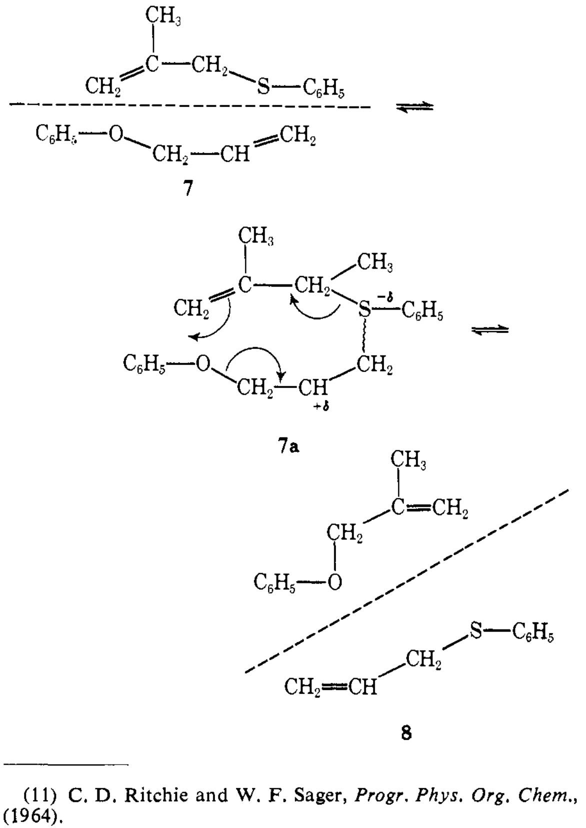
complex **3**. Thus, the conspicuously smaller values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the nonpolar solvent decalin (see Table I) compared to the polar solvents nitrobenzene and *N*-methylacetamide are quite inconsistent with a normal ionization mechanism.[11,12] Clearly, also, they are not characteristic of sigmatropic and electrocyclic rearrangements[1] in which solvent effects are normally absent. Rather than a nonpolar mechanism, these data indicate we are dealing with a unique transition state in which the charge separation of a lower lying intermediate is being destroyed (as illustrated in passing from **3** to **3a** or **3b**) (eq 4), and might be designated more appropriately as an antipolar mechanism. The negative $\Delta S^{\ddagger}$ values for such reactions taking place in the gas phase, and in decalin, are in keeping with the postulated mechanism.

The assumption of an intermediate complex such as **3** or **1a** in thermal allylic rearrangements is compelled by another crossed-product experiment ($\mathbf{7} \rightleftharpoons \mathbf{8}$). Thus, while the oxyallylic rearrangement does not occur in pure allyl phenyl ether, a crossed-product isomerization does take place in the presence of allyl phenyl sulfide (eq 5). Presumably, the principal reason for the (observed) slower reactions here lies in the nature of the mixed complex 7a. Though its formation is made possible by the ability of (one) sulfur to expand its octet,[13] the presence of oxygen instead of a second sulfur (as in 7a) enforces sigmatropic change with a stricter requirement for concertedness.



7

7a

8

(5)

A point of further interest is the effect of the substituent[13] on the sulfur atom. It is found that rearrangement of the homologous compound $C_6H_5CH_2SCH_2CD{=}CD_2$ occurs at a (more than) 50 times slower rate both thermally and photochemically. Apparently the efficiency with which sulfur accepts electronic charge by octet expansion, a necessary step which oxygen cannot accommodate, is somewhat dependent on the nature of the sulfur substituents.

