availability of 1-acetyl*cyclo*heptene of proven structure (Taub and Szmuszkovicz, *J. Amer. Chem. Soc.*, 1952, **74**, 2117), it appeared that this substance would afford a promising starting point for the synthesis of certain non-benzenoid aromatic hydrocarbons. Thus, condensation of 1-acetyl*cyclo*heptene with *cyclo*pentanone might be expected to give rise to (VI*d*) which could be used for the synthesis of the vinylogous (or more precisely, the " butadienylogous ") analogue (I) of azulene (II); with *cyclo*heptanone it might give (VI*b*) which could be used for synthesis of the " butadienylogue " (III) of the still unknown heptalene (IV). These reactions were carried out in view of the analogies developed by Robinson *et al.* for the synthesis of various tricyclic systems (Rapson and Robinson, *J.*, 1935, 1287; cf. Crowfoot, Rapson, and Robinson, *J.*, 1936, 757; Hawthorne and Robinson, *J.*, 1936, 763; Linstead and Walpole, *J.*, 1939, 842).

In principle, one may arrive at a precursor of (I) by using 1-acetyl*cyclo*pentene and *cyclo*heptanone as the starting materials. Although the primary condensation product would be different from that obtained by condensing 1-acetyl*cyclo*heptene with *cyclo*pentanone, the final non-benzenoid hydrocarbon, if ultimately obtained, would be identical.

To complete the picture, it was decided, despite the known difficulties in working with 1-acetyl*cyclo*pentene and with *cyclo*pentanone in an alkaline medium (cf. Wallach, *Ber.*, 1896, **29**, 2955; Kon and Nutland, *J.*, 1926, 3106), to attempt to find conditions for the Michael condensation of these two components, as success in this case might lead to a

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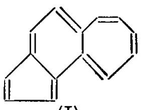
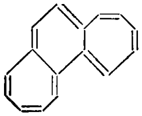
precursor of indacene (V), of very great theoretical interest, which is the " butadienylogue " of the still unknown pentalene.


(I)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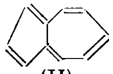
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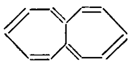
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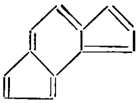
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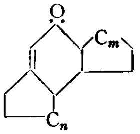
(VI)

(VI*a*) : $m = 2, n = 3$
(VI*b*) : $m = n = 3$
(VI*c*) : $m = 3, n = 2$
(VI*d*) : $m = 3, n = 1$
(VI*e*) : $m = 1, n = 3$

In this communication, we report some of our observations in the preliminary stages of this project, namely, synthesis of (VI*a*—*e*). Further employment of these compounds, in direct and indirect dehydrogenation experiments, will be reported later.

The following Table summarises the light-absorption data (λ in Å; DNPH = dinitrophenylhydrazone).

	Ketones in EtOH		Oximes in EtOH		Semicarbazones in EtOH		2 : 4-DNPH's in $CHCl_3$	
	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε	$\lambda_{max.}$	ε
(VI*a*)	2430	9660	2420	16,000	2705	15,700	3900	26,100
(VI*b*)	2410—2440	8600	2380—2420	11,800	2730	17,100	3900	28,000
(VI*c*)	2400	8500	2370	14,900	2680	24,800	3890	30,900
(VI*d*)	—	—	—	—	—	—	3880	32,000
(VI*e*)			2420—2440	11,600			3960	29,200

Michael condensation of the various 1-acetyl*cyclo*alkenes and *cyclo*alkanones proceeded satisfactorily with the exception of the condensation of 1-acetyl*cyclo*pentene and *cyclo*pentanone. Heating under reflux, in order to complete the dehydration of the aldol which is formed as an intermediate, is necessary, as it was shown in several cases that, when reflux periods shorter than those described in the Experimental section were used, some aldol was present in the product. Thus, for example, after an hour's reflux the infra-red spectrum of the product (VI*c*) showed, besides the band at 1675 cm.$^{-1}$ corresponding to the αβ-ethylenic ketone, bands at 3325 and 1711 cm.$^{-1}$ corresponding to the absorption of the intermediate ketol. When this impure product was heated in benzene with sodium methoxide for an additional hour, dehydration of the aldol was completed and pure αβ-ethylenic ketone was obtained. In this particular case, the intensity of absorption at 2400 Å rose from 7000 to 8500.

EXPERIMENTAL

Infra-red spectra were measured in $CHCl_3$, unless otherwise stated.

