proximately.[1] Changes in a ${}^1H$ nmr signal intensity upon irradiation of a different ${}^1H$ resonance have been observed for cases where both protons are in the same molecule[3-5] and where the observed and irradiated protons are in different molecules.[6-8]

We report here the direct observation of an *inter*molecular ${}^{13}C\{{}^1H\}$ NOE in a $CS_2$-$CHCl_3$ system. The experimental sample consisted of a triple concentric tube arrangement. The innermost region was a sealed 1-mm capillary containing perfluorobenzene which was used as a lock and was centered within a 5-mm (sealed) tube containing perchloroethylene which was used as a standard for integration of peak areas. This arrangement was inserted concentrically into a 10-mm tube that contained a degassed (five freeze–pump–thaw cycles under vacuum) solution of $CS_2$-$CHCl_3$ in a 1:10 mole ratio.

The experiment was performed in the pulse Fourier transform mode on a Bruker HFX-90 spectrometer, interfaced with a Digilab Pulse and FTS/NMR-3 system. The experiment was conducted as follows. First a ${}^{13}C$ spectrum was recorded with the proton decoupler (CW) on, and with its frequency centered on the $CHCl_3$ resonance position, as demonstrated by the collapse of the $CHCl_3$ doublet. Second, the spectrum was recorded with the decoupler switched off.[9] The areas of the $CS_2$ and the $Cl_2C$=$CCl_2$ peaks were determined for both experiments. Then, assuming that the area of the $Cl_2C$=$CCl_2$ signal is independent of ${}^1H$ decoupling, the ${}^{13}CS_2$-$\{CHCl_3\}$ NOE was determined. The results obtained in this manner reveal a *negative* NOE; that is, the $CS_2$ peak area decreases upon irradiation of the proton in $CHCl_3$. When the time between pulses is 220 sec (approximately $5T_1$ for $CS_2$), the decrease in intensity is 30%. As a check, a sample of $CS_2$-$CDCl_3$ was prepared and its spectrum recorded in the same manner; this sample gave essentially no NOE, within the experimental error (about $\pm 5\%$).

An intermolecular ${}^{13}C$-${}^1H$ dipole–dipole mechanism cannot account for a negative NOE. This can be seen from the expression for the Z magnetization of nucleus $I$, in the presence of another spin, $S$, which undergoes saturation (eq 1).[10] In the extreme narrowing case

$$\langle I_z \rangle = I_0 + \xi S_0 I(I+1)/S(S+1) \qquad (1)$$

$\xi$ is $+{}^1/_2$ for dipolar coupling.[10] Balaram, Bothner-By, and Dadok[11] have demonstrated a negative ${}^1H$-$\{{}^1H\}$ NOE that may be of dipole–dipole origin for the case of large correlation times for molecular reorientation. However, Kuhlmann, Grant, and Harris[2] have demonstrated that for dipole–dipole coupling even very large correlation times can lead to only a reduced positive NOE, not a negative value, in the ${}^{13}C$-$\{{}^1H\}$ case. *A priori*, another possible explanation is a dipolar mech-

anism involving the intermediacy of a third spin.[2,4,11] However, this seems unlikely, as the third spin would be ${}^{35}Cl$, which has a rapid (quadrupolar) relaxation mechanism of its own and, thus, could reduce the magnitude of the NOE but could not make it negative.[2]

An alternative explanation is a time-dependent intermolecular scalar coupling, for which $\xi$ in eq 1 is *minus* one in the extreme narrowing case.[10] This mechanism would arise in what is essentially an exchange modulation of the spin–spin coupling due to electron overlap in the collision complex. This may be reasonable for molecules such as $CS_2$, in which the pertinent carbon atom is not severely screened away from neighboring molecules by other atoms, *e.g.*, hydrogens.

Although one cannot, on the basis of the results given here, justify a more definite interpretation, these results clearly establish that intermolecular ${}^{13}C$-$\{{}^1H\}$ NOE's are measurable. Such effects should be useful in studies of intermolecular interactions and molecular reorientation in the liquid state.

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## Mono- and Dideuteriocyclobutadienes[1]

*Sir:*

We wish to report the preparation of monodeuterio-, 1,2-dideuterio-, and 1,3-dideuteriocyclobutadienes. The preparation depends on the synthesis of the appropriate deuterated 2-pyrones,[2] photoisomerization to the $\beta$-lactone, and photoelimination of carbon dioxide.