Finally, we have considered the possibility of a radical pathway analogous to what has been established for certain 1,3-thermal sigmatropic rearrangements occurring in homoallylic systems.[14] The search for identifying emissions in nmr nuclear polarization experiments with substrates like **1** and **3** in solution at various temperatures up to 180° have been unfruitful. Moreover, the total lack of disulfide and other characteristic side products under any of the reaction circumstances discussed in this report comprises the most telling argument against the operation of a radical dissociation–recombination process. Any occurrence of aryl thiyl radicals in the (even neat) bimolecular reaction should certainly have led to some diphenyl disulfides, but no such products, even in traces, were observable. We know of no cases[15] where aryl thiyl radical intermediates have been implicated in which corresponding diaryl disulfides and related side products are not formed. Having applied all presently available criteria to eliminate a radical mechanism of thioallylic rearrangement, we conclude that this hitherto unknown reaction proceeds by a previously unfamiliar reaction course.[16]

Acknowledgment. We are obliged for advice and helpful suggestions made by Professor P. D. Bartlett in the preparation of our manuscript. Support through a grant by the donors of the Petroleum Research Fund of the American Chemical Society is also gratefully acknowledged.

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[11] C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2**, 323 (1964).

[12] W. H. Saunders, Jr., and J. C. Ware, *J. Amer. Chem. Soc.*, **80**, 3328 (1958). The data presented by these authors demontrate that, in a thermal rearrangement involving charge development in the transition state rather than charge destruction, the opposite order of solvent effect is to be observed; *i.e.*, the more polar solvent is associated with smaller $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

[13] The assumption that the sulfur acquires *negative charge* through octet expansion in the complex 7a is supported by two lines of evidence: (1) the oxygen analog in which such octet expansion is not possible does *not* undergo allylic rearrangement except with the assistance of a mole of allyl thiophenyl ether, and (2) substituent effect studies in para-substituted allyl thiophenyl ethers show measurable rate enhancement by electron-withdrawing substituents, $\rho_H \cong +1.0$; these latter results will be considered in detail in a future publication.

[14] J. E. Baldwin and J. E. Brown, *J. Amer. Chem. Soc.*, **91**, 3647 (1969).

[15] See for examples H. Kwart and M. H. Cohen, *J. Org. Chem.*, **32**, 3135 (1967).

[16] Note Added in Proof. The possibility that a thioallylic rearrangement could be made to occur *via* free-radical intermediates involving reaction circumstances other than those discussed in this report is currently under investigation in these laboratories.

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Nitrogen-15 Magnetic Resonance Studies. Further Evidence for the Dependence of $^1J(^{15}NH)$ on the Hybridization of Nitrogen

Sir:

Recently we reported[1] a substituent effect on the one-bond ^{15}N–H coupling constant in a series of aniline derivatives where $^1J(^{15}NH)$ in dimethyl sulfoxide (DMSO) solution was found to vary from 79.4

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[1] T. Axenrod, P. S. Pregosin, M. J. Wieder, and G. W. A. Milne, *J. Amer. Chem. Soc.*, **91**, 3681 (1969).

Table I. Proton Magnetic Resonance Data for Some ^{15}N-Labeled Compounds

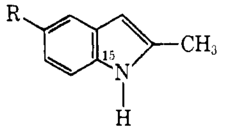
Compound	$^1J(^{15}\text{NH})$[a]	NH[b] chemical shift	Solvent	pK_a
2-Methylindole (Ia)	96.5	10.9	DMSO-d_6	−0.28[c]
2-Methyl-5-nitroindole (Ib)	96.9	11.8	DMSO-d_6	−3.70[c]
2-Methyl-5-nitroindoleninium (IV)	98.0		80% H_2SO_4	
Quinolinium (IIa)	96.0	12.6	$HFSO_3$	4.95[d]
6-Nitroquinolinium (IIb)	96.5	13.0	$HFSO_3$	2.76[d]
Anilinium (IIIa)	76.0	7.45	H_2SO_4	4.60[e]
Aniline[f]	82.6	4.90	DMSO-d_6	
4-Nitroanilinium (IIIb)	76.0	7.76	H_2SO_4	1.00[e]
4-Nitroaniline[f]	89.4	6.63	DMSO-d_6	

[a] Coupling constants are expressed in hertz and the uncertainty is ±0.2 Hz for the measurements in DMSO and ±0.5 Hz in the acid solvents. [b] Chemical shifts are expressed in parts per million from external TMS except for the DMSO solutions where internal TMS was used as the reference. [c] R. L. Hinman and J. Lang, *J. Amer. Chem. Soc.*, **86**, 3796 (1964). [d] W. L. F. Armarego, *J. Chem. Soc.*, 4094 (1962). [e] A. I. Biggs and R. A. Robinson, *ibid.*, 388 (1961). [f] See ref 1.

