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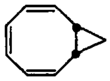
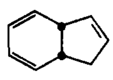
Thermal Isomerization of 1,2,7,8,9,9-Hexadeuterio-*cis*-bicyclo[6.1.0]nona-2,4,6-triene

Sir:

The detailed mechanism of formation of *cis*-dihydroindene (**2**) from *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) remains unsolved.[1] Neither extensive experimental work in many laboratories over the past decade[2] nor the advent of orbital symmetry theory[3] has led to a completely adequate mechanistic rationale for this facile reaction.



1



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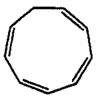
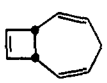


3

The final step in the overall mechanism is thought to involve the symmetry-allowed conversion of *all-cis*-cyclononatetraene (**3**) to dihydroindene (**2**).[2,4] The penultimate step is imagined to be a nonconcerted biradical-mediated link leading from **1**, or some related structure (**4**–**9**) readily accessible through symmetry-allowed valence isomerizations,[3] to the tetraene **3**.



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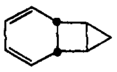

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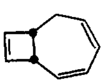

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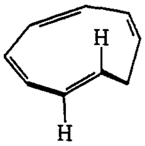

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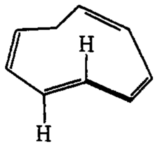

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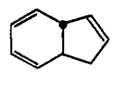
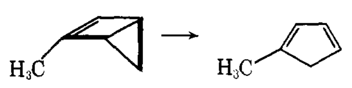


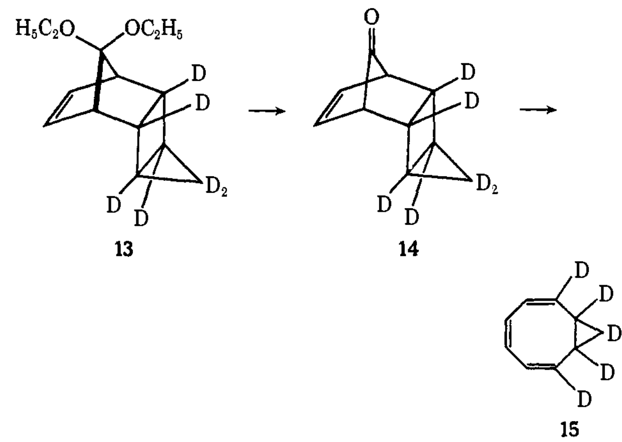
9

Apparently there has been no consideration of concerted [$_\sigma 2_s + {}_\sigma 2_a$] processes which might convert **1** or one of the isomers **4**–**9** directly to **2** or **3**; in view of the recently uncovered [$_\sigma 2_s + {}_\sigma 2_a$] thermal isomerization of 2-methylbicyclo[2.1.0]pent-2-ene (**10**) to 1-methylcyclopentadiene (**11**),[5] analogous reactions seem very reasonable alternatives to the biradical mechanisms commonly invoked as part of the overall **1** → **2** process.



10 **11**

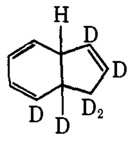
We have prepared and rearranged 1,2,7,8,9,9-hexadeuterio-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**15**) in an initial test for such [$_\sigma 2_s + {}_\sigma 2_a$] reactions.



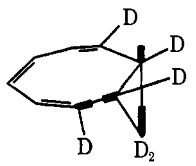
13 **14** **15**

Perdeuteriobicyclo[2.1.0]pent-2-ene[6] and cyclopentadienone diethyl ketal[7] at 4° gave the labeled *endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one (**13**) in quantitative yield; acid-catalyzed hydrolysis of ketal **13** in aqueous methanol–chloroform gave the corresponding ketone **14**. The nmr spectrum of **13** showed only C-1 and C-7 methine protons at τ 7.25 (t, J = 2.5 Hz) and vinyl protons at 3.89 (t, J = 2.5 Hz) in addition to the two sets of absorptions for $-OCH_2CH_3$; the nmr spectrum of **14** had triplets (J = 2.5 Hz) of equal intensity at τ 3.42 and 7.17, while the carbonyl band in the infrared came at 1780 cm^{-1}.[8]

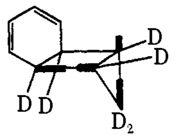
The glpc-purified labeled ketone **14** in thoroughly degassed neutral CCl_4 was decarbonylated[9] at 120° to provide **15**. Further thermolysis converted **15** to a dihydroindene-d_6 which had nmr absorptions at τ 4.1–4.7 and 6.5 in a ratio of 3.0:1. The complex absorptions found centered at τ 6.98, 7.36, and 7.79 for the other allylic protons in unlabeled dihydroindene (**2**) were completely absent, further supporting the assignment of structure to the 1,1,2,3,7,7a-hexadeuterio compound **16**.



