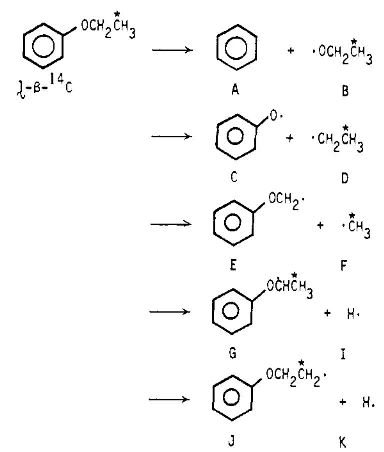
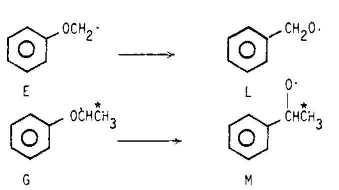
Scheme III

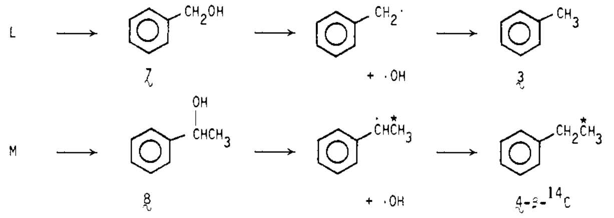


straction by another radical and that homolysis of **1** to A and B is energetically unfavorable. The phenyl radical A, in fact, is most likely formed by decomposition of E to A and formaldehyde.

Benzene and phenol result from the abstraction of hydrogen atoms by A and C, respectively, from tetralin. Toluene (**3**) and ethylbenzene (**4**-β-^{14}C), however, must be produced through intramolecular migration of phenyl from oxygen to carbon in the intermediates E and G; the rearranged radicals L and M

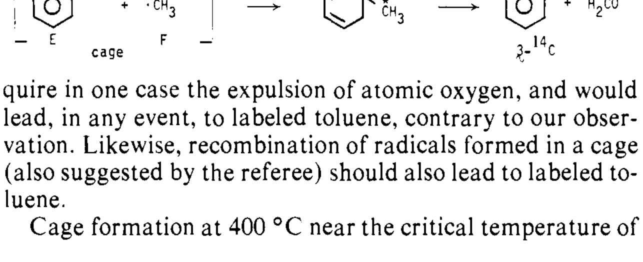


then convert into benzyl alcohol (**7**) and α-phenylethanol (**8**), respectively, which go on to **3** and **4**-β-^{14}C as shown. α-Phenylethanol (**8**) does, in fact, decompose under the conditions of the reaction to yield ethylbenzene and some toluene, as we showed in an independent experiment.

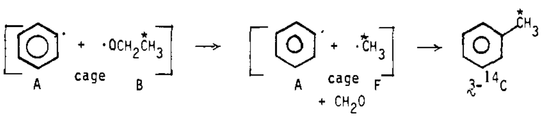


The α- and β-methylnaphthalenes (**5**) and α- and β-ethylnaphthalenes (**6**) are formed intermolecularly through pathways that are not as yet clear.

The fact that toluene (**3**) and ethylbenzene (**4**) are formed through intramolecular reactions (as demonstrated by the crossover experiments, Scheme II) precludes an ipso reaction.[13] A referee has suggested ipso attack by methyl or ethyl radicals from a cage. Such a mechanism has no precedent, would require in one case the expulsion of atomic oxygen, and would lead, in any event, to labeled toluene, contrary to our observation. Likewise, recombination of radicals formed in a cage (also suggested by the referee) should also lead to labeled toluene.



Cage formation at 400 °C near the critical temperature of tetralin is, in any event, highly unlikely.



Although 1,2 shift of phenyl from oxygen to carbon in a free-radical intermediate has been claimed,[14] the evidence is unconvincing and largely circumstantial. In the present work there can be little doubt that 1,2 shift occurs intramolecularly from oxygen to carbon through free-radical intermediates.[15]

Acknowledgment. The authors acknowledge helpful discussions with Dr. M. Poutsma, of Oak Ridge National Laboratory.

References and Notes

(1) Research sponsored by the Division of Chemical Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

(2) See, for example, the discussion of the Pott-Broche process by K. F. Schlupp and H. Wien, *Angew Chem., Int. Ed. Engl.*, **15**, 341-346 (1976).

(3) C. J. Collins, V. F. Raaen, B. M. Benjamin, and G. W. Kabalka, *Fuel*, **56**, 107 (1977).

(4) C. J. Collins, B. M. Benjamin, V. F. Raaen, P. H. Maupin, and W. H. Roark, *ACS Symp. Ser.*, **No. 71**, 165-170 (1978).

(5) B. M. Benjamin, V. F. Raaen, P. H. Maupin, L. L. Brown, and C. J. Collins, *Fuel*, **57**, 269 (1978).

(6) Ethanol-*1*-^{14}C and ethanol-*2*-^{14}C were prepared from appropriately labeled sodium acetates according to A. Murray III and D. L. Williams, "Organic Syntheses with Isotopes", Part I, Interscience, New York, 1958, pp 905, 906. The labeled ethanols were converted to ethyl iodides (H. S. King, "Organic Syntheses", Collect. Vol. II, New York, 1943, p 399) and thence to phenetole-α-^{14}C and phenetole-β-^{14}C through the Williamson synthesis (W. J. Hickinbottom, "Reactions of Organic Compounds", Longmans, Green and Co., New York, 1948, p 91).

(7) A Barber-Coleman 5000 gas chromatograph fitted with radioactivity (carbon-14 and tritium) monitoring accessories was used.

