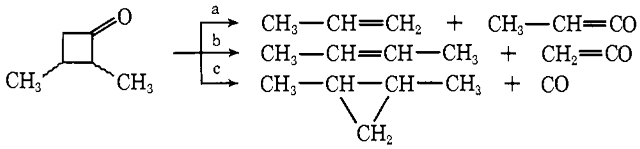
Stereochemistry of the Thermal and Photolytic Decomposition of *cis*- and *trans*-2,3-Dimethylcyclobutanone in the Gas Phase[1]

Sir:

A comparison of the photochemical decomposition modes with the unimolecular, thermal decomposition of cyclobutanone in the gas phase has led to a mechanistic proposal that the internal conversion process ($S_1 \rightsquigarrow S_0$) is surprisingly efficient.[2] Furthermore, the importance of the intersystem crossing process ($S_1 \rightsquigarrow T_1$) in the direct photolysis of cyclobutanone was stressed,[3] on the basis of the result that the triplet benzene photosensitization of cyclobutanone gave $c\text{-}C_3H_6$ and CO exclusively,[3] in contrast to the thermal decomposition, which gave C_2H_4 and CH_2CO, with $E_a = 52.0$ kcal/mol.[4] In order to obtain additional details of this model kinetic system, we have carried out the pyrolysis and photolysis of *cis*- and *trans*-2,3-dimethylcyclobutanone (DMCB),[5] molecules which are capable of providing the crucial stereochemical information about the unimolecular decomposition processes of interest.

The noteworthy results are: (1) pyrolysis at 325° of *cis*- or *trans*-DMCB gives *cis*- or *trans*-2-butene, respectively, with retention of the stereochemical configuration (>98%) during the ring fission path b (see Scheme I); (2) likewise, direct photolysis[6] at 313 nm (23°) gives predominantly retention of configuration in the 2-butene products, *cis*-DMCB giving a *trans*- to *cis*-2-butene ratio of ~0.15, and *trans*-DMCB giving a ratio of ~12; (3) the decarbonylation process c is absent in pyrolysis [c ≤ 0.01(a + b)]; (4) the ring fission processes a and b are absent in the $^3B_{1u}$ benzene-sensitized decomposition of *cis*- and *trans*-DMCB [c ≥ 50(a + b)], and the ratio of *trans*- to *cis*-1,2-dimethylcyclopropane (DMCP) produced is ~2.6; (5) the ring fission processes predominate over the decarbonylation in the direct photolysis (313 nm) [c ≈ 0.12(a + b)]; and (6) the ratio of products a/b is ~1.1 for the pyrolysis of *trans*-DMCB and ~6 for *cis*-DMCB, while this ratio in the direct photolysis is 0.9 and 1.3, respectively.

Scheme I



The most significant conclusion drawn from the above results is that the stereochemistry of the ring fission process b from the ground state is entirely consistent with that predicted for the concerted, cycloreversion process by the conservation of orbital symmetry.[7] We believe that our pyrolysis result, together with the results obtained in the thermal addition of olefins to ketenes,[8] illustrates nicely the reversibility of the cycloaddition–cycloreversion process.

The reason for the negligible participation of the cycloreversion processes (a and b) in the triplet-benzene-sensitized decomposition ($E_T = 85$ kcal/mol) may lie in the fact that the production of an electronically excited ketene (or 2-butene counterpart) from the electronically excited (triplet) DMCB is slightly endothermic and could have an appreciable activation barrier; therefore, an alternative decarbonylation process (c), presumably involving a diradical intermediate, could predominate instead, since the *trans*/*cis* ratio of ~2.6 for DMCP product obtained in observation 4 is nearly equal to the ratio of 2.9 obtained in the triplet CH_2 addition to *cis*- and *trans*-2-butenes involving a diradical intermediate.[9] It is also reassuring to find that observations 2 and 5 are consistent with the earlier proposed photodecomposition mechanism involving the $S_1 \rightsquigarrow S_0$ internal converson process.[2] The observation (6) that the rate of the ring fission mode a in pyrolysis is enhanced for *cis*-DMCB over that for *trans*-DMCB is familiar to the similar observation made for *cis*- and *trans*-1,2-dimethylcyclobutane.[10] However, any simple analogy could be an inadequate explanation, since the cyclobutane pyrolysis involves a nonconcerted, diradical intermediate,[11] unlike the cyclobutanone pyrolysis. We hope that our continued efforts made in the detailed study of this system will bring about a satisfactory understanding of the factors which control the rates in various unimolecular reaction channels of the ground and excited states.

