

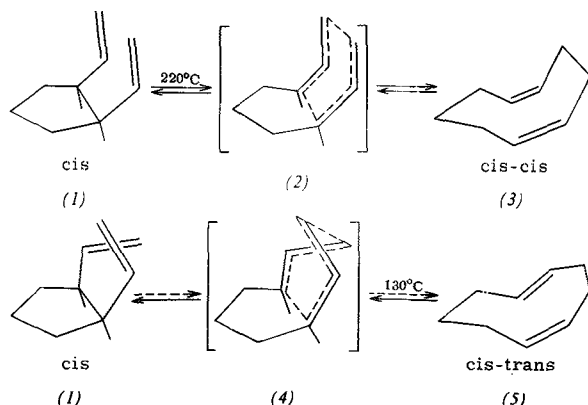
Cyclopentadienone-hydrazone

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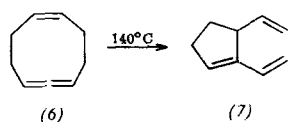
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(intense *cis*-double bond absorption at 740 cm^{-1}) was synthesized independently by reduction of *cis*-cyclonona-1,2,6-triene (6) [2] with sodium in liquid ammonia [3]. When (3) was heated to 220°C , it gave an equilibrium mixture identical with that formed from (1).

The formation of (3) indicates that the Cope rearrangement of *cis*-1,2-divinylcyclopentane proceeds via a six-centred transition state (2) [4] in which the carbon atoms of the di-allyl system are arranged similar to a boat-form. A chair-type, four-centred transition state (4) would be expected to give *cis,trans*-cyclonona-1,5-diene (5) as rearrangement product; according to Dreiding and Stuart models, (5) is more strained than the *cis,cis*-isomer (3).



Compound (5), $n_D^{20} = 1.4949$ (*cis*- and *trans*-double bond absorptions at 720 and 971 cm^{-1} , respectively) [5] was prepared from both homopseudopelletierine (analogous to the preparation of the labile homologue *cis,trans*-cycloocta-1,5-diene) and 6-dimethylamino-*cis*-cyclononene (by Hofmann degradation) [6]. Like its eight-membered homologue, the new hydrocarbon tends to polymerize; it can nevertheless



be isomerized in the gas phase at 130°C under reduced pressure. Like the process starting from (3), this gave gas-chromatographically pure (1) [7].

As is the case with an isocyanate group [8], the allene system can also take part in a valence isomerization of the type of the Cope rearrangement. In a reaction analogous to the rearrangements of (3) and (5), (6) isomerizes at 140°C in the gas phase to give 1,5-divinylcyclopentene (7), b.p. $53^\circ\text{C}/125\text{ mm}$, $n_D^{20} = 1.4972$, as sole product.

Received, October 7th, 1963 [Z 599/430 IE]
German version: Angew. Chem. 75, 1103 (1963)

[1] E. Vogel, K.-H. Ott, and K. Gajek, Liebigs Ann. Chem. 644, 172 (1961).

[2] L. Skatrehöl, Tetrahedron Letters 5, 167 (1961).

[3] This reduction was also effected by D. Devaprabhakar and P. D. Gardner, J. Amer. chem. Soc. 85, 648 (1963).

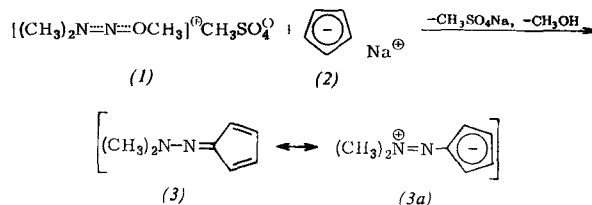
[4] Cf. W. v. E. Doering and W. R. Roth, Tetrahedron 18, 67 (1962).

[5] We have not yet had sufficient substance available for an accurate boiling-point determination.

[6] We obtained this amine from the *cis*-cyclononen-6-one described by D. Devaprabhakar and P. D. Gardner, J. Amer. chem. Soc. 85, 1458 (1963).

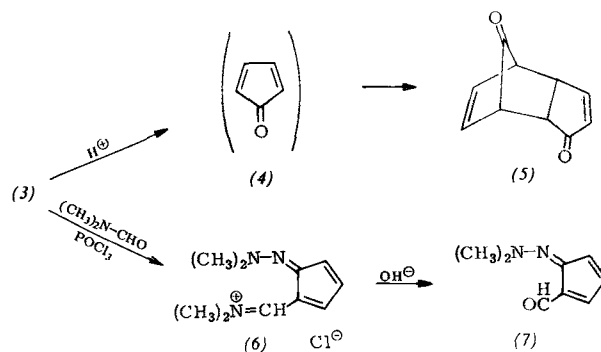
[7] For the analogous isomerization of cyclodeca-1,5-dienes see C. A. Grob, H. Link, and P. W. Schiess, Helv. chim. Acta 46, 483 (1963); G. Wilke, Angew. Chem. 75, 10 (1963); Angew. Chem. internat. Edit. 2, 105 (1963).

[8] E. Vogel, Angew. Chem. 74, 829 (1962); Angew. Chem. internat. Edit. 2, 1 (1963).



Compound (3) is the first cyclopentadienone derivative unsubstituted in the five-membered ring that is stable as the monomer. It can be distilled *in vacuo* without decomposition, and even at 200°C shows no tendency to dimerize or to react with dienophiles. Its dipole moment of 3.3 D indicates definite participation of the dipolar structure (3a) in the ground state of this aza-analogue of 6-dimethylaminofulvene [2].

Hydrolysis of (3) with 2N H_2SO_4 leads immediately via (4) to dimeric cyclopentadienone (5) [3]. Electrophilic reagents substitute (3) in the five-membered ring. For example, Vilsmeier formylation of (3) with dimethylformamide and



phosphorus oxychloride yields the stable aldehyde (7), orange needles, m.p. 65°C , $\lambda_{\text{max}} (\log \epsilon) = 251.8 (4.18), 373.5 (4.35)\text{ m}\mu$ in methanol, via the immonium salt (6), which can be isolated as its perchlorate, orange needles, m.p. 135°C (decomp.).

Received, October 8th, 1963 [Z 596/428 IE]
German version: Angew. Chem. 75, 1104 (1963)

[1] Cf. S. Hünig et al., Angew. Chem. 75, 476 (1963); Angew. Chem. internat. Edit. 2, 327 (1963).

[2] K. Hafner et al., Angew. Chem. 75, 35 (1963); Angew. Chem. internat. Edit. 2, 123 (1963).

[3] K. Hafner and K. Goliasch, Chem. Ber. 94, 2909 (1961); C. H. De Puy et al., J. Amer. chem. Soc. 81, 4629, 4920 (1959).

Light Absorption and Relative Electron Densities of Carbocyanine Dyestuffs

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The relative electron densities at the α -methylene protons of simple pentamethine dyestuffs (1) decrease with increasing bathochromic shift of the longest-wavelength