779. *Carotenoids and Related Compounds. Part IV.* A New Synthesis of the Capsorubin Chromophore.*

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The nonaene diketone (I) has been prepared by condensation of the dimethyloctatrienedial (III) with tiglylidenepinacolone (V).

SYNTHESIS of the nonaene diketone (I), which possesses the same chromophoric system as the natural carotenoid capsorubin (Zechmeister and Cholnoky, *Annalen*, 1934, **509**, 269; 1935, **516**, 30), from the octenedione (II) was described in Part I of this series (*J.*, 1953, 3286). Subsequently it was shown that the dimethyloctatrienedial (III) (Mildner and Weedon, *ibid.*, p. 3294) condenses readily with pinacolone to give the pentaene diketone (IV) (Part III). This new approach to polyenes has now been extended, and affords a much simpler and more convenient route to (I).

$$\mathrm{MeCO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COMe} \quad \text{(II)}$$

$$\mathrm{CMe_3{\cdot}CO{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CO{\cdot}CMe_3} \quad \text{(IV)}$$

$$\text{(V)} \quad \mathrm{CMe_3{\cdot}CO{\cdot}CH{:}CH{\cdot}CMe{:}CHMe} + \mathrm{OCH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CHO} \quad \text{(III)}$$

$$\downarrow$$

$$\mathrm{CMe_3{\cdot}CO{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CMe{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CH{:}CH{\cdot}CO{\cdot}CMe_3} \quad \text{(I)}$$

Treatment of tiglaldehyde with excess of pinacolone in the presence of aluminium *tert.*-butoxide gave crystalline tiglylidenepinacolone (V) in 25% yield. It exhibited maximum light absorption at a wave-length very similar to, but of lower intensity than, that of authentic compounds with similar chromophores (see Table). However, both

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* Part III, *J.*, 1953, 3299.

$\lambda_{max.}$ and $\varepsilon_{max.}$ of its 2 : 4-dinitrophenylhydrazone were markedly less than those of related compounds, but not as low as might be expected if cyclisation had occurred to give a pyrazoline derivative.

	Carbonyl compound *		2 : 4-Dinitrophenylhydrazone †	
	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
CHMe:CH·CH:CH·CHO	270 [a]	26,500	392	43,500
CHMe:CH·CH:CH·COMe	270 [b]	28,500	396	33,500
CHPr:CEt·CH:CH·COMe [c]	282	21,000	396	36,500
CHMe:CMe·CH:CH·CO·CMe$_3$	280	19,000	375	22,500

* In alcohol. † In chloroform.

[a] Hausser, Smakula, Kuhn, and Hoffer, *Z. physikal. Chem.*, 1935, **29**, *B*, 371. [b] Heilbron, Jones, and Richardson, *J.*, 1949, 287. [c] Bharucha and Weedon, *J.*, 1953, 1578.

From its mode of formation the crystalline ketone (V), and hence its derivative, probably possess the *trans*-configuration about each carbon–carbon double bond. A possible explanation of the spectral effects is suggested by a study of scale models. These indicate that there is slight steric interference between the *tert.*-butyl group and the unsaturated side chain in an *s-trans*-configuration of (V). The resulting loss in planarity of the chromophore would lower $\varepsilon_{max.}$ slightly, but not shift $\lambda_{max.}$ (cf. Braude, Jones, Koch, Richardson, Sondheimer, and Toogood, *J.*, 1946, 1890; Bharucha and Weedon, *J.*, 1953, 1571, 1578); this agrees well with observation. With the dinitrophenylhydrazone there is clearly strong interference between the *tert.*-butyl group and the >NH-group, unless the dinitrophenylhydrazine residue is *syn* to the unsaturated side chain. In either event the observed marked lowering of both $\lambda_{max.}$ and $\varepsilon_{max.}$ is to be expected (cf. *locc. cit.*). The alternative explanation that in these compounds the unsaturated side chain is attached by a carbon–carbon bond with an *s-cis*-configuration cannot be definitely excluded (cf. Barton and Brooks, *J.*, 1951, 261; Turner and Voitle, *J. Amer. Chem. Soc.*, 1951, **73**, 1403), but this seems most unlikely with the dinitrophenylhydrazone as steric interference would still preclude planarity of the whole chromophore.

