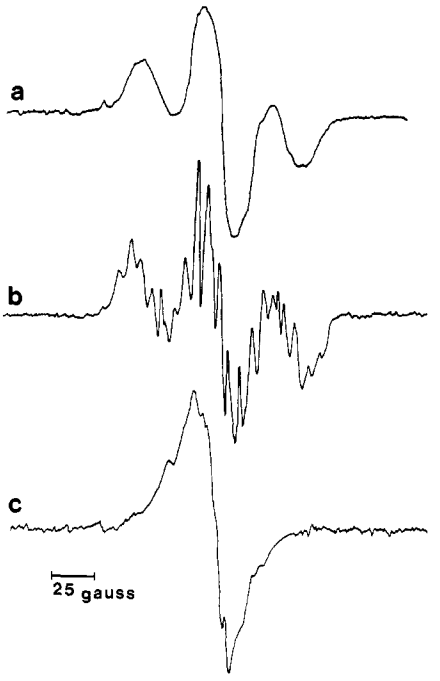
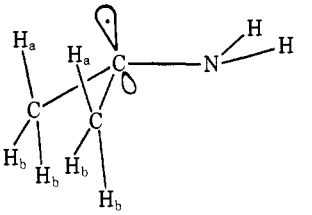


Figure 1. Esr spectrum of the product of the reaction between H· and (a) $(CH_3)_2CHNH_2$; (b) $(CH_3)_2CHND_2$; (c) $(CD_3)_2CDND_2$.

mined that when atomic hydrogen and isopropylamine react in the gas phase, α-aminoisopropyl is the only (>90%) radical produced. Hydrogen atoms generated by electrodeless discharge of molecular hydrogen were allowed to mix with the vapors of isopropylamine in a flow system, and the resulting products were isolated in an argon matrix at 4°K. The esr spectrum of the radical product of this reaction is shown in Figure 1a.[3] A broad triplet (A = 35 G) with an approximately 1:2:1 intensity distribution and centered at a position corresponding to g = 2.002 was observed. This result suggests that the radical formed has the odd electron strongly coupled to two hydrogens and is consistent with either radical A or B (Scheme I, $R_1 = R_2 = CH_3$, R_3 = H). A triplet pattern with this appearance could also arise from coupling to the ^{14}N nucleus (I = 1) if the outer components were broadened by an anisotropic hyperfine interaction. In order to distinguish between these alternatives, the reaction was repeated with isopropylamine-*N*-d_2[4] and isopropylamine-d_9.[5] Figure 1b shows the result when isopropylamine-*N*-d_2 was allowed to react with hydrogen atoms as above. The triplet nature of the spectrum persists, showing that hydrogen bound to nitrogen is not involved in the major hyperfine interaction. Additionally, each triplet component now consists of at least seven resolved lines. With isopropylamine-d_9 as the reactant, the spectrum (Figure 1c) consists of a single broad line showing that the 35 G splitting in Figures 1a and b is due to the methyl hydrogens. These results are best accommodated by structure IV for the radical product. Thus, at 4°K in argon, α-aminoisopropyl assumes a preferred conformation in which one hydrogen of each methyl group becomes eclipsed (or nearly so) with the orbital of the odd

(3) The liquid helium cryostat–X-band esr spectrometer system has been described previously: P. H. Kasai, E. B. Whipple, and W. Weltner, Jr. *J. Chem. Phys.*, **44**, 2581 (1966).
(4) H. J. Emeleus and H. V. A. Briscoe, *J. Chem. Soc.*, 127 (1937).
(5) Prepared by Na–Hg/CH_3OD reduction of hexadeuterioacetone oxime.



IV

electron at the α carbon. These eclipsed hydrogens couple to the electron with A^{H_a} = 35 G; the smaller splittings observed in each triplet component (Figure 1b) are attributed to coupling with the remaining methyl protons ($A^{H_b} \leq 10$ G) and possibly the nitrogen nucleus.