Irradiation of 2-pyrone-5-$d_1$ (84% $d_1$) and 2-pyrone-6-$d_1$ (92% $d_1$) matrix isolated in argon at 8°K gives
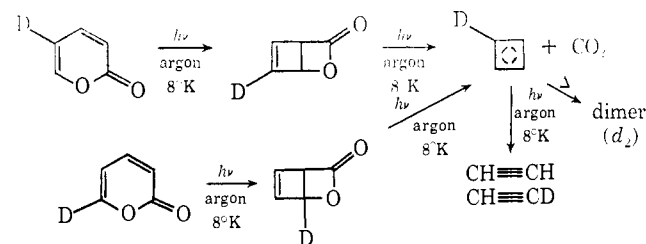


different monodeuterio-$\beta$-lactones but the same monodeuteriocyclobutadiene (1223, 780, 654, 583, 576, 535 cm$^{-1}$). Continued irradiation converts the monodeuteriocyclobutadiene to acetylene (3260, 735 cm$^{-1}$) and monodeuterioacetylene (3330, 2580, 687 cm$^{-1}$).

(4) R. A. Bell and J. K. Saunders, *Can. J. Chem.*, **46**, 3421 (1968).
(5) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).
(6) R. Kaiser, *J. Chem. Phys.*, **42**, 1838 (1965).
(7) E. Lippmaa and M. Alla, *Eesti NSV Tead. Akad. Toim., Fuus, Mat.*, **15**, 473 (1966).
(8) S. I. Chan and G. P. Kreishman, *J. Amer. Chem. Soc.*, **92**, 1102 (1970).
(9) In certain cases the decoupler was not switched off; rather, the ${}^1H$ decoupling frequency was simply moved a few thousand hertz away.
(10) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 312.
(11) P. Balaram, A. A. Bothner-By, and J. Dadok, *J. Amer. Chem. Soc.*, **94**, 4015 (1972).

(1) Photochemical Transformations. XL.
(2) Monodeuterated 2-pyrones were prepared by literature procedures.[3] Dideuterio-2-pyrones were prepared in an analogous manner by halogenation of monodeuterio-2-pyrones followed by reductive incorporation of the second deuterium.
(3) W. H. Pirkle and M. Dines, *J. Org. Chem.*, **34**, 2239 (1969); *J. Amer. Chem. Soc.*, **90**, 2318 (1968).

If a matrix containing monodeuteriocyclobutadiene and the acetylenes is warmed and pumped into a trap (77°K), the mass spectrum (14 eV) of the product shows parent ions for cyclobutadiene dimer containing two deuterium atoms[4] ($m/e$ 106), acetylene ($m/e$ 26), and acetylene-$d_1$ ($m/e$ 27).[5]
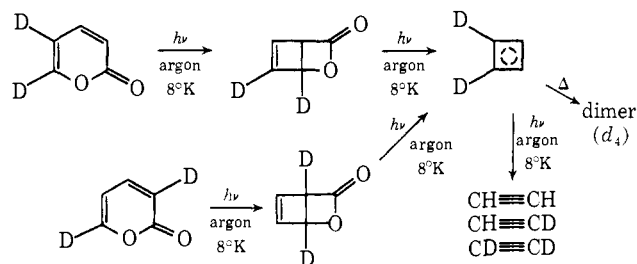


In similar fashion, irradiation of 2-pyrone-5,6-$d_2$ (86% $d_2$, 14% $d_1$) and 2-pyrone-3,6-$d_2$ (81% $d_2$, 19% $d_1$) gives cyclobutadiene-1,2-$d_2$ (1212, 1188, 770, 654, 583, 576 cm$^{-1}$). Irradiation of cyclobutadiene-1,2-$d_2$ gives acetylene (3260, 735 cm$^{-1}$), acetylene-$d_1$ (3330, 2580, 687 cm$^{-1}$), and acetylene-$d_2$ (2420 cm$^{-1}$). The mass spectrum of the product shows the cyclobutadiene-$d_2$ dimer ($m/e$ 108), acetylene, acetylene-$d_1$, and acetylene-$d_2$.[5]
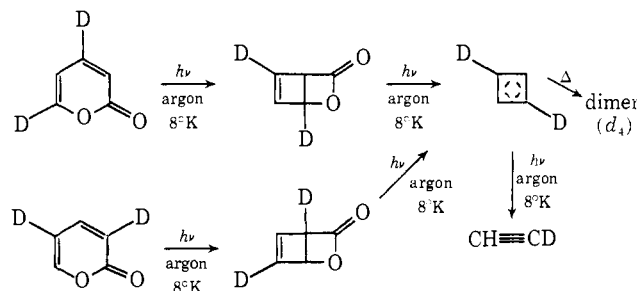