1-*Acetyl*cyclo*alkenes*.—1-Acetyl*cyclo*pentene was prepared by Hawthorne and Robinson's method (cf. Rapson and Robinson, *locc. cit.*). The fraction of b. p. 82—86°/48 mm. was used. A sample was converted into the semicarbazone and the free ketone was regenerated by refluxing with aqueous oxalic acid (45 min.), ether-extraction, and distillation. The ketone, b. p. 80—82°/33 mm., showed carbonyl absorption at 1660 cm.$^{-1}$.

1-Acetyl*cyclo*hexene was prepared by Christ and Fuson's method (*J. Amer. Chem. Soc.*, 1937, **59**, 893). The fraction of b. p. 195—200° was used. A pure sample, obtained by regeneration through the semicarbazone as described above, showed ketonic absorption at 1660 cm.$^{-1}$.

1-Acetyl*cyclo*heptene was prepared by the procedure of Taub and Szmuszkovicz (*loc. cit.*) except that the reaction was carried out at −20°. The fraction boiling at 207—215° was used. The yield reported was raised to 70% by using C.P. sodium carbonate for dehydrochlorination of the intermediate 1-acetyl-2-chloro*cyclo*heptane. A pure sample regenerated through the semicarbazone had b. p. 99—100°/30 mm. and showed ketonic absorption at 1657 cm.$^{-1}$.

Self-condensation of 1-*Acetyl*cyclo*pentene*.—A solution of 1-acetyl*cyclo*pentene (5·5 g.) and potassium *tert.*-butoxide (prepared from 2·1 g. of potassium) in dry benzene (25 ml.) was refluxed for 1 hr. After cooling, acetic acid (4 ml.) was added. The mixture was washed with water and distilled under reduced pressure. Two impure fractions, b. p. 135—160°/1 mm. (1·7 g.) and 160—220°/1 mm. (1·1 g.), were obtained, and a gummy residue (2·3 g.). Each of the fractions

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consisted of material of varying degrees of polymerisation. No crystalline derivatives could be obtained.

Self-condensation of cyclo*Pentanone*.—A solution of *cyclo*pentanone (4·2 g.) and potassium *tert.*-butoxide (from 2 g. of potassium) in benzene (25 ml.) was refluxed for 1 hr. The mixture was worked up as described for 1-acetyl*cyclo*pentene. *cyclo*Pentylidene*cyclo*pentanone, b. p. 99—101°/2 mm. (1·6 g.), n_D^{20} 1·5262, was obtained. Wallach (*loc. cit.*) reports b. p. 117—119°/12 mm. and n_D^{20} 1·52095. The 2 : 4-*dinitrophenylhydrazone* formed maroon needles, m. p. 222·5—223·5° (from ethyl acetate–ethanol) (Found : C, 58·1; H, 5·4; N, 16·9. $C_{16}H_{18}O_4N_4$ requires C, 58·2; H, 5·5; N, 17·0%). Light absorption in $CHCl_3$: $\lambda_{max.}$ = 3990 Å (ε 25,100). The oxime formed needles, m. p. 120—121° (from ethanol). Light absorption in EtOH : $\lambda_{max.}$ = 2560 Å (ε 11,400). Wallach (*loc. cit.*) reports m. p. 123—124°.

A second fraction (2·2 g.), b. p. 165—170°/2 mm., was obtained. This was 2 : 5-di*cyclo*pentylidene*cyclo*pentanone and had m. p. 82·5—83·5° (from methanol) (Found : C, 83·5; H, 9·2. Calc. for $C_{15}H_{20}O$: C, 83·3; H, 9·3%). Wallach (*loc. cit.*) reports b. p. 190°/12 mm., m. p. 76—77°.

Self-condensation of cyclo*Heptanone*.—A solution of *cyclo*heptanone (5·6 g.) and potassium *tert.*-butoxide (from 2·1 g. of potassium) in dry benzene (25 ml.) was refluxed for 4·5 hr. The mixture was treated as above. Distillation afforded fractions including (*a*) *cyclo*heptanone, b. p. 180—185°/760 mm. (0·7 g.), and (*b*) *cyclo*heptylidene*cyclo*heptanone, b. p. 130—135°/0·9 mm. (2·6 g.), n_D^{19} 1·52122 [light absorption in EtOH : $\lambda_{max.}$ 2530 Å (ε 2870); infra-red absorption in CCl_4 : no OH band, 1688 cm.$^{-1}$ ($-C{=}C-C{=}O$); Godchot and Brun (*Compt. rend.*, 1922, **174**, 618) report b. p. 143—145°/8 mm., n_D^{14} 1·5144]. The 2 : 4-*dinitrophenylhydrazone* of the latter formed yellow needles, m. p. 144—145° (from ethyl acetate–methanol) (Found : C, 62·0; H, 6·9; N, 14·7. $C_{20}H_{26}O_4N_4$ requires C, 62·2; H, 6·8; N, 14·5%). Upon admixture with *cyclo*heptanone 2 : 4-dinitrophenylhydrazone, m. p. 143—144° (from ethyl acetate–ethanol), the m. p. was depressed to 134—135°. Light absorption in $CHCl_3$: $\lambda_{max.}$ 3740 Å (ε 22,300).