16



17



18

This labeling result complements earlier studies limited to tracing the fate of substituents at C-9 in bicyclononatrienes.[2] It conclusively rules out a number of [$_\sigma 2_s + {}_\sigma 2_a$] mechanisms for the rearrangement, including those abbreviated through structures **17** and **18**. The experimental finding is consistent with the various nonconcerted mechanisms proposed in the literature as well as with the [$_\sigma 2_s + {}_\sigma 2_a$] symmetry-allowed and connectivity-permuting isomerization of

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(1) J. C. Barborak, T.-M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *J. Amer. Chem. Soc.*, **93**, 279 (1971).

(2) Reference 1 includes an extensive listing of pertinent articles.

(3) R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, **91**, 1560 (1969); P. Radlick and G. Alford, *ibid.*, **91**, 6529 (1969).

(5) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

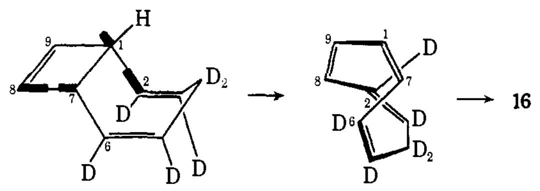
(6) A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., *Org. Syn.*, submitted for publication; J. E. Baldwin and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **92**, 5247 (1970); J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *ibid.*, **92**, 5249 (1970).

(7) E. L. Allred and C. Anderson, *J. Org. Chem.*, **32**, 1874 (1967); P. E. Eaton and R. A. Hudson, *J. Amer. Chem. Soc.*, **87**, 2769 (1965).

(8) The unlabeled analogs of **13** and **14** were thoroughly characterized by mass spectrometric and spectral data; *cf.* J. E. Baldwin and A. H. Andrist, *Spectrosc. Lett.*, in press.

(9) J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966), and references therein.

the bicyclo[5.2.0]nona-2,5,8-triene form of the labeled substrate (**19** → **20** → **16**).



19 **20**

Further labeling studies to distinguish between these two distinctly different types of mechanism are underway.[10]

Acknowledgment. This work was supported by the Cities Service Oil Co., the Du Pont Co., and the National Science Foundation.

(10) 3,6-Dideuteriobicyclo[6.1.0]nona-2,4,6-triene rearranges to 3a,6-dideuteriodihydroindene. This qualitative finding by R. K. Pinschmidt, Jr., is now being placed on a firm quantitative basis.

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Received March 8, 1971

On the Quenching of Photochemical Reactions and of Fluorescence of Alkanones by 1,3-Cyclohexadiene and *cis*-1,3-Pentadiene

Sir:

One of the most powerful techniques in investigating the mechanism of photochemical reactions of carbonyl compounds is the study on the energy transfer from excited states of carbonyl compounds to conjugated dienes which was developed in Hammond's laboratory.[1] The singlet energy level of dienes is above that of carbonyl compounds. However, the energy spacing between the singlet and the triplet states of carbonyl compounds is relatively small, while that between dienes is large. The triplet energy level of dienes is thus lower than that of carbonyl compounds. Therefore, dienes may readily accept energy from the triplet state of carbonyl compounds thus quenching it, while they have little effect on the behavior of the singlet state of carbonyl compounds. However, Hammond and coworkers found that dienes quenched the fluorescence of aromatic hydrocarbons.[2] Recently, Wettack, Turro, and their coworkers demonstrated that dienes also quenched the fluorescence of aliphatic and alicyclic ketones, but the quenching efficiency for fluorescence was much lower than that for the $^3n,\pi^*$ of ketones.[3] Many conjugated dienes have been used in the investigation on the mechanism of photochemical reactions and 1,3-pentadienes and 1,3-cyclohexadiene are among the most commonly used. This communication demonstrates that 1,3-cyclohexadiene is more efficient than *cis*-1,3-pentadiene in quenching the fluorescence and photochemical processes of alkanones.

