328. *Studies in the Polyene Series. Part II.*

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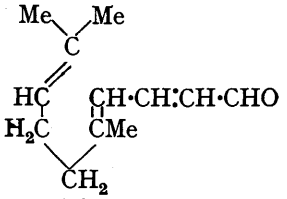
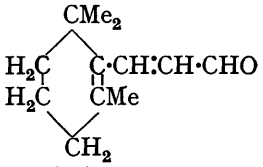
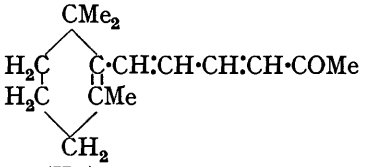
Whereas ψ-ionone on cyclisation with concentrated phosphoric acid is known to yield almost exclusively α-ionone, ψ-ionone semicarbazone is now found to give mainly the β-isomer. Citrylideneacetaldehyde semicarbazone similarly gives β-*cyclo*citrylideneacetaldehyde (*semicarbazone*, m. p. 186—187°).

Hibbert and Cannon (*J. Amer. Chem. Soc.*, 1924, **46**, 119) have shown that cyclisation of ψ-ionone with syrupy phosphoric acid gives practically pure α-ionone. We have confirmed this result and found further that similar treatment of ψ-ionone semicarbazone gives an excellent yield of an ionone shown by spectroscopic comparison with the pure compound to consist almost exclusively of the β-isomer. This was confirmed by conversion of the ketone into its characteristic semicarbazone and by the formation of geronic acid in high yield on ozonolysis.

This led us to investigate the cyclisation of citrylideneacetaldehyde (I) in the hope of obtaining β-*cyclo*citrylideneacetaldehyde (II). When the crude semicarbazone obtained


(I.)


(II.)


(III.)

after cyclisation was distilled with steam in the presence of phthalic anhydride, a volatile aldehyde was obtained as a pale yellow oil ($\lambda_{max.}$ 2930 A.). This readily formed a *semi-*

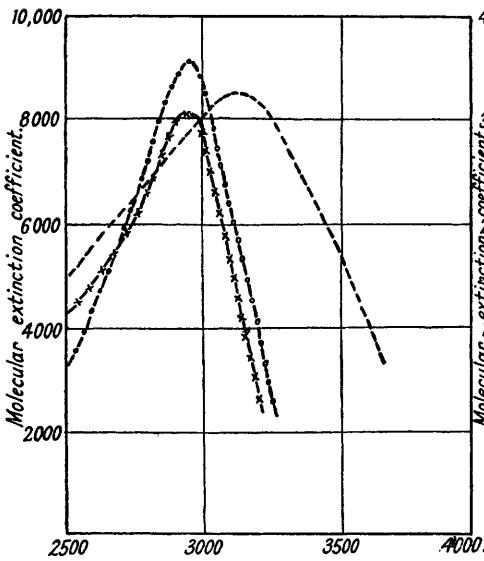
carbazone, m. p. 186—187°, which gave a large depression in melting point on admixture with the semicarbazone, m. p. 167°, of the acyclic aldehyde. Comparison of the absorption spectra (Table I) of β-ionone and the above product leaves little room for doubt that it is

TABLE I.

			Semicarbazone.	
	$\lambda_{max.}$	$\epsilon_{max.}$	$\lambda_{max.}$	$\epsilon_{max.}$
(i) ψ-Ionone	2910	21,800	2995	45,400
(ii) β-Ionone	2935	9,200	2765	23,300
(iii) Citrylideneacetaldehyde	2900	15,960	3045	47,200
(iv) β-*cyclo*Citrylideneacetaldehyde	2930	8,000	2950	27,000
(v) Ketone (III)	3190	8,280	3160	38,000
(vi) α-Ionone	2285	14,300	—	—

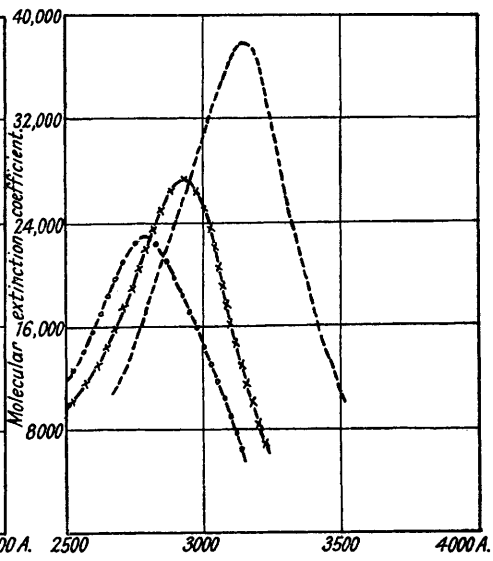
actually β-*cyclo*citrylideneacetaldehyde. The same product was obtained by cyclisation of the semicarbazone of a specimen of citrylideneacetaldehyde prepared by distillation of

FIG. 1.



–o–o– β-*Ionone*.
–×–×– β-cyclo*Citrylideneacetaldehyde*.
– – – – *Ketone* (III).