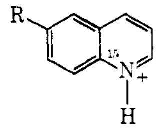
Hz in *p*-methoxyaniline to 89.4 Hz in *p*-nitroaniline.[2] The Fermi contact term is generally accepted as the dominant factor in the coupling mechanism. The coupling constant is considered to be proportional to the per cent s character in the N–H bond and inversely proportional to the mean triplet excitation energy, ΔE. To the extent that ΔE is constant, $^1J(^{15}\text{NH})$ has proved to be a useful parameter with which the hybridization at nitrogen can be investigated,[3,4] although exceptions which seem to correlate with unexpectedly low nitrogen chemical shifts have been observed.[5] However, Grant and Litchman have calculated that in some simple aliphatic halides changes in the effective nuclear charge of carbon can account for the changes in $^1J(^{13}\text{CH})$ and that changes in the hybridization are not necessarily involved.[6] Thus, the substituent effect on the $^1J(^{15}\text{NH})$ in the aniline derivatives can be explained in terms of either an enhanced planarity at the amino group brought about by increased p–π interaction of the nitrogen lone pair with electron-withdrawing substituents (resonance effect), or by an increase in the effective nuclear charge at the nitrogen and concomitant contraction of the s orbitals induced by electron-withdrawing substituents (inductive effect).[7]

To provide information which might bear on these points, we have investigated the effect of the introduction of a nitro substituent on the $^1J(^{15}\text{NH})$ values of 2-methylindole and the quinolinium and anilinium ions. All of the labeled compounds (I–III) contained a nitrogen-15 enrichment to the extent of 95 atom % or greater and were prepared by conventional synthetic procedures.

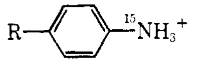
The results are summarized in Table I. Although the magnitude of the $^1J(^{15}\text{NH})$ is markedly dependent on the nature of the solvent,[8] the relative effect of a particular substituent remains the same in different solvents.[1,2] It may be seen that within each of the three systems investigated the introduction of the nitro group in place of a hydrogen atom has virtually no effect on the magnitude of the ^{15}N–H coupling. In the indoles and protonated quinolines a large change in the bond order at nitrogen caused by the substituent would not be expected, since the nitrogen atoms are presumably essentially sp^2 hybridized. This is substantiated by the similarity in the $^1J(^{15}\text{NH})$ values for the indoles and the quinolinium ions. Even in acid medium, where it has been shown by ultraviolet[9] and nmr[10] studies that indoles are protonated at the 3 position to give indoleninium cations, the conversion of Ib into IV does not significantly alter the ^{15}N–H coupling.[11] Similarly, in the sp^3 cases of the anilinium ions the coupling constant, 76.0 Hz, is found to be identical in the parent and in the 4-nitro-substituted ions, which contrasts with the substituent effect that exists in the free bases.



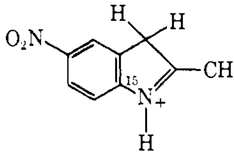
Ia, R = H
Ib, R = NO$_2$



IIa, R = H
IIb, R = NO$_2$



IIIa, R = H
IIIb, R = NO$_2$



IV

Thus, if we are correct in our interpretation, these observations suggest that the substituent effect on the $^1J(^{15}\text{NH})$ previously found in anilines[1] can be primarily attributed to the change in hybridization at the nitrogen, and that the inductive effect or field effect of the substituent has only a negligible influence, if any, on the coupling.

On the other hand, the chemical shift of the ^{15}N-bound proton appears at lower field in each system when a hydrogen atom is replaced by an electron-withdrawing nitro group. It is interesting to note

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(2) A similar observation has been reported by M. Bramwell and E. W. Randall, *Chem. Commun.*, 250 (1969).

