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# Reactions of $CH_3^+$ ($CD_3^+$) with $C_3H_6O$ Isomers

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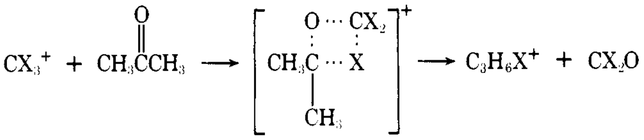
**Abstract:** Product distributions for the near thermal translational energy (≤0.1 eV) reactions of $CH_3^+$ and $CD_3^+$ with propionaldehyde, propylene oxide, trimethylene oxide, and allyl alcohol are reported and compared to previous results for acetone. With the exception of allyl alcohol, each of the $C_3H_6O$ isomers exhibits a reaction pathway with $CD_3^+$ leading to formation of a $CD_3OCH_2^+$ ionic product. Other ionic reaction products include $C_2H_5^+$, $CH_3O^+$, $C_3H_5^+$, $C_3H_7^+$, $CH_3CO^+$, $C_3H_5O^+$, and $C_3H_6O^+$. The results are generally consistent with $CH_3^+$ attack at the oxygen atom and formation of a short-lived intermediate adduct in approximately 80% of the reactive collisions; less important reaction channels include charge exchange, hydride transfer, and attack at sites other than oxygen.

A recent study by Smith, Herold, Elwood, and Futrell[1] of ion–molecule reactions of $CH_3^+$ ($CD_3^+$) with acetone (and acetone-$d_6$) demonstrated that no less than ten primary bimolecular reactions occur. The remarkably rich chemistry indicated by this work contrasts sharply with recent studies[2,3] of halomethyl ion ($CF_3^+$, $CF_2Cl^+$, etc.) reactions with acetone. In these cases Ausloos et al.[3] found $C_3H_6X^+$ (X = F or Cl) to be the dominant reaction product. This reaction presumably occurs via a four-center mechanism;[3]



$$CX_3^+ + CH_3\overset{\overset{O}{\|}}{C}CH_3 \longrightarrow \left[\begin{array}{c} O\cdots CX_2 \\ \vdots \quad\;\; \vdots \\ CH_3C\cdots X \\ | \\ CH_3 \end{array}\right]^+ \longrightarrow C_3H_6X^+ + CX_2O \tag{1}$$

For the most exothermic reactions involving the $CF_3^+$ reactant ion a $C_3H_5^+$ product, corresponding to HX elimination from the highly excited $C_3H_6X^+$ ion generated in reaction 1, was also observed.

Corresponding products ($C_3H_7^+$ and $C_3H_5^+$) were observed in the tandem Dempster–ion cyclotron resonance (ICR) study of $CH_3^+$ ($CD_3^+$) reactions with acetone; however, the analogous product from reaction 1 ($C_3H_7^+$) accounts for only 12% of the total products. A moderate amount of $C_3H_5^+$ was also observed (8%) but was attributed to

$$CD_3^+ + CH_3COCH_3 \rightarrow C_3H_5^+ + CD_3OH + 1.7\text{ eV} \tag{2}$$

since H, D isotopic scrambling (which is known to occur in deuterium labeled propyl cations *prior* to $H_2$ or HD elimination[4]) was not observed.

An unexpected reaction of $CD_3^+$ ($CH_3^+$) with acetone results in elimination of an ethylene molecule from an intermediate adduct as follows:

$$CD_3^+ + CH_3COCH_3 \rightarrow CD_3OCH_2^+ + C_2H_4 \tag{3}$$

Remarkably, while this reaction requires extensive rearrangement of the intermediate it accounts for 11% of all reaction products and occurs totally *without* H, D isotopic scrambling.[1]

To elucidate the mechanism of this reaction it was considered desirable to examine reactions of $CH_3^+$ ($CD_3^+$) with other $C_3H_6O$ isomers, on the assumption that the relative ease with which the intermediate was formed in reaction 3 might provide information concerning its structure. In this work we present branching ratios obtained for $CH_3^+$ ($CD_3^+$) reactions with propionaldehyde, trimethylene oxide, propylene oxide, and allyl alcohol. It will be shown that the several reactions can be partitioned into those occurring via direct reaction channels (proton transfer, charge transfer, and possibly hydride ion abstraction) and those involving an intermediate adduct, which can be rationalized on the basis of plausible structures of the respective reaction intermediates. Although several of the reaction products can be rationalized in terms of an intermediate resulting from attack at the oxygen atom, in several cases attack at other sites must also be considered.

