(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-divinylcyclopentene 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 Dreding and Stuart models, (5) is more strained than the cis,cis-isomer (3).

\[
\text{cis-cis} \quad \xrightarrow{220^\circ C} \quad \text{cis-trans} \quad \xrightarrow{140^\circ C} \quad \text{cis-cis} 
\]

Compound (5), \(n^\text{D} = 1.4949\) (cis- and trans-double bond absorptions at 720 and 971 cm\(^{-1}\); respectively) [5] was prepared from both homopseudopelleteriene (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, \(n^\text{D} = 1.4972\), as sole product.

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

Cyclopentadienone-hydrazone

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Alkylation of dimethylaminosamine with dimethyl sulfate affords trimethylammonium 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, \(\lambda_{\text{max}}\) (log e) = 267.7 (3.31), 326.5 (4.41) m\(\mu\) in n-hexane.

\[
\begin{align*}
\text{(1)} & \quad \text{(4)} & \quad \text{(5)} \\
\text{(2)} & \quad \text{(3)} & \quad \text{(6)} \\
\text{(7)} & \quad \text{(8)} & \quad \text{(9)}
\end{align*}
\]

Compound (3) is the first cyclopentadienone derivative unsubstituted in the five-membered ring that is stable as the monomer. It can be distilled \textit{in vacuo} without decomposition, and even at 200 °C shows no tendency to dimerize or to react with dienophiles. Its dipole moment moment of 3.3 D indicates definite participation of the dipolar structure (1a) in the ground state of this aza-analogue of 6-dimethylamino-fulvene [2].

Hydrolysis of (3) with 2N H\(\text{2}\)SO\(\text{4}\) 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 e) = 251.8 (4.18), 373.5 (4.35) m\(\mu\) in methanol, via the immoniuni salt (6), which can be isolated as its perchlorate, orange needles, m.p. 135 °C (decomp.).

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Light Absorption and Relative Electron
Densities of Carbocyanine Dyestuffs

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