69. *The Self-condensation of Acetyl*cyclo*hexene.*

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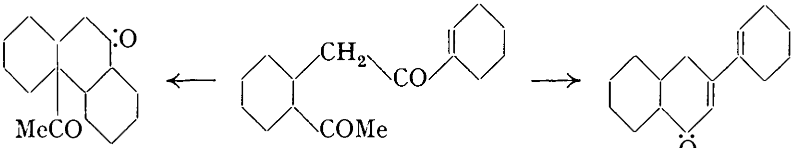
The two dimerides formed by the action of sodamide on acetyl*cyclo*hexene (Rapson and Robinson, J., 1935, 1285) are stereoisomeric saturated perhydrophenanthrene diketones of structure (II). They both yield phenanthrene on dehydrogenation, show no high intensity absorption in the ultra-violet, and form only monoketonic derivatives. A third self-condensation product has also been isolated for which the constitution 1-*keto*-3-cyclo*hexenyl*-Δ^2-*octahydronaphthalene* (III) is proposed, since on dehydrogenation it yields 2-phenylnaphthalene.

IN an abortive attempt to condense 2-methyltetralone with acetyl*cyclo*hexene in the presence of sodamide Rapson and Robinson (J., 1935, 1285) observed the formation of two dimerides of the unsaturated ketone which were assumed to be *cis*- and *trans*-isomerides of structure (I), each yielding one mol. of acetic acid on oxidation by the Kuhn–Roth micro-method. Since we have encountered both isomers, together with yet another self-condensation product, to a greater or lesser extent in a number of experiments involving condensation with acetyl*cyclo*hexene in the presence of sodamide, we have undertaken a more detailed investigation of the constitutions of these compounds.

By the action of sodamide on acetyl*cyclo*hexene in ethereal solution we have isolated, in addition to the two dimerides, m. p.'s 205° and 130°, described by Rapson and Robinson, a third and more soluble compound of m. p. 85°.



(II.) (I.) (III.)

The dimerides of m. p. 205° and 130° form only *monoximes* and *mono*-2 : 4-*dinitrophenylhydrazones*, they exhibit no selective absorption in the ultra-violet of greater intensity than $E^{1\%}_{1\,\text{cm.}} = 50$ between 2000 and 3000 A., and on dehydrogenation with selenium, phenanthrene is produced. A diketone of structure (I) would probably yield a dioxime and would certainly exhibit light absorption properties characteristic of an αβ-unsaturated ketone. The two dimerides in question are now to be considered as stereoisomeric α- and β-12-acetyl-9-ketotetradecahydrophenanthrenes (II) respectively, formed by an internal Michael reaction from the hypothetical intermediate diketone (I). Heilbron and his collaborators (J., 1927, 1888; 1928, 2323) obtained saturated dimerides of styryl methyl ketones in the presence of piperidine for which *cyclo*butane structures were suggested. It now seems probable that these compounds (which form only monoketonic derivatives) are similar in type to (II).

The third product of the self-condensation is an unsaturated ketone, $C_{16}H_{22}O$, which has been characterised by the preparation of an *oxime*, m. p. 232° (decomp.), a *semicarbazone*, m. p. 213°, and a 2 : 4-*dinitrophenylhydrazone*, m. p. 228°. The absorption spectra of the ketone and of its three derivatives (see Experimental) provide conclusive evidence that the carbonyl group is conjugated with a diene system and the isolation of 2-phenylnaphthalene on catalytic dehydrogenation of the ketone in the presence of palladium–norit indicates the carbon skeleton. On this evidence it is suggested that this third self-condensation product is 1-*keto*-3-cyclo*hexenyl*-Δ^2-*octahydronaphthalene* (III) produced by the intramolecular aldol condensation of the intermediate diketone (I), the latter reaction finding analogies in the intramolecular cyclisation of azafrinone to anhydroazafrinone (Kuhn and Brockmann, *Annalen*, **1935**, **516**, 95) and of capsanthinone to anhydrocapsanthinone (Zechmeister and von Cholnoky, *ibid.*, **1936**, **523**, 101). The self-condensation of β-methylcrotonaldehyde to 4 : 6 : 6-trimethyl-$\Delta^{1:3}$-*cyclo*hexadien-1-al (Fischer and Lowenberg, *ibid.*, 1932, **494**, 263) presumably takes place by a similar series of reactions.