Pinacolone (0.80 *M* in *n*-hexane) was used for the study on the type I process (reaction 1), and the reaction was followed by the consumption of pinacolone by gas chromatography using *n*-undecane as the internal standard.[4] 2-Hexanone (0.83 *M* in *n*-hexane) was used for the study on the type II process (reaction 2), and the reaction was followed by the formation of acetone.[5,6] The quenching studies were carried out with various concentrations of either diene at 313 nm using an apparatus previously described.[6] The data for quenching of pinacolone were taken from our earlier work and verified at a few selected diene concentrations.[4] The Stern–Volmer plots are presented in Figures 1 and 2. The plots were analyzed on the basis of two reactive states, the $^1n,\pi^*$ and the $^3n,\pi^*$, and the results are presented in Table I.[3,7] The quenching of fluorescence of alkanones was carried out in a conventional spectrofluorimeter using exciting light at 313 nm and *n*-hexane as the solvent. The results are also summarized in Table I.

$$CH_3COC(CH_3)_3 \xrightarrow{h\nu} CH_3CO\cdot + (CH_3)_3C\cdot \tag{1}$$

$$CH_3CO(CH_2)_3CH_3 \xrightarrow{h\nu} CH_3C(OH){=}CH_2 + CH_3CH{=}CH_2 \tag{2}$$

Our results clearly indicated that 1,3-cyclohexadiene is a more efficient quencher than *cis*-1,3-pentadiene for both the fluorescence and the photochemical reactions of alkanones. Since the photochemical reactions studied occur from both the $^1n,\pi^*$ and the $^3n,\pi^*$,[4,5] while the fluorescence occurs only from the $^1n,\pi^*$, *the higher quenching efficiency of cyclohexadiene may be attributed to its enhanced ability in quenching the* $^1n,\pi^*$ *of alkanones*. However, a minor discrepancy remains in the experimental results that *cis*-1,3-pentadiene appears to be a more efficient quencher than 1,3-cyclohexadiene at low concentrations for the type II process of 2-hexanone. Since the E_T (triplet energy) for both dienes are appreciably lower than the E_T for 2-hexanone, both quenching rates for the $^3n,\pi^*$ should approach that of a diffusion-controlled process. However, 1,3-cyclohexadiene is known to undergo sensitized dimerization at a very high quantum efficiency whereas 1,3-pentadienes do not.[2b,8] The concentration of 1,3-cyclohexadiene will decrease as the quenching proceeds, and the effective quencher concentration during the irradiation will be less than the starting quencher concentration. We suggest that the apparent lower efficiency of 1,3-cyclohexadiene in this case may be due to its consumption during the irradiation.

Hammond and his coworkers showed that 1,3-cyclohexadiene quenched the fluorescence of aromatic hydrocarbons more efficiently than do most acyclic dienes, and they also suggested that an exciplex between the excited state of the aromatic hydrocarbon and the diene was involved in the deactivation of the excited state.[2] Evans suggested that the initial complex formed underwent electron transfer from the diene as the donor to give an electron-transfer complex which subsequently deactivated to the ground state.[9] Recently Barltrop and Carless reported that dienes reacted with the $^1n,\pi^*$ of alkanones to form oxetanes.[10] The mechanism of

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(1) For a review on energy transfer to 1,3-dienes, see A. A. Lamola in "Energy Transfer and Organic Photochemistry," A. A. Lamola and N. J. Turro, Ed., Interscience, New York, N. Y., 1969, p 96.

(2) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665, 3893 (1966); L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969).

(3) F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1794 (1970).

(4) N. C. Yang and E. D. Feit, *ibid.*, **90**, 504 (1968).

(5) P. J. Wagner and G. S. Hammond, *ibid.*, **88**, 1245 (1966).

(6) D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

(7) J. C. Dalton and N. J. Turro, *Mol. Photochem.*, **2**, 133 (1970).

(8) D. Valentine, N. J. Turro, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5022 (1964).

(9) T. R. Evans, *ibid.*, **93**, 2081 (1971).