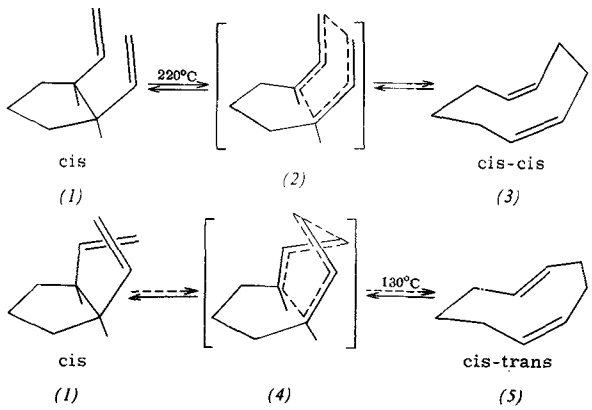
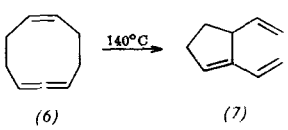
(intense *cis*-double bond absorption at 740 cm^{-1}) was synthetized independently by reduction of *cis*-cyclonona-1,2,6-triene *(6)* [2] with sodium in liquid ammonia [3]. When *(3)* was heated to 220 °C, it gave an equilibrium mixture identical with that formed from *(1)*.

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 diallyl 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 °C/125 mm, n_D^{20} = 1.4972, as sole product.

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

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

[3] This reduction was also effected by *D. Devaprabhakara* 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. Devaprabhakara* 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).

Cyclopentadienone-hydrazone

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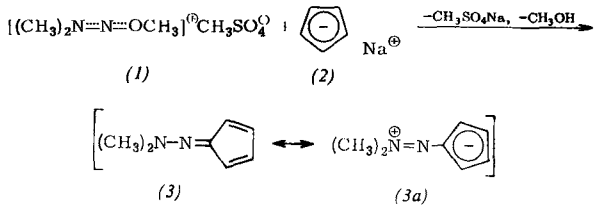
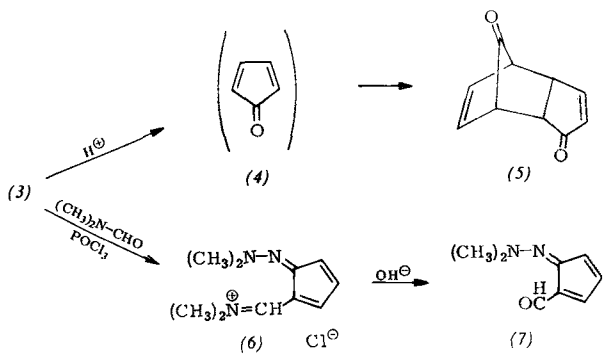
Alkylation of dimethylnitrosamine with dimethyl sulfate affords trimethylnitrosimmonium methylsulfate *(1)* [1]. This compound reacts with cyclopentadienylsodium *(2)* in tetrahydrofuran to give monomeric cyclopentadienone *N,N*-dimethylhydrazone *(3)*, orange leaflets, m.p. 14 °C, b.p. 107–108 °C/10 mm, λ_{max} (log ε) = 267.7 (3.31), 326.5 (4.41) mμ in n-hexane.



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, λ_{max} (log ε) = 251.8 (4.18), 373.5 (4.35) mμ in methanol, via the immonium salt *(6)*, which can be isolated as its perchlorate, orange needles, m.p. 135 °C (decomp.).

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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