## Experimental Section

In this work we have utilized a tandem Dempster–ICR mass spectrometer, described elsewhere,[5] to study the near thermal energy (≤0.1 eV average translational energy—laboratory frame) reactions of mass-selected $CH_3^+$ and $CD_3^+$ ions. Such studies, under single collision conditions, avoid mass discrimination effects present in most tandem instruments, the integrations required in crossed-beam experiments, and the artifacts common to more conventional ICR-double resonance studies.

The mass-selected $CH_3^+$ ($CD_3^+$) ions are decelerated to ≤0.1 eV and injected into an ICR cell where reaction occurs with the $C_3H_6O$ isomer (typically at a pressure of $10^{-6}$ Torr). Ions are detected using a variable frequency marginal oscillator calibrated for each ion frequency.[5] Total absolute $CH_3^+$ ($CD_3^+$) rate constants were not determined; however, all were fast, on the order of $10^{-9}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, consistent with previous studies of $CF_3^+$ reactions with acetone.[2,3]

$CH_3^+$ ($CD_3^+$) reactant ions were prepared by 25-eV electron impact on $CH_4$ ($CD_4$). The ions are probably internally excited, although recent work[6] indicates that electronic excitation is unlikely on the present reaction time scale ($10^{-3}$ s). While $CH_3^+$ vibrational energy may affect the branching ratios, preliminary results for reactions with a number of molecules show that it is rather unusual for nominally endothermic $CH_3^+$ reactions to account for more than 10–15% of the

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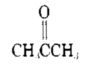
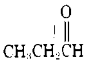
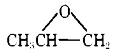
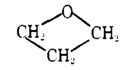
Table I. Product Distributions for Methyl Cation Reactions with $C_3H_6O$ Isomers

| | Percent abundance for $C_3H_6O$ neutral reactant | | | | |
|---|---|---|---|---|---|
| | Acetone | Propionaldehyde | Propylene oxide | Trimethylene oxide | |
| Reaction products[a] |  $CH_3C(=O)CH_3$ |  $CH_3CH_2C(=O)H$ |  |  | Allyl alcohol $CH_2{=}CHCH_2OH$ |
| $C_2H_5^+ + C_2H_4O$ | 9 | 10 | 16 | 13 | 0 |
| $CH_3O^+ + C_3H_6$ | 7 | 1 | 5 | 0 | 14 |
| $C_3H_5^+ + CH_3OH$ | 8 | 29 | 17 | 10 | 72 |
| $C_3H_7^+ + CH_2O$ | 12 | 0 | 0 | 0 | 0 |
| $CH_3CO^+ + C_2H_6$ | 28 | 2 | 8 | 0 | 0 |
| $C_2H_5O^+ + C_2H_4$ | 11 | 53 | 53 | 59 | 0 |
| $C_3H_5O^+ + CH_4$ | 5 | 5 | 1 | 16 | 14 |
| $C_4H_7^+ + H_2O$ | 6 | 0 | 0 | 0 | 0 |
| $C_3H_6O^+ + CH_3$ | 9 | 0 | 0 | 2 | 0 |
| $C_3H_7O^+ + CH_2$ | 5 | 0 | 0 | 0 | 0 |

[a] Identity of ionic species determined by use of $CD_3^+$ reactants; neutral species cannot be precisely characterized in all cases (see text). Ion concentrations have been corrected for naturally occurring $^{13}C$ in the $C_3H_6O$ neutral.