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[1] This research has been supported by National Science Foundation Grant No. GP 11390.

[2] (a) N. E. Lee, H. O. Denschlag, and E. K. C. Lee, *J. Chem. Phys.*, **48**, 3334 (1968); (b) N. E. Lee and E. K. C. Lee, *ibid.*, **50**, 2094 (1969).

[3] H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 3628 (1968).

[4] (a) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *ibid.*, **76**, 6271 (1954); (b) A. T. Blades, *Can. J. Chem.*, 47, 615 (1969).

[5] Our assignments of the isomeric *cis* and *trans* structures (based on nmr, ir, and order of vpc elution) are consistent with the assignments made by N. J. Turro and R. B. Gagosian, *J. Amer. Chem. Soc.*, **92**, 2036 (1970), and J.-L. Ripoll and J. M. Conia, *Bull. Chim. Soc. Fr.*, 2755 (1965).

[6] *cis–trans* isomerization of the starting ketones was not detected under our photolysis conditions.

[7] See R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969); the orbital symmetry of the reaction is of the type $[\sigma 2_s + \sigma 2_a]$, suprafacial with respect to the olefinic product and antarafacial with respect to the ketene product.

[8] (a) R. Huisgen, L. Feiler, and G. Binsch, *ibid.*, 3, 753 (1964); (b) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *J. Org. Chem.*, 30, 4309 (1965); (c) R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, 7, 221 (1968); (d) G. Binsch, L. A. Feiler, and R. Huisgen, *Tetrahedron Lett.*, 4497 (1968).

[9] C. McKnight, P. S. T. Lee, and F. S. Rowland, *J. Amer. Chem. Soc.*, **89**, 6802 (1967).

[10] H. R. Gerberich and W. D. Walters, *ibid.*, 83, 3935, 4884 (1961).

[11] (a) A. T. Cocks, H. M. Frey, and I. D. R. Stevens, *Chem. Commun.*, 458 (1969); however see (b) J. E. Baldwin and P. W. Ford, *J. Amer. Chem. Soc.*, **91**, 7192 (1969).

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Carbon-13 Fourier-Transform Nuclear Magnetic Resonance. I. Comparison of a Simple Spin–Echo Procedure with Other Methods

Sir:

Interest in Fourier-transform nuclear magnetic resonance (FT nmr) as an alternative to continuous-wave high-resolution nmr (CW nmr) for nuclei with poor sensitivity and low natural abundance is due to the expectation of large improvements in signal-to-noise

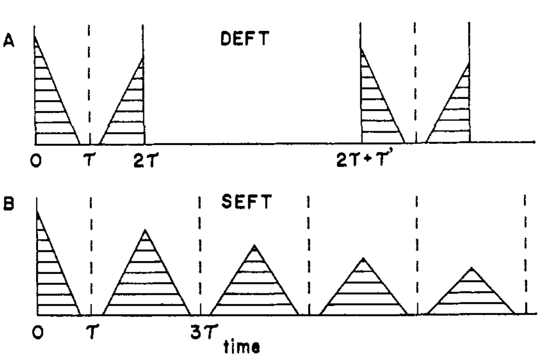

Figure 1. Symbolic representation of the multiple-pulse sequences used in the Fourier-transform nmr. Solid and broken vertical lines represent 90 and 180° pulses, respectively. The shaded areas are linear representations of the upper portions of signal envelopes. (A) A few pulses of a DEFT sequence. (B) The Carr-Purcell sequence used in SEFT. The 90° pulse is 90° out of phase with the 180° pulses (Meiboom-Gill modification).