FIG. 2.



–o–o– β-*Ionone semicarbazone*.
–×–×– β-cyclo*Citrylideneacetaldehyde semicarbazone*.
– – – – *Semicarbazone of* (III).

Solvent, EtOH.

the barium salt of the corresponding acid with barium formate under reduced pressure (J., 1937, 755).

The presence of the β-ionone ring was established by the fact that both specimens of the cyclic aldehyde gave geronic acid on ozonolysis. Von Braun and Kurtz (*Ber.*, 1937, **70**, 1009) claim to have prepared β-*cyclo*citrylideneacetaldehyde by reduction of the phenylimidochloride of the corresponding acid by means of chromous chloride, but unfortunately they were apparently unable to prepare any solid derivatives of the aldehyde, nor do they record any spectrographic data. In these circumstances it is impossible to make any deductions as to the possible identity of the two products.

β-*cyclo*Citrylideneacetaldehyde condenses readily with acetone in presence of sodium ethoxide, giving the ketone (III) ($\lambda_{max.}$ 3190 A.), characterised by a *semicarbazone*, m. p. 186°. The absorption maximum of the latter is located at 3160 A., compared with 3200 A. (approx.) for the semicarbazone of β-ionylideneacetaldehyde (Kuhn, J., 1938, 613), although the extinction coefficient is considerably lower.

Experimental.

Cyclisation of ψ-Ionone Semicarbazone.—The finely powdered semicarbazone (20 g., m. p. 142°) was added during ½ hour with stirring at room temperature to phosphoric acid (200 c. c., *d* 1·75), stirring being continued for a further hour. The clear solution was poured into water, the semi-solid product extracted with ether, solvent removed, and the residue distilled with steam in the presence of phthalic anhydride (50 g.). When the distillate was worked up in the normal manner, a pale yellow oil (14 g.) was obtained, the molecular extinction of its absorption maximum at 2940 A. being 8500 (cf. pure β-ionone, Table I). The corresponding semicarbazone had m. p. 148°, in agreement with that given by Kuhn and Morris (*Ber.*, 1937, **70**, 856).

Cyclisation of Citrylideneacetaldehyde Semicarbazone.—The semicarbazone (3·5 g.), cyclised as above, gave the cyclic aldehyde as a pale yellow oil (1 g.), readily convertible into its *semicarbazone*, which separated from methyl alcohol as a pale yellow, microcrystalline solid, m. p. 186—187° (Found: C, 66·5; H, 8·9; N, 17·8. $C_{13}H_{21}ON_3$ requires C, 66·4; H, 8·9; N, 17·9%).

Ozonolysis of β-cyclo*Citrylideneacetaldehyde.*—A solution of the aldehyde (0·8 g.) in carbon tetrachloride (40 c.c.) was treated with ozonised oxygen for 24 hours. The precipitated ozonide was dissolved by addition of glacial acetic acid (40 c.c.), and the ozonolysis continued for a further 24 hours. The solution was then refluxed with water (300 c.c.) for 1 hour and evaporated under reduced pressure to a thick syrup. Water (150 c.c.) was added, and the process repeated, the residue being extracted repeatedly with ether. The combined extracts were washed several times with small quantities of a saturated solution of sodium bicarbonate, the alkaline washings acidified with phosphoric acid, and the product again extracted repeatedly with ether. Removal of solvent from the combined extracts gave a viscous oil, which was extracted with hot water, and the extract treated with a solution of semicarbazide hydrochloride (1 g.) and sodium acetate (2 g.) in water. The solution immediately became cloudy and deposited a solid after standing for 24 hours at 0°; repeated crystallisation from ethyl acetate gave geronic acid semicarbazone as small needles, m. p. 159—160°, not depressed by an authentic specimen, m. p. 162°.

Condensation of β-cyclo*Citrylideneacetaldehyde with Acetone.*—The aldehyde (5·5 g., regenerated from the semicarbazone) was condensed with acetone (30 c.c.) in presence of alcoholic sodium ethoxide (0·7 g. in 10 c.c. of absolute alcohol) exactly as described (preceding paper) for the condensation of citrylidenecrotonaldehyde *a* with acetone. The resulting ketone (2·7 g.) was a pale yellow oil, b. p. 140—145°/0·17 mm., exhibiting a rather broad absorption band with its head at 3190 A. With chloroformic antimony trichloride the ketone gave a clear red colour with an intense absorption band at 5420 A. The *semicarbazone* crystallised from aqueous methyl alcohol in colourless prisms, m. p. 186°, which turned yellow in light (Found: C, 69·9; H, 9·2; N, 15·5. $C_{16}H_{25}ON_3$ requires C, 69·8; H, 9·2; N, 15·3%).

Cyclisation of ψ-Ionone.—When ψ-ionone was cyclised according to the method of Hibbert and Cannon (*loc. cit.*), the product was practically pure α-ionone, as shown by the absorption spectrum: $\lambda_{max.}$ 2285 A., $\epsilon_{max.}$ 13,500 (cf. Table I).

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