(3) G. Binsch, J. B. Lambert, B. W. Roberts, and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 5664 (1964).

(4) A. J. R. Bourn and E. W. Randall, *Mol. Phys.*, **8**, 567 (1964).

(5) J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Nat. Acad. Sci. U. S.*, **51**, 735 (1964).

(6) D. M. Grant and W. Litchman, *J. Amer. Chem. Soc.*, **87**, 3994 (1965).

(7) Alternatively, changes in the chemical shifts of a nitrogen nucleus whose lone pair can be delocalized have been interpreted in terms of changes in ΔE when the lone pair is removed by protonation or quaternization.[5] A referee has pointed out that similar considerations may apply to the coupling constant.

(8) E. D. Becker and L. Paolillo, *J. Magn. Resonance*, **2**, 168 (1970).

(9) G. Berti, A. Da Settimo, and D. Segnini, *Gazz. Chim. Ital.*, **91**, 571 (1961).

(10) R. L. Hinman and E. B. Whipple, *J. Amer. Chem. Soc.*, **84**, 2534 (1962).

(11) The small increase in coupling (∼1 Hz) can probably be attributed to the differences in solvent effects in DMSO as compared to 80% H_2SO_4.

that the effect of the substituent on the NH shift parallels the profound influence that these substituents are known to have on the base strengths in these systems. Studies are in progress to measure the nitrogen-15 chemical shifts in these compounds.

Finally, the $J(^{14}NH)$ in pyrrole has been variously reported to be 55,[12] 60,[13] and 69.5 Hz.[14] These values correspond to a ^{15}N–H coupling constant of 77, 84, and 97.4 Hz, respectively.[15] Our findings for the indoles are consistent with this latter value and with the contention that the nitrogen atom is sp^2 hybridized.[3] This conclusion is further supported by microwave studies[16] and the recently reported[17] investigation of 2,5-di-*tert*-butylpyrrole-^{15}N.

[12] J. D. Roberts, *J. Amer. Chem. Soc.*, 78, 4495 (1956).

[13] B. Dischler and G. Englert, *Z. Naturforsch. A*, 16, 1180 (1960).

[14] E. Rahkamaa, *J. Chem. Phys.*, **48**, 531 (1968).

[15] Calculated from the ratio of magnetogyric constants $\gamma^{15}/\gamma^{14} = 1.4$.

[16] B. Bak, D. Christiansen, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, 24, 720 (1956).

[17] D. Gagnaire, R. Ramasseul, and A. Rassat, *Bull. Soc. Chim. Fr.*, 415 (1970).

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Isomerization of Conjugated Dienes *via* Photolysis of Metal Carbonyl–Diene Complexes

Sir:

Interest has been shown in the photochemistry of metal carbonyls, especially as photosubstitution reactions provide a synthetic tool for preparing new metal carbonyl–olefin complexes.[1–3] Many molybdenum and tungsten carbonyl–olefin complexes have been reported, and the photochemistry is known to proceed as in eq 1 and 2.[1,4,5] Subsequent photolysis of the metal carbonyl–olefin complexes has received

$$M(CO)_6 \xrightarrow{h\nu} M(CO)_6^* \longrightarrow M(CO)_5 + CO \qquad (1)$$

$$M(CO)_5 + \text{olefin} \longrightarrow [M(CO)_5(\text{olefin})] \qquad (2)$$

relatively little attention. Photoexchange reactions have been reported,[1,6–8] and dimerization of norbornadiene *via* photolysis of norbornadiene–chromium tetracarbonyl has recently been reported.[9] We have initiated a study of the photochemistry of tungsten, molybdenum, and chromium hexacarbonyls and their olefin derivatives and wish to report here our preliminary results with the tungsten carbonyl–conjugated diene system.