2 : 3 : 4 : 5 : 7 : 8 : 9 : 10 : 11 : 4a : 11a : 11b-*Dodecahydro*-5-*oxo*-1H-cyclo*hepta*[a]*naphthalene* (VI*a*).—A solution of *cyclo*heptanone (5·6 g., 0·05 mole) in dry benzene (5 ml.) was added with swirling to a suspension of potassium *tert.*-butoxide [from 2·1 g. (0·0525 g.-atom) of potassium] in dry benzene (20 ml.). To this was immediately added a solution of 1-acetyl*cyclo*hexene (6·2 g., 0·05 mole) in dry benzene (5 ml.). The mixture became warm and the alkoxide slowly dissolved. To complete the reaction, the solution was refluxed for 2 hr. After cooling, acetic acid (4 ml.) was added, followed by water (20 ml.) and ether (50 ml.). The ether–benzene extract was washed twice with water and dried (Na_2SO_4), and the solvents were removed. The oily residue was distilled at reduced pressure, giving a forerun of unchanged ketones, b. p. 60—85°/30 mm. (2·5 g.). Upon distillation in a high vacuum and redistillation, the αβ-ethylenic *ketone*, b. p. 150—151°/0·9 mm. (6·1 g., 55·5%), n_D^{20} 1·5342, was obtained (Found : C, 82·4; H, 10·0. $C_{15}H_{22}O$ requires C, 82·5; H, 10·2%). Infra-red absorption : 1666 cm.$^{-1}$ ($-C{=}C-C{=}O$). The *oxime* formed colourless prismatic needles, m. p. 198·5—199·5° (from ether) (Found : C, 77·0; H, 9·9; N, 6·2. $C_{15}H_{23}ON$ requires C, 77·2; H, 9·9; N, 6·0%). The *semicarbazone* crystallised in colourless needles, m. p. 189—190° (from methanol–chloroform) (Found : C, 70·3; H, 9·9; N, 15·3. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·2; N, 15·3%). The orange 2 : 4-*dinitrophenylhydrazone* had m. p. 196—197° (from ethyl acetate–ethanol) (Found : C, 62·8; H, 6·7; N, 14·4. $C_{21}H_{26}O_4N_4$ requires C, 63·3; H, 6·6; N, 14·1%).

2 : 3 : 4 : 6 : 7 : 8 : 9 : 10 : 11 : 6a : 11a : 11b-*Dodecahydro*-6-*oxo*-1H-cyclo*hepta*[a]*naphthalene* (VI*c*).—The condensation of 1-acetyl*cyclo*heptene with *cyclo*hexanone was carried out as described above, using the corresponding molar quantities of reactants. The αβ-ethylenic *ketone* (VI*c*) had b. p. 149—152°/0·8 mm. (6 g., 54·5%) (Found : C, 82·1; H, 10·5%). Infra-red absorption : 1675 cm.$^{-1}$ ($-C{=}C-C{=}O$). The *oxime* formed long colourless rectangular plates, m. p. 164—165° (from ethyl acetate) (Found : C, 76·9; H, 9·8; N, 5·3%). The colourless *semicarbazone* crystallised in needles, m. p. 110—111° (from methanol–chloroform), m. p. 194—195° after drying at 100°/2 mm. for 2 hr. (Found : C, 70·2; H, 9·8; N, 15·1%). The bright orange 2 : 4-*dinitrophenylhydrazone* formed shiny prisms, m. p. 200—200·5° (from ethyl acetate–methanol) (Found : C, 62·8; H, 6·6; N, 14·3%).