Table II. Heats of Reaction for Various $CH_3^+ + C_3H_6O$ Reaction Pathways

| | Reaction enthalpy for indicated neutral reactant, eV | | | | |
|---|---|---|---|---|---|
| Reaction products | Acetone | Propionaldehyde | Propylene oxide | Trimethylene oxide | Allyl alcohol |
| $C_2H_5^+ + \overline{CH_2CH_2O}$ | −1.2 | −1.4 | −2.5 | −2.4 | −2.1 |
| $C_2H_5^+ + CH_3CHO$ | −0.1 | −0.2 | −1.4 | −1.3 | −0.9 |
| $C_2H_5^+ + CH_2O + H_2$ | −0.7 | −0.9 | −2.0 | −1.9 | −1.6 |
| $CH_3O^+ + C_3H_6$ | −1.0 | −1.15 | −2.30 | −2.22 | −1.86 |
| $C_3H_5^+ + CH_3OH$ | −1.7 | −1.8 | −3.0 | −2.9 | −2.6 |
| $C_3H_5^+ + CH_2O + H_2$ | −0.9 | −1.0 | −2.2 | −2.1 | −1.8 |
| $CH_3CO^+ + C_2H_6$ | −3.3 | −3.45 | −4.6 | −4.5 | −4.2 |
| $CH_3CO^+ + 2CH_3$ | +0.6 | +0.5 | −0.6 | −0.5 | −0.2 |
| $C_2H_5O^+ + C_2H_4$ | −2.2 | −2.4 | −3.5 | −3.4 | −3.1 |
| $C_3H_5O^+ + CH_4$ | −3.6[b] | −3.7[b] | −4.9[b] | −4.8[b] | −4.4[b] |
| $C_3H_7^+ + CH_2O$ | −2.0 | −2.1 | −3.3 | −3.2 | −2.8 |
| $C_4H_7^+ + H_2O$ | −2.5[b] | −2.6[b] | −3.8[b] | −3.7[b] | −3.3[b] |
| $C_3H_6O^+ + CH_3$ | −0.17 | +0.13 | +0.40 | −0.16 | −0.15 |
| $C_3H_7O^+ + CH_2$ | +0.17[c] | [a] | [a] | [a] | [a] |

[a] Reliable proton affinities are not available. [b] Denotes considerable uncertainty in assigned heat of reaction. [c] Calculated using a proton affinity of 195.8 kcal/mol for acetone. Quoted in ref 11.

total products.[7] Studies of collisional deactivation of $CH_3^+$ were precluded in the present work by the collision-limited reaction of $CH_3^+$ with $CH_4$ to yield $C_2H_5^+$.

While nearly all the reactions observed in the present study may be rationalized by exothermic reactions (for ground-state ions), the excess internal energy of the $CH_3^+$ ($CD_3^+$) ions almost certainly affects the branching ratios. The average translational energies (≤0.1 eV lab) employed in these studies are sufficiently low that the differences with conventional ICR studies may be considered negligible. Indeed, a precise comparison of branching ratios between the tandem Dempster-ICR and conventional pulsed ICR experiments is difficult because of artifacts induced by the ion heating or ion ejection techniques employed in conventional ICR mass spectrometers. If it were possible to produce ground state $CH_3^+$ ions by conventional ICR experiments and determine branching ratios with sufficient accuracy, any difference in the branching ratios could be assumed to be due to excess internal energy in the present experiments. (Relaxed $CH_3^+$ ions can be produced by a mixture of methane in a large excess of hydrogen; however, this experiment is precluded in the Tandem instrument by the poor differential pumping for hydrogen and would complicate conventional ICR experiments due to the higher pressures and subsequent reactions of ionic products with hydrogen.)

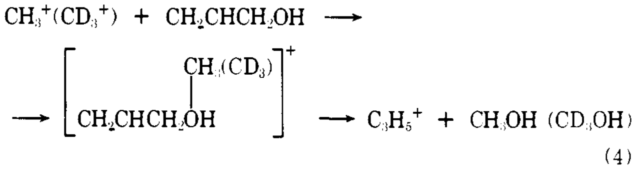
## Results and Discussion

Product distributions for the reactions of $CH_3^+$ with the five $C_3H_6O$ isomeric species studied (including previous results for acetone[1]) are given in Table I. Some of the data in this table were derived from studies of the reaction of $CD_3^+$ with these compounds, which provided an unambiguous assignment of ionic empirical formulas. These isotopic studies also provided information regarding the reaction mechanism and an indication of the extent of hydrogen atom rearrangement.

The enthalpies of reaction (in electron volts) corresponding to the reactions in Table I are given in Table II, and were calculated using the thermodynamic values given in ref 8. These values assume ground state reactants and products, and were calculated for the products indicated in Table II.