Wood has shown that the (bent) α-aminoisopropyl radical has an *isotropic* coupling constant of 18.27 G for protons bound to the *freely rotating* methyl groups.[6] For alkyl radicals, $A_\beta^H \approx B \cos^2 \theta$, where B is constant and θ is the dihedral angle between the C_β–H_β bond and the orbital of the odd electron;[7] for freely rotating methyl groups $A_\beta^H \sim {}^1/_2B$. In the present case θ (for the H_a's) is ~0, and the large triplet splitting is not surprising. Indeed, our observed value of 35 G provides additional support for structure IV.

In summary, mercury photosensitized oxidation of primary and secondary aliphatic amines to give imines proceeds by a free-radical mechanism in which both Hg ^3P atoms and H atoms function as hydrogen abstractors. To the extent that results obtained with isopropylamine are general, hydrogen atoms react with primary and secondary aliphatic carbinamines to give α-aminoalkyls. These data will be elaborated in our full paper.[2]

(6) D. E. Wood and R. V. Lloyd, *J. Chem. Phys.*, **53**, 3932 (1970).
(7) See, for example, J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

Anthony A. Baum,* Linda A. Karnischky
D. McLeod, Jr., Paul H. Kasai
Union Carbide Research Institute, Tarrytown Technical Center
Tarrytown, New York 10591
Received August 19, 1972

Homonuclear Decoupling and Peak Elimination in Fourier Transform Nuclear Magnetic Resonance

Sir:

If a system is subjected to a periodic time-dependent perturbation $\mathcal{H}'(t)$ with period T seconds, the spectrum in the limit $T \rightarrow 0$[1] consists of a central component together with a large number of side bands at the frequencies $\pm n/T$ Hz from the central (n = 0) component. The central component in the spectrum corresponds to the Hamiltonian $\mathcal{H}_0 + \overline{\mathcal{H}}'$, where $\mathcal{H}_0$ is the unperturbed Hamiltonian and $\overline{\mathcal{H}}'$ is the average of $\mathcal{H}'(t)$ over the period T.[2] In the Fourier mode, the dwell time used for recording the free induction decay can be shared between a perturbation $\mathcal{H}'$ and the receiver so that there is no direct interaction between the receiver and the perturbation. The dwell time is then the period T.

In this note we describe two applications of this technique in which the perturbation $\mathcal{H}'(t)$ is a contin-

(1) The $T \rightarrow 0$ limit is approached if $T \ll$ typical relaxation times and $T \ll 1/[\mathcal{H}'(t)]$.
(2) For a detailed discussion, see U. Haeberlen and J. S. Waugh, *Phys. Rev.*, **175**, 453 (1968).

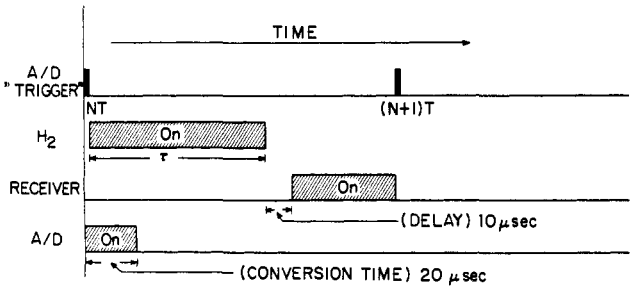


Figure 1. Timing scheme for Fourier mode homonuclear decoupling and selective saturation experiments.

uous coherent electromagnetic field (H_2) of frequency ω_2 which is gated so that it influences the spin system only during the first τ seconds of the period T (Figure 1). Since the dwell time is usually very small compared to the relaxation times, the condition $T \ll T_2$ is well satisfied; on the other hand, the condition $T \ll 1/[\mathcal{H}'(t)]$ is more stringent.[3] If the $T \rightarrow 0$ limiting condition is closely approached, the spectrum recorded after Fourier transforming the FID corresponds to that observed in the cw mode with a second rf field of magnitude $H_2\tau/T$ at frequency ω_2.