1 : 2 : 3 : 4 : 5 : 6 : 8 : 9 : 10 : 11 : 12 : 5a : 12a : 12b-*Tetradecahydro*-6-*oxodi*cyclo*hepta*[a,c]-*benzene* (VI*b*).—The condensation of 1-acetyl*cyclo*heptene with *cyclo*heptanone was carried out as described above, using the corresponding molar quantities of reactants. The αβ-ethylenic *ketone* (VI*b*) had b. p. 166—167°/0·4 mm. (6·2 g., 57%), $n_D^{20\cdot3}$ 1·5346 (Found : C, 82·1; H, 10·1. $C_{16}H_{24}O$ requires C, 82·7; H, 10·4%). Infra-red absorption in CCl_4 : 1668 cm.$^{-1}$. The *oxime* formed fine colourless needles, m. p. 157·5—158·5° (from ethyl acetate) (Found : C, 78·2; H,

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10·3; N, 5·5. $C_{16}H_{25}ON$ requires C, 77·7; H, 10·2; N, 5·7%). The *semicarbazone* crystallised in colourless needles, m. p. 182—183° (from methanol–chloroform) (Found: C, 70·8; H, 10·2; N, 14·6. $C_{17}H_{27}ON_3$ requires C, 70·6; H, 9·4; N, 14·5%). The 2 : 4-*dinitrophenylhydrazone* formed orange needles, m. p. 190—191° (from ethyl acetate–methanol) (Found: C, 63·8; H, 6·3; N, 13·8. $C_{22}H_{28}O_4N_4$ requires C, 64·1, H, 6·8; N, 13·6%).

1 : 2 : 3 : 4 : 6 : 7 : 8 : 9 : 10 : 3a : 10a : 10b-*Dodecahydro*cyclo*hept*[e]*inden*-4-*one* (VI*e*).—The following conditions were found to be the most satisfactory: Potassium *tert.*-butoxide (from 2·1 g. of potassium) was covered with dry benzene (30 ml.), and the mixture was cooled to 5°. A cold solution (5°) of *cyclo*heptanone (5·6 g.) in dry benzene (10 ml.) was added with stirring, followed by a cold solution (5°) of 1-acetyl*cyclo*pentene (5·5 g.) in dry benzene (10 ml.). The solution was kept at 5° for an additional hr. The alkoxide dissolved completely after the first 20 min. of stirring. The solution was refluxed for 20 min., then cooled, acetic acid (4 ml.) was added, and the whole was worked up as usual. During distillation, considerable resinification occurred, but a fraction containing the desired αβ-ethylenic ketone (VI*e*), b. p. 146—150°/1·2 mm (4·2 g., 41%), was isolated (infra-red absorption in CCl_4: 1662 cm.$^{-1}$) and characterised by means of the *oxime*, colourless needles, m. p. 187·5—188·5° (Found: N, 6·2. $C_{14}H_{21}ON$ requires N, 6·4%). The 2 : 4-*dinitrophenylhydrazone* crystallised as dark-red needles, m. p. 147—148°, from ethyl acetate–methanol (Found: C, 62·0; H, 6·2; N, 15·0. $C_{20}H_{24}O_4N_4$ requires C, 62·5; H, 6·3; N, 14·6%).

Conditions similar to those used for the condensation of 1-acetyl*cyclo*hexene with *cyclo*heptanone (see above) afforded the ketone in only 24% yield.

1 : 2 : 3 : 5 : 6 : 7 : 8 : 9 : 10 : 5a : 10a : 10b-*Dodecahydro*cyclo*hept*[e]*inden*-5-*one* (VI*d*).—Owing to the ready self-condensation of *cyclo*pentanone in the presence of alkali-metal alkoxides, considerable difficulties were encountered in this reaction. The conditions found to be most satisfactory were the following: Sodium methoxide (2·83 g., 0·0525 mole) was covered with dry benzene (30 ml.); the mixture was cooled to 5° and stirred vigorously. A mixture of *cyclo*pentanone (4·2 g.) and 1-acetyl*cyclo*heptene (6·9 g.) in dry benzene (10 ml.) was cooled to 5° and added in one portion. The mixture was stirred for 35 min. at 5° and acetic acid (4 ml.) was added. After the usual working up and removal of a forerun at 30 mm., a fraction, b. p. 150—170°/1 mm. (2·1 g.), was collected. Redistillation of this fraction did not lead to much improved fractionation and the material boiled over a 20° range. This fraction, n_D^{20} 1·5357 (infra-red absorption in CCl_4: 1667 cm.$^{-1}$), was undoubtedly contaminated with di*cyclo*pentylidene*cyclo*pentanone but gave the 2 : 4-*dinitrophenylhydrazone* of the αβ-ethylenic ketone (VI*d*), which crystallised as dark red plates, m. p. 157—159° (from ethyl acetate–methanol) (Found: C, 62·5; H, 6·4; N, 14·7. $C_{20}H_{24}O_4N_4$ requires C, 62·5; H, 6·3; N, 14·6%).

When potassium *tert.*-butoxide was used in the condensation, as described above for the condensation of 1-acetyl*cyclo*pentene with *cyclo*heptanone, employing 0·05 molar quantities of reactants, the fraction of b. p. 150—170°/1 mm. was again obtained (1·8 g.).

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