Dehydration of 4-Hydroxy-2,3,4-triphenylcyclopentenone

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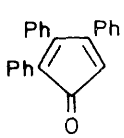
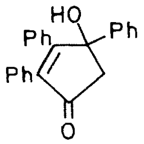
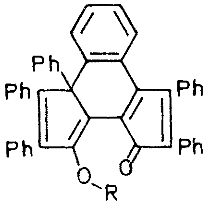
Summary Chemical and spectral evidence indicate that the blue-black crystalline product from dehydration of the title alcohol with acetic acid–sulphuric acid is the dehydro-dimer (III).

2,3,4-TRIPHENYLCYCLOPENTADIENONE (I) is potentially a useful diene. The n.m.r. spectrum of the ring proton in its Diels–Alder adducts and their decarbonylated derivatives would be expected to yield information not available from the corresponding tetracyclone adducts. Boiling a solution of the title alcohol (II) in acetic acid–sulphuric acid 10 : 1 for a few minutes gave a blue-black crystalline compound,† m.p. 284—287° in 35% yield, easily separable because of its sparing solubility. On the basis of spectral evidence and the transformations given below, this product is formulated as the dehydro-dimer (III).

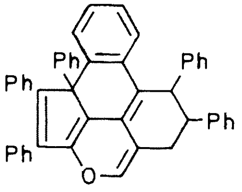

(I)

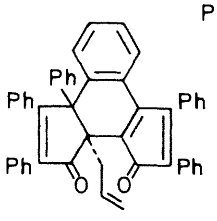

(II)

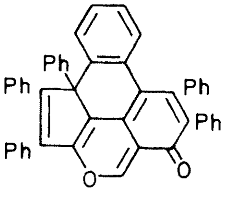

(III) R = H
(IV) R = $COCH_3$
(V) R = $CH_2CH{=}CH_2$

The i.r. spectrum ($CHCl_3$) shows a carbonyl band at 1686 cm^{-1} (tetracyclone 1715 cm^{-1}) and a hydroxyl band at 3260 cm^{-1} which dilution studies show to be intramolecularly hydrogen-bonded. In the n.m.r. spectrum ($CDCl_3$) the hydrogen bonded proton is visible as a low-field (τ 0·01) singlet removed on addition of trifluoroacetic acid; all other protons were aromatic. Acetylation gave a red crystalline acetate (IV), m.p. 294—300° which was re-converted into the dehydro-dimer (III) on base hydrolysis. In the i.r. spectrum (Nujol) of this acetate the hydroxyl band has been replaced by an enolic acetate band at 1755 cm^{-1}, the cyclopentadienone carbonyl stretching frequency (1707 cm^{-1}) becomes characteristic of tetracyclone (1704 cm^{-1}, Nujol). Further support for the presence of a cyclopentadienone ring in acetate (IV) comes from the u.v.‡ spectrum showing a broad longest-wavelength band (λ_{max} 535 nm, log ϵ 3·51) similar in appearance and position to tetracyclone (λ_{max} 508 nm, log ϵ 3·10). Dehydro-dimer (III) shows a hypsochromic shift in its longest-wavelength band (λ_{max} 273, 305, and 626 nm, log ϵ 4·18, 4·29, and 3·6) of 90 nm on acetylation.

Allylation of the dehydro-dimer (III) with sodium hydride and allyl bromide in dimethylformamide gave red allyl ether (V), m.p. 216—217° in 70% yield. Brief heating of this allyl ether at its melting point gave the Claisen rearrangement product (VI), m.p. 277—280° (λ_{max} 502 nm, log ϵ 3·23)—the phenyl and allyl groups assumed *trans*.


(VII)


(VI)


(VIII)

This rearrangement product was itself unstable on further heating at 290° for 2 min. A yellow crystalline product, m.p. 302—305° was isolated by chromatography in 20% yield. Mass-spectral data showed that this compound still contained the allyl residue but had lost carbon monoxide. The i.r. spectrum indicated that the remaining oxygen was present as an enol (ν_{max} 1641 cm^{-1}, medium intensity). Structure (VII) accommodates the n.m.r. data and accounts for the deep red colour produced on addition of acid giving the corresponding pyrrilium salt. Furthermore, oxidation of this yellow pyrolysis product with selenium dioxide in acetic acid gave a more polar yellow crystalline product m.p. 333—335°, formulated as the ketone (VIII), having i.r. ν_{max} 1631 cm^{-1} (strong) and showing only a singlet proton at τ 1·35 ($CDCl_3$) in the n.m.r. spectrum besides aromatic protons. The pyrolysis product (VII) is probably formed from the allylated dehydro-dimer (V) by an intramolecular Diels–Alder addition followed by decarbonylation and hydrogen rearrangement. It was produced directly from (V) by heating at the higher temperature.

The mass spectrum of the dehydro-dimer (III) (M^+ 614·22505; calc. for $C_{46}H_{30}O_2$ 614·22457) and of (IV), (VII), and (VIII) all show a major fragmentation by loss of a phenyl group, but labelling experiments indicated that randomisation of the cyclopentadiene substituents occurs prior to fragmentation.[2] However, the position of the angular phenyl group given is the most reasonable on mechanistic grounds.[3]

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† This product has similarities to a 'bright blue' compound, m.p. 292—294° previously isolated from this same reaction and formulated as triphenylcyclopentadienone (I).[1] Although the carbonyl stretching frequencies in the i.r. spectrum are closely similar, there are gross differences in the u.v. spectrum. In particular, the reported band at 940nm was absent in our compound. Using the dehydration and work-up procedure given, a lower yield of blue product, identical in all respects to that discussed in this paper, was isolated.

‡ U.v. spectra run in chloroform.

2,3,4-Triphenylcyclopentadienone (I) has been trapped as its decarbonylated adducts with various acetylenes[4] but evidently possesses considerably less stability as a monomer than tetracyclone as does 2,3,5-triphenylcyclopentadienone.[5]

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[2] M. M. Bursey and T. A. Elwood, *J. Amer. Chem. Soc.*, 1969, **91**, 3812.

[3] The initial dimerisation is formally similar to the dimerisation of 2-phenylindenone. S. Wawzonek, G. R. Hauser, and A. R. Zigman, *Chem. Comm.*, 1969, 6.

[4] F. Feher and H. Berthold, *Z. anorg. Chem.*, 1956, **284**, 60.

[5] W. Dilthey and W. Schommer, *J. prakt. Chem.*, 1933, **136**, 293.