The application of this technique to homonuclear decoupling is illustrated in Figure 2. Spectra were taken on a Bruker HFX 90 using a Digilab NMR 3 data system.[4] The upper part of Figure 2 shows the Fourier mode ^{31}P nmr of an aqueous solution of $K_5P_3O_{10}$. It consists of an AB_2 pattern approaching the AX_2 limit (δ_A = 20.3 ppm, δ_B = 5.9 ppm from 85% H_3PO_4 J_{AB} = 19 Hz). The lower part of the figure shows the spectrum obtained in the homonuclear decoupling mode. The frequency of the H_2 field has been set at the center of the A triplet and the B doublet has been collapsed.

An exactly analogous approach can be used to eliminate a solvent or impurity peak of large intensity by saturation with the H_2 field set at resonance with the peak to be eliminated. An example is given in Figure 3. The upper part of the figure shows the Fourier mode ^1H nmr spectrum of a solution of 1% ethyl benzene and 2% TMS in carbon tetrachloride. In the lower part of the figure the perturbing rf field has been used to selectively saturate the TMS peak. This approach offers at least a partial solution to the dynamic range problem often encountered in Fourier transform systems with limited computer word length.

A problem arises in these experiments in choosing the duty cycle for the decoupler generating the perturbation. In order to attain maximum signal/noise, the fraction of the dwell time used for signal detection should be as long as possible, *i.e.*, τ (the time the decoupler is on) should be as short as possible. On the other hand, in some applications, it is necessary to have $\overline{\mathcal{H}'}$ as large as possible. Since $\overline{\mathcal{H}'} = H_2\tau/T$, the effective decoupling power is only $(\tau/T)^2$ of that available in a comparable cw experiment[5] with the decoupler

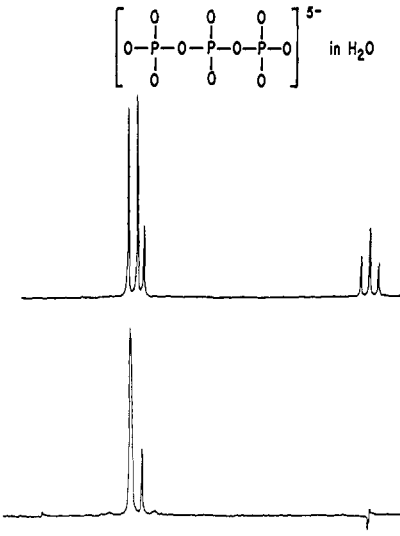


Figure 2. The Fourier mode ^{31}P nmr spectrum of aqueous $K_5P_3O_{10}$ with (lower part) and without homonuclear decoupling. In recording these spectra a dwell time (T) of 500 μsec was used and 2048 points were recorded in the FID. In the homonuclear decoupled spectrum the decoupler was on for 350 out of the 500 μsec and the FID was sampled for 140 μsec. The additional peak close to the doublet is due to an impurity.

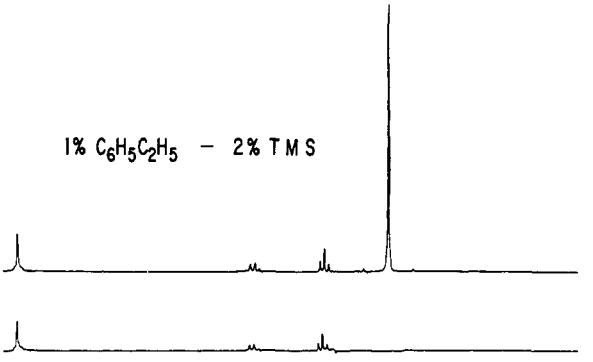


Figure 3. The Fourier mode ^1H nmr spectrum of a solution of 1% ethyl benzene and 2% TMS in CCl_4. The dwell time (T) was 500 μsec. In the selective saturation experiment (lower part) the decoupler was on for 400 out of the 500 μsec and the receiver sampled the FID for 90 μsec. For both spectra 2048 data points were recorded.

on all the time. In those experiments where only a small effective perturbing field is required (spin tickling and selective peak saturation, for example) there is no problem. A small τ can be chosen and the H_2 level can be raised to compensate for the τ/T factor. It may be noted that the same duty cycle problem arises in a simple time sharing experiment as well as in the Fourier experiment. In a time sharing spectrometer the duty cycle of the transmitter is usually set at about one-tenth of the time sharing cycle; gating the decoupler in the same manner will reduce the decoupling power in the center band by a factor of 100 relative to a comparable cw experiment. In the Fourier experiments shown in Figures 2 and 3, the duty cycle was much higher than $^1/_{10}$.