On condensation of the dimethyloctatrienedial (III) with tiglylidenepinacolone (V), in the presence of alcoholic alkali, the pure nonaene diketone (I) crystallised from the reaction mixture in 1—2% yield, *i.e.*, about ten times the overall yield achieved in the six-stage synthesis from (II).

EXPERIMENTAL

All operations were carried out in an atmosphere of nitrogen.

2 : 2 : 6-*Trimethylocta*-4 : 6-*dien*-3-*one* (*Tiglylidenepinacolone*).—A mixture of tiglaldehyde (32 g.) (Bernhauer and Skudrzyk, *J. pr. Chem.*, 1940, **155**, 310), pinacolone (90 c.c.) and aluminium *tert.*-butoxide (50 g.) in benzene (300 c.c.) was heated under reflux for 15 hr. and then cooled. Decomposition of the complex, and isolation of the product in the usual way, gave the *ketone* (15 g.), b. p. 57—58°/1 mm., which crystallised in needles, m. p. 15°, unchanged on recrystallisation from pentane (Found: C, 79·45; H, 11·1. $C_{11}H_{18}O$ requires C, 79·45; H, 10·9%). Light absorption: see Table. The 2 : 4-*dinitrophenylhydrazone* crystallised from methanol in orange needles, m. p. 112—113° (Found: N, 16·45. $C_{17}H_{22}O_4N_4$ requires N, 16·2%). Light absorption: see Table.

The 2 : 4-*dinitrophenylhydrazone* of crotonylideneacetone crystallised from ethyl acetate in red needles, m. p. 205—206° (Found: N, 19·4. $C_{13}H_{14}O_4N_4$ requires N, 19·3%). Light absorption: see Table.

2 : 2 : 6 : 10 : 15 : 19 : 23 : 23-*Octamethyltetracosa*-4 : 6 : 8 : 10 : 12 : 14 : 16 : 18 : 20-*nonaene*-3 : 22-*dione*.—Methanolic potassium hydroxide (1 c.c.; 5% w/v) was added to a solution of 2 : 7-dimethylocta-2 : 4 : 6-triene-1 : 8-dial (40 mg.) in tiglylidenepinacolone (1 c.c.) and the mixture was kept for 20 hr. at 20°. More methanolic potassium hydroxide (5 c.c.; ~2·5% w/v) was then added. When the resulting solution was kept at 20° for a period which varied from 4 to 48 hr. in different experiments, the nonaene diketone (1—1·5 mg.) crystallised out and had m. p. 220—221° (Kofler block). Light absorption in benzene: maxima, 486 and 518 mμ. The product was identified by a mixed m. p. determination, and by a mixed chromatogram with the specimen described in Part I which had the same m. p. and light absorption properties.

When a solution of the dimethylocatrienedial (40 mg.) in tiglylidenepinacolone (1 c.c.) was added to methanolic potassium hydroxide (6 c.c.; ~2·5% w/v), spectroscopic examination of the resulting mixture (kept at 20°) at intervals up to 20 hr. revealed none of the nonaene diketone. Chromatography of the crude product gave an orange-yellow band which exhibited maximum light absorption (in $CHCl_3$) at 425 mμ, probably due to a hexaene keto-aldehyde formed by condensation of the starting materials in equimolar proportions. [A similar condensation of the dimethyloctatrienedial with crotonylidenepinacolone (2 : 2-dimethylocta-4 : 6-dien-3-one) also gave a half condensation product (in 5% yield); it crystallised from chloroform–pentane and had m. p. 149—152°. Light absorption (in $CHCl_3$) : maxima, 395, and 416 mμ; $\varepsilon = 90,000$ and 88,000 respectively.]

An attempt to condense dimethyloctatrienedial with tiglylidenepinacolone in the presence of aluminium *tert.*-butoxide in benzene was unsuccessful.

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