Comparison of the product distributions given in Table I shows a strong similarity of the results for the reactions of $CH_3^+$ with propionaldehyde, trimethylene oxide, and propylene oxide. The reactions are qualitatively similar to the major reactions observed with acetone[1] and markedly dissimilar to those of allyl alcohol. Accordingly the results for these three molecules are grouped and discussed in a later section.

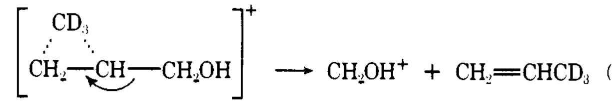
**Allyl Alcohol.** For reaction of $CH_3^+$ with allyl alcohol the major product (72%) is $C_3H_5^+$, presumably formed via a reaction involving complex formation with subsequent fragmentation.



$$CH_3^+(CD_3^+) + CH_2CHCH_2OH \longrightarrow \left[CH_2CHCH_2\overset{\overset{\displaystyle CH_3(CD_3)}{|}}{O}H\right]^+ \longrightarrow C_3H_5^+ + CH_3OH\ (CD_3OH) \quad (4)$$

*Smith et al. / Reactions of $CH_3^+$ ($CD_3^+$) with $C_3H_6O$ Isomers*

This reaction occurs without detectable H, D scrambling and is consistent with the reactivities of other alcohols with $CH_3^+$.[7,9] The remaining products are $CH_3O^+$ and $C_3H_5O^+$; isotopic studies suggest that the latter results from a simple hydride ion abstraction. The mechanism for $CH_3O^+$ formation is presently undetermined. A plausible mechanism is $CD_3^+$ attack at the double bond:


(5)

However, the possibility that $CH_3O^+$ results from dissociative hydride ion abstraction via reaction 6 cannot be ruled out on thermodynamic grounds.

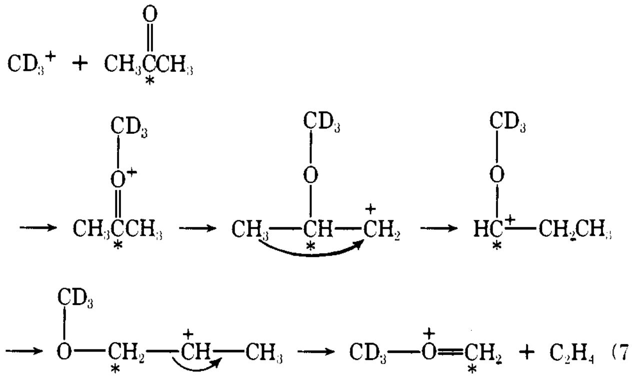
$$CH_3^+ + CH_2CHCH_2OH \rightarrow [C_3H_5O^+ + CH_4] \rightarrow CH_3O^+ + C_2H_2 + CH_4 \quad (6)$$

This mechanism is considered less likely as recent work[10] suggests that hydride abstraction processes deposit a relatively small amount of excess energy in the ionic products. Further experiments with selectively labeled neutrals (i.e., $CH_2CHCD_2OH$) are required to clarify the mechanism unambiguously.

**Propionaldehyde, Trimethylene Oxide, and Propylene Oxide.** As noted above, the reactions of $CH_3^+$ ($CD_3^+$) with propionaldehyde, trimethylene oxide, and propylene oxide are qualitatively similar; consequently their reactions will be discussed as a group.

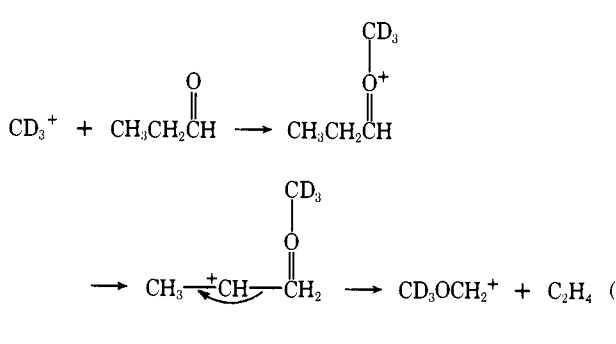
The most interesting aspect of the product distributions given in Table I is the fact that $C_2H_5O^+$ is the major product (50-60% abundance) for reaction with each of these species. As with acetone, reaction 3 occurs without H, D isotopic scrambling (i.e., only $C_2D_3H_2O^+$ is observed as a product).

