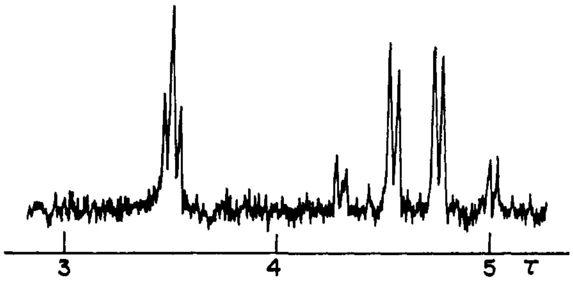
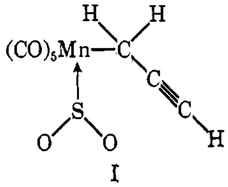


Figure 1. Proton magnetic resonance spectrum of $Mn(CO)_5SO_2$-C_3H_3 (recorded on a Varian Associates A-60 spectrometer in $CDCl_3$ solution).

The chemical shift of the unique proton (X) precludes retention of the $-CH_2C\equiv CH$ structure by the C_3H_3 fragment upon insertion but is compatible with either an SCH= or an OCH= linkage.[13,15] The hydrogens A and B absorb in the region assigned to olefinic or allenic protons,[15] and their nonequivalence may be due to the presence of the asymmetric sulfur in the compound.[16]

The proposed $(CO)_5MnS(O)OCH{=}C{=}CH_2$ structure is consistent with the absence of a C≡C stretching frequency in the infrared spectrum of **2**; interestingly, however, there is no absorption which could be assigned to a carbon–carbon stretching frequency of an allenic moiety. Nevertheless, it appears reasonable that such a band may be hidden underneath a very intense carbonyl stretching absorption at 2010 cm^{-1}.

The formation of $(CO)_5MnS(O)OCH{=}C{=}CH_2$ rather than the corresponding sulfinate may be rationalized in terms of the geometry of the parent 2-propynyl complex and a relatively facile 2-alkynyl to 1,2-alkadiene rearrangement. Assuming that the SO_2 sulfur interacts with manganese in the initial step of the insertion, the C(3) atom of C_3H_3 is placed in an unfavorable position for migration onto that sulfur because of the linearity of the C—C≡CH moiety (I). By way of contrast, the SO_2 oxygens are in a close proximity to the C(3) atom and can accept the migrating C_3H_3 fragment. The alternative route—direct insertion of SO_2 into the Mn-CH_2 bond—is apparently energetically less favorable than the concerted process leading to rearrangement.



I

Finally, two remarks are in order. First, the course of this insertion indicates that sulfur dioxide may function as an electrophilic rather than a nucleophilic reagent toward the metal,[17] assuming, of course, that the mechanism proposed above is operative. Second, the formation of a complex containing an S-O-C linkage demonstrates that such derivatives may, with certain systems, be the kinetically favored products which once formed exhibit a high degree of thermodynamic stability. Indeed, all attempts at isomerization of $(CO)_5MnS(O)OCH{=}C{=}CH_2$ to the corresponding S-sulfinate by heating it in chlorobenzene, benzene, tetrahydrofuran, and chloroform proved unsuccessful.

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Received January 31, 1968

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[15] L. M. Jackman, ref 14, pp 60–62.

[16] Although, to our knowledge, organic allenes with such asymmetry have not been investigated, there are numerous examples of magnetic nonequivalence of methylene protons adjacent to an asymmetric center; see L. M. Jackman, ref 14, pp 99–103.

[17] Electrophilic attack of SO_2 on $C_5H_5Rh(C_2H_4)_2$ to give C_5H_5Rh-$(C_2H_4)(SO_2)$ has been recently suggested by Cramer.[18]

[18] R. Cramer, *J. Am. Chem. Soc.*, **89**, 5377 (1967).

Radical Transfer in a CIDNP Raser

Sir:

Ward and Lawler recently predicted[1] that pmr emission should be observed for products, in addition to the alkenes, which are formed from radical intermediates of alkyllithium–bromoalkane reactions. This radiofrequency amplification by stimulated emission of radiation (raser) produced by chemically induced dynamic nuclear polarization (CIDNP) was confirmed in their subsequent report.[2] They reported CH_2 emission for ethylbenzene formed by treating 2-bromoethylbenzene and *t*-butyllithium. However, each of the products observed to date as an emitter has as a structural component one of the initially generated radicals. Therefore, I wish to report raser action in a compound formed by radical transfer.