(S/N) ratios.[1,2] Ernst and Anderson[1] have shown that the advantage of FT nmr is lost when the ratio of longitudinal to transverse relaxation times, T_1/T_2^*, becomes large. In ordinary FT nmr, $1/T_2^*$ is the sum of $1/T_2$, the "natural" transverse relaxation rate, and $1/T_2'$, the dephasing contribution from the inhomogeneity of the magnetic field. For spin $^1/_2$ nuclei, T_2 is usually equal to T_1 (exceptions are discussed below), but the contribution of $1/T_2'$ to $1/T_2^*$ is normally dominant, yielding T_1/T_2^* ratios much larger than unity and limiting the usefulness of ordinary FT nmr. Recently, Becker, Ferretti, and Farrar[3] have shown that a refocusing multiple-pulse scheme (Figure 1A) which they called driven-equilibrium Fourier-transform nmr (DEFT) yields S/N ratios dependent on T_1/T_2 instead of T_1/T_2^*.

We have employed a different pulse sequence to accomplish the same purpose, namely the Meiboom-Gill modification[4] of the familiar Carr-Purcell spin-echo train[5] (Figure 1B). The digital averager is triggered by each 180° pulse or slightly thereafter and *the echoes themselves* are accumulated. We call this method spin-echo Fourier-transform nmr (SEFT). If we now define time zero as the time at each echo maximum, both the "positive" and "negative" sides of the accumulated sum of echoes can be Fourier transformed (Figure 2).

The pulse experiments were performed at 9.8 MHz on a modified Magnion pulsed nmr apparatus.[6] A Fabri-Tek 1074 digital averager was used for signal accumulation. The advantages of proton decoupling, field-frequency lock, and sample spinning were not available. We obtained good natural-abundance carbon-13 spectra by digital cosine transforms without the need for any phase corrections.[1] A typical result is shown in Figure 2.