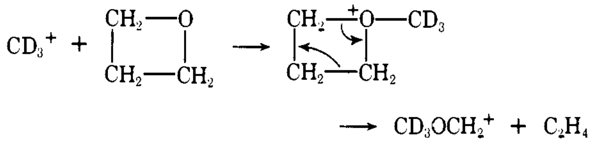
A study of the reaction of $CH_3^+$ with acetone, labeled with $^{13}C$ at the carbonyl position, shows that the $C_2H_4$ molecule eliminated from the adduct is unlabeled. This may occur via a 1,2 methyl shift, as follows:

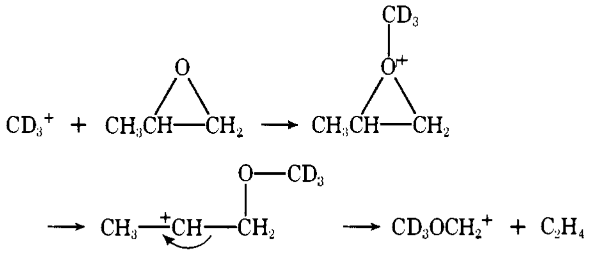

(7)

This mechanism is consistent with both the $^{13}C$ and deuterium labeling studies.[1]

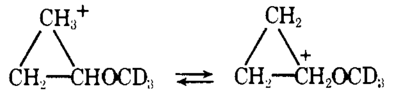
By analogy we can propose the following mechanisms for the reaction of $CD_3^+$ with propionaldehyde, trimethylene oxide, and propylene oxide, e.g.


(8)


(9)


(10)

Further justification of the proposed mechanisms must await the appropriate $^{13}C$ labeling experiments. An alternate rationalization of these reactions, invoking a protonated cyclopropane intermediate structure, is also plausible.



An experimental method for distinguishing between this and the $CH_3OCH_2CHCH_3^+$ intermediate is being pursued. For the present, we assume that these mechanisms are correct and postulate a common intermediate (possibly $CD_3OCH_2CHCH_3^+$) for reactions 7, 8, and 10.

Other significant products for $CH_3^+$ reacting with propionaldehyde, trimethylene oxide, and propylene oxide are $C_3H_5O^+$, $C_3H_5^+$, and $C_2H_5^+$. Since the $CD_3^+$ reaction does not lead to detectable $C_3H_4DO^+$, we assume that the first product results exclusively from hydride ion abstraction rather than proton transfer followed by $H_2$ (HD) elimination.

$$CD_3^+ + C_3H_6O \rightarrow C_3H_5O^+ + CD_3H \quad (11)$$

Reaction 11 is 3.7, 4.8, and 4.9 eV exothermic for propionaldehyde, trimethylene oxide, and propylene oxide, respectively. Hydride abstraction results in very stable products from the reaction with trimethylene oxide (and allyl alcohol, as discussed earlier), while the other $C_3H_6O$ isomers show considerably reduced yields of the $C_3H_5O^+$ product. In contract with acetone,[1] products corresponding to elimination of a methane molecule from the adduct were not found for other $C_3H_6O$ isomers.

The product at *m/e* 41 is assigned to $C_3H_5^+$ since $C_2HO^+$ formation required considerably more energy, even for formation via a dissociative hydride abstraction process ($CH_4$ elimination from $C_3H_5O^+$). Additionally, this species was definitely shown to be $C_3H_5^+$ in the $CD_3^+$-acetone-$d_6$ system studied previously. Experiments with $CD_3^+$ show no D-atom retention in the ionic products. Since the $C_3H_5^+$ ion abundances are in opposite order to that anticipated from energetics for the respective reactions, it appears that other factors, such as structure of the reaction intermediate, determine the product ratios.

The mechanism of $C_3H_5^+$ formation may be visualized as an alternate decomposition pathway for the postulated intermediate species of reactions 7, 8, and 10, viz.

$$CD_3^+ + C_3H_6O \rightarrow C_3H_5^+ + CD_3OH \quad (12)$$

Similarly, the $C_2H_5^+$ may also be rationalized as resulting from the decomposition of the same reaction complex:

$$CD_3^+ + C_3H_6O \rightarrow C_2H_5^+ + C_2D_3HO \quad (13)$$

As with $C_3H_5^+$ products, use of $CD_3^+$ reactant ions did not result in detectable deuterium incorporation in this product.