The system which gave a radical-transfer product was comparable to that previously reported.[1] However, a change in the Lewis base, employed to depolymerize the alkyllithium hexamer with concomitant enhancement of the radical-generation reaction, gave additional negative pmr peaks. Figure 1 shows the pmr spectra, measured on a Varian A-60A spectrometer, for the system *n*-butyllithium in hexane (0.6 ml of 1.5 *M*, Foote Mineral Co.), 1-bromobutane (60 μl), and anhydrous triethylamine (0.25 ml).[3] Although the order of mixing these components was unimportant, in the example 1-bromobutane was added to the *n*-butyllithium solution (Figure 1.1) to give a mixture of the radical generation reagents (Figure 1.2). The triethylamine was then rapidly added, and repeated scans were run over the pmr region from δ 6.5 to 3.0 ppm.[4] The series of absorption and emission bands (Figure 1.3)[5] built up in 2–3 min and then slowly decreased, giving the weak absorption spectrum in Figure 1.4 after 10 min.

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[1] H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967).

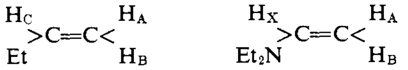
[2] *Chem. Eng. News*, 46, 40 (Jan 15, 1968).

[3] Considerable variation in the quantities of 1-bromobutane and triethylamine showed qualitative concentration effects including the loss of raser action where the reaction rate was very slow. High concentrations led to uncontrollably fast reactions or reactions which were complete in less than the pmr scan times.

[4] Other regions of the spectrum were searched, including the $-CH_2Li$ range, δ 0 to -2, but no additional emission bands were detected. The regions 0.7–1.9 and 2.3–2.7 were not accessible because of solvent and triethylamine ($-CH_2N$) absorption, respectively. TMS was used as an internal calibration standard in most experiments.

[5] Scan time for this sweep was approximately 2 min and was started at 0.8 min after mixing of triethylamine.

In Figure 1.3, the bands at b, d, and e are the characteristic remnants of 1-butene raser action;[1] the ABC pattern here is broken down into an absorption and an emission peak for each of the protons with the negative peak downfield from the positive peak. Thus e con-

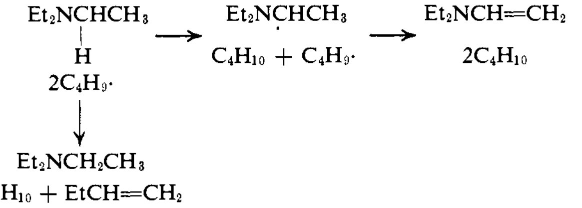


$$\overset{H_C}{\underset{Et}{}}\!>\!C{=}C\!<\!\overset{H_A}{\underset{H_B}{}} \qquad \overset{H_X}{\underset{Et_2N}{}}\!>\!C{=}C\!<\!\overset{H_A}{\underset{H_B}{}}$$

tains all the peaks of H_A and H_B, which have overlapping positive bands coupled by J_{AC} and J_{BC} with the two downfield negative multiplets. The chemical shift for H_C accounts for both b and d, but net cancelation of two of the normal triplets leaves only the outside emission and absorption pair. The other immediately assigned band was h, which, aside from the distortion of g, was obviously the unreacted 1-bromobutane H_X band.

The remaining bands, a, c, f, and g, showed the reverse relationship of absorption to emission pairs, *i.e.*, negative peak upfield from the positive peak, the inverse of b, d, and e. However, the same basic, if somewhat simplified, relationships hold for splitting, indicating an ABX system. H_A (upfield band of f, and g) is at δ 3.43 ppm, H_B (downfield band of f, and g) is at δ 3.49 ppm, and H_X (a and c) is at δ 5.92 ppm, with coupling constants of J_{AB} = 0 cps, J_{AX} = 9.5 cps, and J_{BX} = 15 cps. Although the pmr spectrum of the simplest vinylamine which might be anticipated in this system has not been reported,[6] it is possible from data on related amines[7] to justify the assignment of these bands to N,N-diethylvinylamine.

Chemically the origin of these compounds can be postulated by the reaction sequence 1. In this se-



(1)

quence the initial radical pair is generated from the reaction of *n*-butyllithium and 1-bromobutane. Since a Lewis base is required to depolymerize the *n*-butyllithium hexamer,[8] the radical pair probably forms in the immediate vicinity of a triethylamine molecule. These radicals, polarized in the magnetic field, react with one another to form predominantly *n*-octane[9] plus a small amount of 1-butene[10] and butane. A ready alternative to attack on a butyl radical is hydrogen abstraction from the available triethylamine. This should form the more stable α-amine radical, which undergoes subsequent loss of a second hydrogen to give the vinylamine observed in Figure 1.3. The absence of an emission band in the characteristic triplet of h confirms[11] the negligible amount of halogen–metal interchange, at least by radical processes.