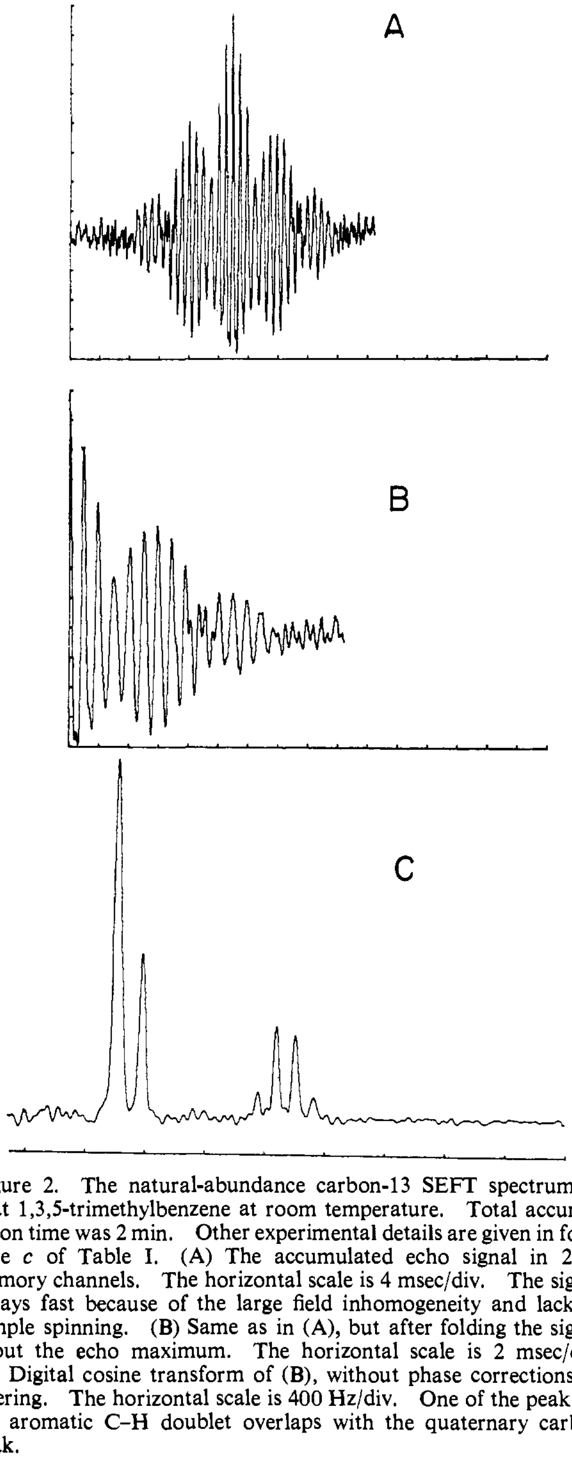

Figure 2. The natural-abundance carbon-13 SEFT spectrum of neat 1,3,5-trimethylbenzene at room temperature. Total accumulation time was 2 min. Other experimental details are given in footnote *c* of Table I. (A) The accumulated echo signal in 2048 memory channels. The horizontal scale is 4 msec/div. The signal decays fast because of the large field inhomogeneity and lack of sample spinning. (B) Same as in (A), but after folding the signal about the echo maximum. The horizontal scale is 2 msec/div. (C) Digital cosine transform of (B), without phase corrections or filtering. The horizontal scale is 400 Hz/div. One of the peaks of the aromatic C-H doublet overlaps with the quaternary carbon peak.

For purposes of comparison, ordinary CW nmr spectra were measured on a modified Varian DA-60 spectrometer,[7] at 15.07 MHz, using digital frequency sweep, field-frequency lock, and sample spinning. Although proton decoupling was available, it was not used. Some results are shown in Table I. It is obvious that SEFT can lead to very significant reductions in the time required to obtain good spectra, even for carbons expected to have long T_1 values, such as carbonyls and quaternaries. The observed six- to tenfold improvement in S/N of SEFT over CW nmr (Table I), which is comparable to the experimental improvement obtained by Ernst and Anderson[1] in proton Fourier-transform nmr, should be considered a lower limit. In any case, a given S/N ratio in carbon-13 nmr can be obtained at least 40-100 times faster by SEFT than by CW nmr. This is well below the expected theo-

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(1) R. R. Ernst and W. A. Anderson, *Rev. Sci. Instrum.*, 37, 93 (1966).

(2) T. C. Farrar, *Anal. Chem.*, **42,** 109A (1970).

(3) E. D. Becker, J. A. Ferretti, and T. C. Farrar, *J. Amer. Chem. Soc.*, **91,** 7784 (1969).

(4) S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **29,** 688 (1958).

(5) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **94,** 630 (1954).

(6) A. Allerhand, *J. Magn. Resonance*, **1,** 488 (1969).

(7) A. O. Clouse, D. Doddrell, S. B. Kahl, and L. J. Todd, *Chem. Commun.*, 729 (1969).

Table I. Comparison of CW and SEFT Nmr Signal-to-Noise

	CW nmr[b]		SEFT nmr[c]		
Compound[a]	Total time, min	S/N[e]	Total time, min	S/N[e]	Improvement[d]
Acetic acid	17	12[f]	2	44[f]	11
3 *M* acetic acid (aq)	53	4[f]	6	11[f]	8
1,3,5-Trimethylbenzene	53	16[g]	2	28[g]	9
Hexamethylbenzene, 21 mol % in $CHCl_3$	23	8[g]	6	24[g]	6

[a] Neat liquid unless otherwise indicated. Room temperature. [b] At 15.07 MHz. See text and ref 7. 11.6-mm i.d. sample tubes were used. Sweep width was 2000 Hz. Sweep time was 50 sec/scan. [c] At 9.8 MHz. See text and ref 6. 12.8-mm i.d. sample tubes were used. τ was 23 msec, there were 66 echoes per burst, and the recycle time between bursts was about 20 sec. The output filter time constant was 40 μsec. [d] Ratio of S/N values for SEFT and CW nmr, for equal total accumulation times. [e] Using the "practical" definition of 2.5 times the peak height divided by the peak-to-peak noise. [f] Carbonyl peak. [g] Inner peak of methyl quartet.

retical improvement,[1] but sufficient to be of great interest to the user of carbon-13 nmr.

We have also made some ordinary Fourier-transform nmr determinations. As expected, S/N ratios were appreciably lower than with SEFT for comparable total scan times, except in molecules with very short T_1 and T_2 values, such as glycerin, where ordinary FT nmr would be indicated.