1-Acetyl-2-methyl*cyclo*hexene does not undergo self-condensation when treated with sodamide in ethereal solution.

EXPERIMENTAL.

Self-condensation of 1-*Acetyl*cyclo*hexene.*—1-Acetyl*cyclo*hexene (44 g.) (Ruzicka, Koolhaas, and Wind, *Helv. Chim. Acta*, 1931, **14**, 1157) was stirred with sodamide (10 g.) in dry ether (1000 c.c.) for 18 hours at 20° and was then refluxed for 2 hours. The product was isolated in the usual manner after addition of ice and ammonium chloride and on distillation gave a small quantity of starting material (2 g.) and then a viscous gum (32 g.), b. p. 160—170°/0·05 mm., which did not crystallise spontaneously even after long standing. Trituration with light petroleum (b. p. 40—60°) gave a solid (A) (16 g.), m. p. 122—127°, and evaporation of the petroleum solution gave a residue (B) which crystallised partially on standing for some hours at 0°.

α-12-*Acetyl*-9-*ketotetradecahydrophenanthrene* (II).—Repeated crystallisation of the solid (A) from alcohol gave the α-isomer (2·5 g.) in fine needles, m. p. 205° (Robinson and Rapson, *loc. cit.*, give m. p. 205—206°) (Found : C, 77·3; H, 10·0. Calc. for $C_{16}H_{24}O_2$: C, 77·4; H, 9·8%). The substance contained no active hydrogen (Zerewitinoff) and showed no absorption in the ultra-violet greater than $E^{1\%}_{1\,\text{cm.}} = 50$, between 2000 and 3000 A. *Monoxime* : Prepared in the usual manner, this separated from alcohol in fine needles, m. p. 251° (decomp.) (Found : N, 5·4. $C_{16}H_{25}O_2N$ requires N, 5·3%). Oximation in pyridine solution gave the same oxime, m. p. 254° (decomp.), undepressed on admixture with the above specimen (Found : N, 5·2%). The 2 : 4-*dinitrophenylhydrazone* crystallised from acetic acid in yellow micro-needles, m. p. 293° (Found : N, 12·4. $C_{22}H_{28}O_5N_4$ requires N, 13·1%). *Light absorption in alcohol* : Maximum, 3700 A.; log ε = 4·38.

Dehydrogenation of the α-Dimeride.—A mixture of the α-dimeride (2·4 g.) and selenium (3 g.) was heated for 24 hours at 300° and a light petroleum (b. p. 40—60°) extract of the product was percolated through a column of alumina. Evaporation of the eluate yielded a solid (200 mg.) which on crystallisation from aqueous methyl alcohol (90%) yielded phenanthrene, m. p. 98° (picrate, m. p. 144°). These m. p.'s were not depressed by authentic specimens.

β-12-*Acetyl*-9-*ketotetradecahydrophenanthrene* (II).—After removal of the less soluble α-dimeride from the solid (A) the residue (12 g.), when crystallised from petroleum (b. p. 80—100°), gave the β-dimeride (9·5 g.) in fine needles, m. p. 130° (Robinson and Rapson, *loc. cit.*, gave m. p. 126—127°) (Found : C, 77·5; H, 9·8. Calc. for $C_{16}H_{24}O_2$: C, 77·4; H, 9·8%). This substance exhibited no absorption in the ultra-violet greater than $E^{1\%}_{1\,\text{cm.}} = 50$, between 2000 and 3000 A. *Monoxime :* Prepared in the usual manner, this separated from aqueous alcohol (75%) in clusters of fine needles, m. p. about 250° (decomp.). Mixed with the oxime of the α-dimeride, it had m. p. 240° (decomp.) (Found : N, 5·2. $C_{16}H_{25}O_2N$ requires N, 5·3%). The 2 : 4-*dinitrophenylhydrazone* crystallised from aqueous alcohol (85%) as an orange micro-crystalline powder, m. p. 212—213° (Found : N, 13·7. $C_{22}H_{28}O_5N_4$ requires N, 13·1%). *Light absorption in alcohol :* Maximum, 3680 A.; log ε = 4·42.