Other methods of combatting the dynamic range problem have been introduced by Pratt and Sykes[6] and by Berg, Feeney, and Roberts.[7] These lack generality

(3) The difficulty in satisfying the condition $T \ll 1/[\mathcal{H}'(t)]$ may limit the applicability of this technique. In analyzing the results of experiments of this type, corrections can be made to the effective averaged Hamiltonian.[1] The first-order correction is of the order of magnitude $[\mathcal{H}']^2T$.

(4) Similar experiments have been performed in the Bruker Scientific applications laboratories (C. Tanzer, private communication).

(5) The Fourier coefficients for the side bands are given by $A_n = \sin(\pi n\tau/T)/\pi n$. This indicates that τ/T of the available power goes into the $n = 0$ center band and the rest into the side bands.

(6) S. L. Pratt and B. D. Sykes, *J. Chem. Phys.*, 56, 3182 (1972).

(7) F. W. Berg, J. Feeney, and G. C. K. Roberts, *J. Magn. Resonance*, 8, 114 (1972).

in that the peaks to be eliminated must have different relaxation characteristics to those which are to be observed. The approach described in this communication and that described by Shaefer[8] (in which the solvent or impurity peak is selectively saturated before each pulse is applied) do not have this limitation. A choice between these latter two methods will depend on the particular system under study.

Of course, unlike the ^{31}P experiment described here, none of the earlier experiments mentioned in the last paragraph are applicable to homonuclear decoupled Fourier transform nmr.

(8) J. Schaefer, *J. Magn. Resonance*, 6, 670 (1972).

J. P. Jesson,* P. Meakin
Central Research Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

G. Kneissel
Digilab, Inc.
Cambridge, Massachusetts 02139

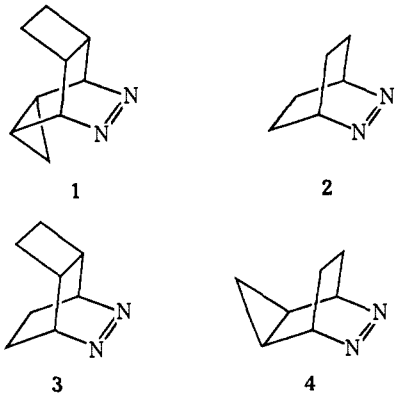
Received November 6, 1972

Orientational Effects on Cyclopropyl Participation in the Thermolysis of Azo Compounds. Assessment of the Endo Configuration

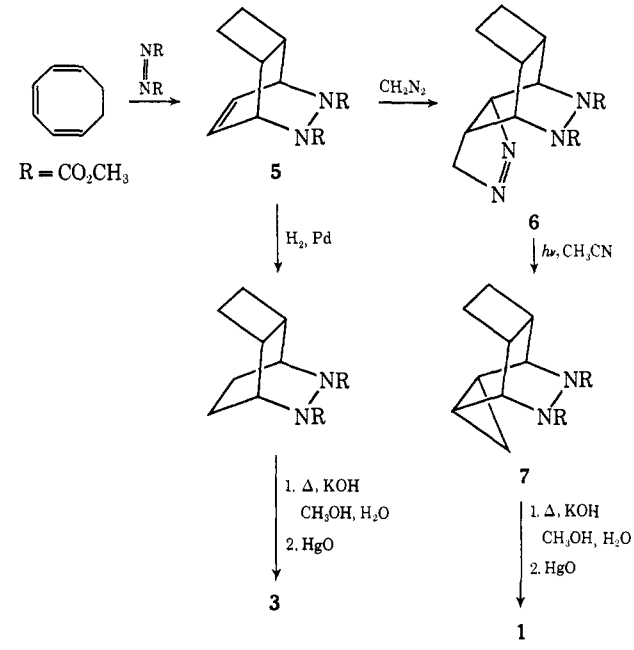
Sir:

Recent thermolysis studies of azo compounds have proven to be uniquely informative about the influence of geometry on the contribution made by edge cyclopropyl electrons to chemical reactivity.[1-3] For the case of the exo configuration,[4] changes in the dihedral angle between the plane of the cyclopropane ring and the rest of the structure produce very substantial differences in reactivity.[1] Surprisingly, there has been no comparison of the reactivities of the endo and exo arrangements. We now report a quantitative assessment of the influence of an *endo*-cyclopropane ring on the thermal reactivity of azo compounds.[5] The structures we use for this purpose are azo compound **1** and the known compounds **2**,[2,6] **3**,[2,7] and **4**.[2]

Scheme I outlines the synthetic sequence used to prepare **1**. Compound **1** is characterized by mp 59.5–60.5° (from dichloromethane–pentane); $\lambda_{max}^{isooctane}$ 383 (ϵ 294) and 372 nm (sh) (ϵ 112);[6] λ_{max}^{KBr} 6.63 μ (–N=N–);[6] and nmr, τ ($CDCl_3$) 10.29 (1 H, overlaid triplets), 9.85 (1 H, overlaid triplets complicated by additional small couplings), 8.44 (2 H, multiplet), 7.96 (6 H, singlet), and 4.94 (2 H, broad singlet).[8] The stereochemistry of the cyclobutane ring in **5**, **6**, **7**, and **1** was shown to be exo by the conversion of **5** into a product which had physical and spectral properties identical with those of



Scheme I



authentic **3**.[2,9] The assignment of the endo configuration to the cyclopropane ring in **1** is supported by three lines of evidence: (a) examination of models clearly shows that diazomethane is blocked from addition to the exo side of the double bond of **5** by the proximate cyclobutyl group; (b) an nmr signal above τ 10 indicates the juxtaposition of this cyclopropyl proton and the azo linkage;[10,11] and (c) an enormous difference in the thermolysis rates of **1** and **4** establishes that the cyclopropyl groups of the two compounds are of different orientations.

The first-order rate constants for the thermolysis of **1** in the range of 177–199° were measured by a previously described method.[6] These results, along with a comparison of reactivity between **1**, **2**, **3**, and **4**,[12] are

(1) E. L. Allred and A. L. Johnson, *J. Amer. Chem. Soc.*, 93, 1300 (1971).
(2) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969).
(3) E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Amer. Chem. Soc.*, 91, 3382 (1969).
(4) The designation exo refers to the relationship between the cyclopropane ring and the –N=N– group.
(5) An *endo*-cyclopropyl azo compound has been decomposed [L. A. Paquette and M. J. Epstein, *J. Amer. Chem. Soc.*, 93, 5936 (1971)]; however, a phenyl group at each C–N carbon and the lack of a corresponding *exo*-cyclopropyl compound precludes any quantitative evaluation of the effect of a cyclopropane ring in the endo configuration.
(6) S. G. Cohen and R. Zand, *ibid.*, 84, 586 (1962).
(7) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 387 (1972).
(8) Products **1** and **6** (mp 133.5–135°) gave satisfactory elemental analyses, and all compounds gave spectral data in accord with their assigned structures.
(9) R. C. Cookson, S. S. H. Giliani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967); A. B. Evnin, R. D. Miller, and G. R. Evanega, *Tetrahedron Lett.*, 5863 (1968).
(10) This cyclopropyl proton signal is at least 0.4 ppm upfield from any cyclopropyl proton of **4**: M. Martin and W. R. Roth, *Chem. Ber.*, 102, 811 (1969).
(11) The shielding effect of the –N=N– structure is well established. For example, see : (a) J. J. Uebel and J. C. Martin, *J. Amer. Chem. Soc.*, 86, 4618 (1964); (b) R. J. Crawford, A. Mishra, and R. Dummel, *ibid.*, 88, 5959 (1966); (c) W. R. Roth and M. Martin, *Justus Liebigs Ann. Chem.*, 702, 1 (1967).
(12) This comparison necessitates extrapolation of the kinetic data between gas- and liquid-phase conditions. Previous control experiments have demonstrated that the decomposition rates of such azo compounds are not appreciably greater in solution than in the gas phase.[1,2]