Cyclobutadiene-1,3-$d_2$ (1216, 1182, 781, 654, 633, 583, 576, 535 cm$^{-1}$) has been generated by irradiation of 2-pyrone-4,6-$d_2$ (85% $d_2$, 14% $d_1$) and 2-pyrone-3,5-$d_2$ (64% $d_2$, 33% $d_1$). Photochemical cleavage of cyclobutadiene-1,3-$d_2$ gives only acetylene-$d_1$ (3330, 2580, 687 cm$^{-1}$). The mass spectrum of the product confirms the presence of acetylene-$d_1$ and shows the parent ion of cyclobutadiene-$d_2$ dimer ($m/e$ 108).

The formation of the same deuterated cyclobutadiene from different precursors in the three cases cited above leaves no room for doubt that the product formed from 2-pyrone is indeed cyclobutadiene.[6,7] The photochemical cleavage of cyclobutadiene-1,2-$d_2$ to acetylene, acetylene-$d_1$, and acetylene-$d_2$ also provides convincing evidence that the product is cyclobutadiene. The cleavage of cyclobutadiene-1,3-$d_2$ to only acetylene-$d_1$ shows clearly that tetrahedrane is not an intermediate in the photochemical conversion of cyclobutadiene to acetylene. A further interesting observation comes from these studies. The rate of photochemical cleavage of the cyclobutadienes is 1,3-$d_2$ > 1,2-$d_2$ > $d_1$ > $d_0$. This could be due to an isotope effect on the rate constant

cleavage, but it is more likely due to an increase in the excited state lifetime in the deuterated cyclobutadienes.

The dideuteriocyclobutadienes give further insight into the details of the cyclobutadiene structure. The leading candidates for the structure have $D_{4h}$ (square planar) and $D_{2h}$ (rectangular planar) symmetries, respectively. If the structure of cyclobutadiene has $D_{4h}$ sym-



metry, only one 1,2-dideuteriocyclobutadiene and one 1,3-dideuteriocyclobutadiene are possible. If the structure has $D_{2h}$ symmetry, two 1,2-dideuteriocyclobutadienes and one 1,3-dideuteriocyclobutadiene are possible.
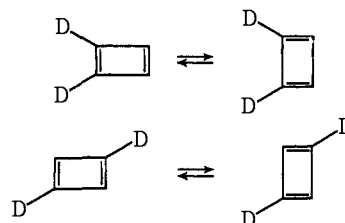


The infrared spectrum of 1,2-dideuteriocyclobutadiene is very similar to that of 1,3-dideuteriocyclobutadiene. No evidence for the presence of two 1,2-dideuteriocyclobutadienes is observed. This fits with our tentative conclusion based on the infrared spectrum that cyclobutadiene has $D_{4h}$ symmetry.

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## Cycloadditions and Reactivity of 2-Methoxyallyl Halides

*Sir:*

The 2-methoxyallyl halides **1a-c** represent a novel class of organic compounds which have recently become accessible by two independent and efficient routes.[1] In studying the chemical properties of these compounds two questions seemed to us of special interest: (1) what is the reactivity of **1a-c** when compared with conven-



1a, Hal = Cl
b, Hal = Br
c, Hal = I
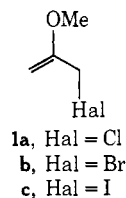
tional allyl halides and (2) can the 2-methoxyallyl cation be generated and captured with a conjugated diene according to eq 1?

(4) The element composition of this ion ($C_8H_6D_2$) was established by exact mass determination.

(5) The ratio of the deuterated to nondeuterated acetylene determined by mass spectrometry was that expected on the basis of the deuterium incorporation in the starting 2-pyrone in each case.

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