We have observed that irradiation of solutions containing $W(CO)_6$ and either of the isomeric 1,3-pentadienes (piperylenes) or the isomeric 2,4-hexadienes leads to cis–trans isomerization.[10] The quantum yields are time dependent, first increasing and then gradually declining. The cis → trans quantum yields are generally much higher than the trans → cis reactions. We have observed net isomeric conversion of more than five molecules of piperylene per molecule of $W(CO)_6$ present in the system.

In Table I we report cis → trans quantum yields for the piperylene system in three solvents and for two irradiation times. In Table II we present quantum yield data for the isomers of 2,4-hexadiene. The quantum yields vary only slightly with changes in diene concentration over the range 0.01–0.1 *M*.

Table I. Quantum Yields for 0.05 *M* *cis-* → *trans*-Piperylene Conversion

Solvent	Irradiation time, min	[*trans*] formed, *M*	$\Phi_{c\to t}$
Pentane	180	1.90×10^{-3}	0.082
	460	4.16×10^{-3}	0.070
Dodecane	180	1.52×10^{-3}	0.066
	460	3.42×10^{-3}	0.058
Hexadecane	180	1.97×10^{-3}	0.085
	460	3.90×10^{-3}	0.066

Table II. Quantum Yields for 0.088 *M* 2,4-Hexadienes in Pentane

Irradiation time, min	$\Phi_{tt\to ct}$	$\Phi_{tt\to cc}$	$\Phi_{cc\to ct}$	$\Phi_{cc\to tt}$	$\Phi_{ct\to tt}$	$\Phi_{ct\to cc}$
175	0.038	*a*	0.053	0.019	0.046	0.005
460	0.026	*a*	0.085	0.019	0.065	0.010

[a] $\Phi_{tt\to cc}$ is less than 0.002.

The use of infrared spectroscopy for structural characterization in such systems has been demonstrated.[2–5] Irradiation of solutions of the piperylene and $W(CO)_6$ results in appearance of the new carbonyl peaks tabulated in Table III. The positions of the

Table III. Ir Data for $W(CO)_6$–Piperylene Irradiations

Starting material	Band (intensity), cm⁻¹		
cis-Piperylene	2080 (w)	1967.9 (s)	1950.2 (s)
trans-Piperylene	2080 (w)	1965.5 (s)	1949.0 (s)
70% *trans*-, 30% *cis*-piperylene	2080 (w)	1966.8 (s)	1949.2 (s)

[1] W. Strohmeier, *Angew. Chem.*, 76, 873 (1964).

[2] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *Inorg. Chem.*, 2, 1264 (1963).

[3] I. W. Stolz, H. Haas, and R. K. Sheline, *J. Amer. Chem. Soc.*, 87, 716 (1965).

[4] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *ibid.*, 84, 3589 (1962).

[5] I. W. Stolz, G. R. Dobson, and R. K. Sheline, *ibid.*, **85**, 1013 (1963).

[6] W. Strohmeier and R. Muller, *Z. Phys. Chem. (Frankfurt am Main)*, 28, 112 (1961).

[7] W. Strohmeier and D. v. Hobe, *Z. Naturforsch., B*, **18**, 770 (1963).

[8] W. Strohmeier and D. v. Hobe, *ibid.*, *B*, **18**, 981 (1963).

[9] W. Jennings and B. Hill, *J. Amer. Chem. Soc.*, **92**, 3199 (1970).

[10] Irradiations were carried out at 313 nm in a merry-go-round apparatus[11] at 27°. The samples were thoroughly degassed, and aliphatic hydrocarbon solvents were used with diene concentrations of 0.05–0.10 *M* and a $W(CO)_6$ concentration of 2.3×10^{-3} *M*. Conversion was generally less than 5%. Light intensity was measured by benzophenone-sensitized isomerization of *cis*-piperylene.[12] Dienes were analyzed by vpc on a 25-ft × 1/8 in. β,β'-ODPN column at 50°. The ir data were obtained using a Perkin-Elmer 225 grating infrared spectrophotometer. Quantum yields were ±10%.

[11] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

[12] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).