$CH_3O^+$ (or $CH_2OH^+$) was a minor product of the reaction with propionaldehyde (~1%) and with propylene oxide (5%), and not detected for reaction with trimethylene oxide. A larger amount of $CH_3O^+$ (7%) was observed for reaction of $CH_3^+$ with acetone but a high degree of H, D isotopic scrambling was noted when $CD_3^+$ reactant ions were used. This contrasts to the present study in which these $C_3H_6O$ isomers produce a negligible amount of deuterium atom labeling of the $CH_3O^+$ ionic product. Further studies with double labeling will be required before a definite mechanism can be proposed.

$CH_3CO^+$ was produced by a direct reaction of methyl cation with acetone (28% abundance), propylene oxide (8% abundance), and propionaldehyde (2% abundance), but not for trimethylene oxide or allyl alcohol. This reaction always occurs without deuterium atom incorporation in the ionic product, implying a direct reaction such as $CH_3^-$ "pickup" from neutral species with a readily available methyl group. An alternative mechanism is dissociative charge transfer, provided one makes the not-unreasonable assumption that the reactant ion beam contains some number of excited $CH_3^+$ ions and that the excess energy is available to drive the reaction. Again no correlation of reaction exothermicity with products is noted in Table II.

The fact that $C_4H_7^+$ (representing $H_2O$ elimination from the complex) is not observed as a product for any of the $C_3H_6O$ isomers except acetone is best explained as increased competition of alternate channels such as reactions 8-10.

In conclusion, the present work has examined the product distributions for $CH_3^+$ ($CD_3^+$) reactions with four $C_3H_6O$ isomers in relation to previous results for acetone. The reactions with allyl alcohol are dissimilar to the other isomers studied, as expected, and are consistent with the reactions of other alcohols with methyl cations.[7,9] Propionaldehyde, propylene oxide, and trimethylene oxide react with $CH_3^+$ ($CD_3^+$), with reactions 8-10 being the major pathway (50-60%). Reactions of the alcohol, aldehyde, and oxide isomers are simpler than that of acetone. The fact that a more complex set of reactions occurs with acetone, often involving extensive H, D randomization, is consistent with the complexity of reaction 7, compared to reactions 8-10. A methyl shift or formation of the alternative protonated cyclopropane structure intermediate, followed by $C_2H_4$ elimination, are undoubtedly slow, rate-determining processes which allow sufficient time for alternate reaction pathways to become important.

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# Novel Aromatic Systems. 7.[1a] Benzo- and Dibenzocyclobutadiene Dications[1b]

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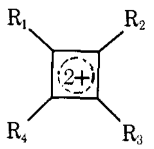
*Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.* *Received January 18, 1977*

**Abstract:** Benzo- and dibenzocyclobutadiene dications were prepared in $SbF_5$-$SO_2ClF$ solution at low temperatures. The dications are characterized from their proton and carbon-13 NMR spectra as fully delocalized closed-shell six and ten π-electron aromatic systems, respectively.

Hückel's "4*n* + 2" rule[2] accurately predicts the enhanced stability of conjugated cyclic polyolefins (annulenes) containing (4*n* + 2) π electrons and thus their "aromaticity".[3] Cyclobutadiene (**1**) is known to be extremely reactive and elusive; its isolation was only achieved by using matrix isolation techniques at low temperatures.[4] Two-electron oxidation of **1** should result in the formation of a closed-shell 2π Huckeloid cyclobutadiene dication (**2**) with aromatic character.[5] Although to date the parent dication **2** has not been directly obtained, a number of substituted cyclobutadiene dications **3** are known.[6] In accord with the theoretical prediction,[5] cyclobutadiene dications are static, nonequilibrating 2π Hückeloid systems.

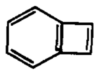
**1**

**2**

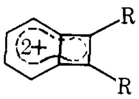


**3**

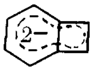
The monobenzo derivative of cyclobutadiene, benzocyclobutadiene (**4**), has also been a subject of extensive search,[3a,5,7]



**4**



**5**, R = H
**6**, R = $CH_3$



**7**