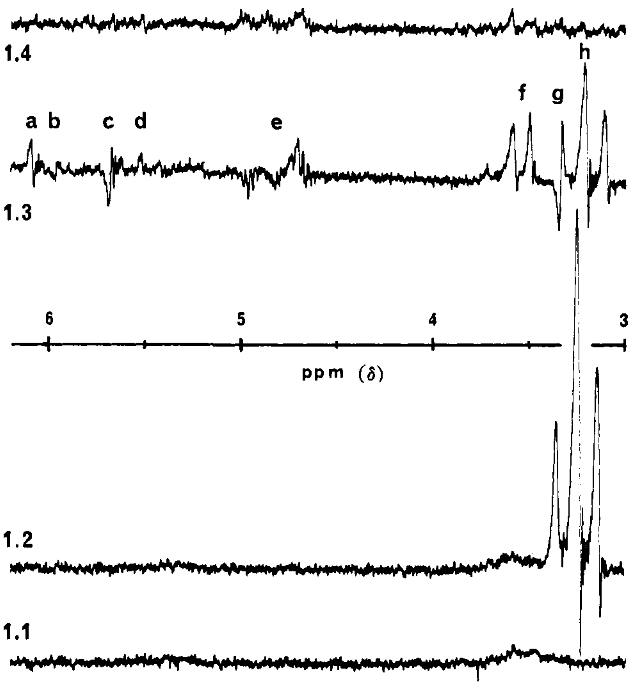


Figure 1. Proton magnetic resonance in the range δ 3–6.3 ppm for 0.5 ml of 1.5 *M n*-butyllithium in hexane (1.1), the addition of 0.07 ml of 1-bromobutane to this solution (1.2), and time scans (1.3 at 0.8 min and 1.4 at 10 min) after the addition of 0.25 ml of triethylamine.

Two mechanisms might account for the emission as well as absorption bands in the vinylamine produced. Either the intermediate amine radical is formed in an unpolarized state, but with a lifetime in the range necessary to allow its polarization,[2,12] or the polarization of the original butyl radical, which abstracts the hydrogen, is transmitted in the process of forming the amine radical. However, until more is known about the stabilities of such radicals and the emission–absorption relationships in the spectra, it is not possible to differentiate between these routes to polarization.[13]

Other amines tested as radical-generation initiators were either so efficient that they could not be used in significant quantities[14] or so inefficient[15] that a more reactive halide was required.

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(6) For a recent summary of data on this compound see: L. Spailter and J. A. Pappalardo, "The Acyclic Aliphatic Tertiary Amines," The Macmillan Co., New York, N. Y., 1965, p 130.

(7) A. N. Kurtz, W. E. Billups, R. B. Greenlee, H. F. Hamil, and W. T. Pace, *J. Org. Chem.*, 30, 3141 (1965); M. L. Farmer, W. E. Billups, R. B. Greenlee, and A. N. Kurtz, *ibid.*, 31, 2885 (1966).

(8) G. G. Screttas and J. F. Eastham, *J. Amer. Chem. Soc.*, **87**, 3276 (1965), and references cited therein.

(9) A. R. Lepley and W. A. Khan, unpublished work.

(10) 2-Butene was not detected.[9]

(11) D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, **85**, 743 (1963).

(12) R. G. Lawler, *ibid.*, **89**, 5519 (1967).

(13) The formation of this radical from the butyl radical and the increased radical stability with chain branching in simple hydrocarbon systems may support the first of these, but the characteristics of the last step in the reaction are unknown.

(14) Comparable reaction times to those reported here were encountered with 25 μl of tetramethylethylenediamine.

(15) N,N-Dimethylaniline.

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The Nuclear Magnetic Resonance Spectrum of a Phenoxy Radical. Di-*t*-butyl Nitroxide as a Spin Relaxer

Sir:

The nmr spectra of organic radicals provides a means of determining both the sign and magnitude of electron–nuclei coupling constants.[1] One observes single

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(1) R. W. Kreilick, *J. Chem. Phys.*, 46, 4260 (1967); **45**, 1922 (1966); H. H. Hausser, H. Brunner, and J. C. Jochims, *Mol. Phys.*, **10**, 253 (1966).