Calculations by Waugh[8] indicate that under *optimum conditions* DEFT should be slightly more efficient than SEFT. The important advantage of SEFT, however, is that the signal at $t = 0$ (the time of the accumulated echo maximum) is not obscured by a strong rf pulse. Both in ordinary FT nmr and in DEFT, the rf pulse causes an uncertainty in $t = 0$ (the start of the accumulated free-induction decay) and a feedthrough of the excitation pulse, especially if long accumulation times are used. This causes frequency-dependent phase errors and spurious spectral features.[9] In using SEFT, we have found no base-line problems and no need for phase corrections. The cosine transform in Figure 2C is typical.

So far, we have made no measurements on samples more dilute than 1 *M* owing to a lack of field-frequency lock, which has prevented us from using accumulation times of more than about 15 min. We plan to do further SEFT experiments with improved instrumentation.

Finally, we wish to discuss those cases for which T_1/T_2 is appreciably larger than unity, and to present experimental evidence for the loss of effectiveness of Fourier-transform nmr in such cases, as predicted by Ernst and Anderson.[1] There are two possible contributions to $1/T_2$ that usually do not affect $1/T_1$. One is modulation of chemical shifts or coupling constants through intermolecular or intramolecular chemical exchange.[10] The other is residual broadening from scalar coupling to a quadrupolar nucleus undergoing rapid relaxation,[11] such as ^{35}Cl or ^{14}N.

We believe we have encountered the effect of exchange in the case of cyclohexane, which yielded a relatively poor SEFT spectrum. Since much larger S/N ratios were obtained with cyclohexane-d_{12}, this is evidence for a modulation of carbon–hydrogen coupling by the chair–chair isomerization process, the effect being observable in spite of the very fast rate at room temperature.[12] Modulation of carbon–hydrogen coupling by chemical exchange will not affect the S/N ratio if proton decoupling is used.

In many instances carbons directly bonded to nitrogen or chlorine yielded relatively weak signals. Since the shortening of the carbon-13 T_2 by a quadrupolar nucleus is proportional to the relaxation time of the latter and the square of the coupling constant,[11] the loss of intensity can vary.

In some compounds, such as amino acids, both the exchange and quadrupolar effects appear to be operating.[13]

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(8) J. S. Waugh, *J. Mol. Spectrosc.*, in press.

(9) I. Salmeen and M. P. Klein, presented in part at the 11th Experimental Nmr Conference, Pittsburgh, Pa., April 1970.

(10) C. S. Johnson, Jr., *Advan. Magn. Resonance*, **1**, 33 (1965).

(11) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, Oxford, 1961.

(12) A. Allerhand, F. M. Chen, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3040 (1965); F. A. L. Anet and A. J. R. Bourne, *J. Amer. Chem. Soc.*, **89**, 760 (1967).

(13) A. Allerhand and D. W. Cochran, unpublished.

(14) National Institutes of Health Predoctoral Fellow, 1967–1970.

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Nuclear Magnetic Resonance Spectroscopy. Observation of Carbon-13 Resonances in a Paramagnetic Transition Metal Complex. Nickel(II) N,N′-Di(*p*-tolyl)aminotroponiminate[1]

Sir:

The discovery[2] of the extraordinary chemical shifts of the proton magnetic resonances of paramagnetic Ni(II) aminotroponiminates has been of great value for probing the nature of metal–ligand bonding especially because sharp resonances are observed as the result of the short electronic relaxation times of the tetrahedral forms[3] which are associated with the square-planar (diamagnetic) $\rightleftharpoons$ tetrahedral (paramagnetic) equilibria. These complexes are expected to provide a useful starting point for natural-abundance ^{13}C nmr studies of paramagnetic transition metal complexes. We report in this study observation of eight of the possible nine carbon resonances of the N,N′-di(*p*-tolyl) derivative **1**, and present evidence for nonzero spin density in the σ framework of the ligand.

Typical carbon spectra of the complex and the ligand are shown in Figure 1, and a summary of the

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(1) Supported by the National Science Foundation and by the Public Health Service (Grant No. 11072), Division of Research Grants, National Institutes of Health.

(2) (a) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, **37**, 347 (1962); (b) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Amer. Chem. Soc.*, **85**, 397 (1963); (c) D. R. Eaton, A. D. Josey, and R. E. Benson, *ibid.*, **89**, 4040 (1967); (d) for a review, see R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969).

(3) G. N. La Mar, *J. Amer. Chem. Soc.*, **87**, 3567 (1965).