Dehydrogenation of the β-*Dimeride.*—The β-dimeride (7 g.) was heated with selenium (12 g.) for 24 hours at 350°, the residue was thoroughly extracted with ether, and the gum obtained on evaporation of the ethereal solution was dissolved in benzene–light petroleum (b. p. 40—60°) (1 : 1) and percolated through a column of alumina. Evaporation of the eluate gave a white residue (3 g.) which contained a trace of a hydrocarbon insoluble in light petroleum (b. p. 40—60°) and alcohol but which crystallised from benzene in fine matted needles, m. p. 306° This material exhibited light absorption properties characteristic of a highly condensed polycyclic hydrocarbon. The main bulk of the product (2·3 g.) had m. p. 60—80°, and resisted further purification by either chromatography or crystallisation but readily yielded phenanthrene picrate, m. p. 144°, from which phenanthrene (0·7 g.), m. p. 98°, was regenerated. Neither the picrate nor the hydrocarbon gave any depression in m. p. on admixture with authentic specimens.

1-*Keto*-3-cyclo*hexenyl*-Δ^2-*octahydronaphthalene* (III).—A solution of the semi-solid material (B) in light petroleum (b. p. 40—60°) was percolated through a column of alumina and evaporation of the eluate yielded a solid which on crystallisation from aqueous methyl alcohol gave 1-*keto*-3-cyclo*hexenyl*-Δ^2-*octahydrophenanthrene* (4 g.) in flakes, m. p. 85° (Found : C, 83·6; H, 9·8. $C_{16}H_{22}O$ requires C, 83·5; H, 9·6%). *Light absorption in alcohol :* Maximum, 2815 A.; log ε = 4·25. The *oxime*, prepared in the usual manner, separated from alcohol in needles, m. p. 232° (decomp.) (Found : N, 5·75. $C_{16}H_{23}ON$ requires N, 5·7%). *Light absorption in alcohol :* Maximum, 2750 A.; log ε = 4·41. The *semicarbazone* was obtained from aqueous alcohol (85%) as an amorphous powder, m. p. 213° (Found : N, 14·6. $C_{17}H_{25}ON_3$ requires N, 14·6%). *Light absorption in alcohol :* Maximum, 3000 A.; log ε = 4·40. The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in red micro-crystals, m. p. 228° (Found : N, 13·8. $C_{22}H_{26}O_4N_4$ requires N, 13·7%). *Light absorption in alcohol :* Maximum, 3980 A.; log ε = 4·53.

Dehydrogenation of 1-*Keto*-3-cyclo*hexenyl*-Δ^2-*octahydronaphthalene.*—Extensive decomposition occurred on attempted selenium dehydrogenation. The ketone (460 mg.) and palladium–norit (400 mg. ; 10%) were heated at 340° in an atmosphere of carbon dioxide, the hydrogen evolved being collected in a nitrometer. After 2 hours 90% of the theoretical amount of hydrogen had been collected and the reaction mixture was cooled and extracted with ether. After being washed with aqueous sodium hydroxide, the ethereal solution was dried and evaporated and a solution of the residual solid in benzene–light petroleum (b. p. 40—60°) (1 : 1) was passed through an alumina column. The eluate was evaporated, and the residual solid purified further by readsorption on alumina from light petroleum solution. Crystallisation of the final residue (90 mg.) from methyl alcohol gave 2-phenylnaphthalene, m. p. 100°, undepressed by an authentic specimen.

The authors express their thanks to Professor I. M. Heilbron, D.S.O., F.R.S., for his interest in this work and to the University of London for the award of a Postgraduate Studentship.

IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON, S.W. 7. [*Received, February* 20*th*, 1942.]