(8) The dry combustion method with Borkowski ion chamber and vibrating reed electrometer was used. The method is described in Chapter 11, by V. F. Raaen, G. A. Ropp, and H. P. Raaen, "Carbon-14", McGraw-Hill, New York, 1968.

(9) The method used was that of L. Slaugh, *J. Am. Chem. Soc.*, **81**, 2262 (1959).

(10) Phenetole-α-^{14}C was converted[5] to toluene-^{14}C and ethylbenzene-^{14}C (4.46 mCi/mol). Benzoic-^{14}C acid was obtained from toluene, 4.11 mCi/mol, and benzoic-^{14}C acid from ethylbenzene, 4.04 mCi/mol. The discrepancies with the data in *Scheme I* are due to isotope effects during the oxidations to benzoic acid. See, for example, W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 2308 (1953).

(11) When phenetole and tetralin-*1*-^{14}C (C. J. Collins, *J. Am. Chem. Soc.*, **73**, 1038 (1951)) were heated at 400 °C, the alkylnaphthalenes were all of essentially the same carbon-14 content as the reactant tetralin-^{14}C.[7]

(12) The *p*-xylene was identified by its GC retention times and by admixture with an authentic sample. The *p*-ethyltoluene, however, was isolated by preparative GC (Varian Aerograph, Series 2800) and identified by NMR Varian XL-100. Radioactivity determinations were by GC fitted with a carbon-14 monitor.[7]

(13) See, for example, C. R. Everly and J. G. Traynham, *J. Am. Chem. Soc.*, **100**, 4316 (1978).

(14) M. F. R. Mulcahey, B. G. Tucker, D. J. Williams, and J. R. Wilmshurst, *Chem. Commun.*, 609-610 (1965). See also the review by J. W. Wilt, "Free Radicals", J. K. Kochi, Ed., Wiley, New York, 1973, Chapter 8, pp 353-356.

(15) The carbon-14 (6%) found in the α position of ethylbenzene (Scheme I) is as yet unexplained. In this connection it is significant that, in an experiment in which anisole and tetralin were heated at 400 °C for 23 h, toluene and ethylbenzene were formed, among other products (GC analysis) in a ratio of ~4:1. See also J. W. Wilt and M. W. Stumpf, *J. Org. Chem.*, **30**, 1256 (1965).

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The Nonclassical Brexyl Cation. A Reassessment[1]

Sir:

In two recent papers,[2,3] the Blys and co-workers reported results of solvolyses of deuterium- and carbon-13-labeled β-

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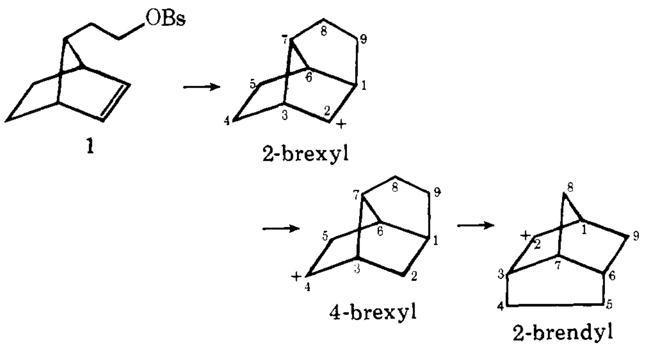

(*syn*-7-norbornenyl)ethyl *p*-bromobenzenesulfonates (**1**), which lead directly to labeled 2-brexyl ions.[4-7] The 2-brexyl ion is potentially degenerate through Wagner–Meerwein rearrangement, but is not itself captured by nucleophiles; instead it undergoes hydride shift to the 4-brexyl which can suffer Wagner–Meerwein rearrangement to produce the 2-brendyl cation. Both the 4-brexyl and the 2-brendyl cations are captured by nucleophiles to yield products. By determining the position of carbon-13 or deuterium in the solvolysis products and analyzing the resulting data, the Blys came to two important conclusions: (1) that the 2-brexyl cation is completely degenerate and (2) that there is a large counterion effect which partially controls product formation.[8] They also argue strongly[3] that their data support the intervention of nonclassical 2-brexyl cations. *It is this latter conclusion with which I disagree, and against which I now offer compelling arguments.* The classical and nonclassical schemes (Schemes I and II[3]) are not incorrect but present, nonetheless, an incorrect picture since they imply that each mechanism can be portrayed by four cations, whereas, in fact, Scheme I (classical) contains only two isotopically distinguishable cations and Scheme II (nonclassical) contains three. In Charts I and II, I have rewritten each scheme to show the minimum number of distinguishable intermediates. This is an important point, for the Blys, using a computer treatment, adjusted the concentrations of each ion as well as the values for the rate constants, by use of appropriate coefficients, and showed that the nonclassical scheme better fit their data. Since the nonclassical scheme contains three cations and the classical only two, it is clear that the former is inherently more capable of optimizing the data by providing more parameters to vary independently until the "best" answer is obtained.

That the data presented[2,3] allow no choice between the two mechanisms can be seen by reference to Charts I and II. To simplify the analysis, the complicated mixtures of products have been designated m_a, m_b, m_c, and m_d. These are mole fractions of product: m_a is the average of 4-brexyl-*4*-^{13}C and 2-brendyl-*1*-^{13}C; m_b of 4-brexyl-*9*-^{13}C and 2-brendyl-*5*-^{13}C; m_c of 4-brexyl-*8*-^{13}C and 2-brendyl-*4*-^{13}C; and finally, m_d of 4-brexyl-*5*-^{13}C and 2-brendyl-*8*-^{13}C. The averages are portrayed in Table I. Isotopic distributions in the 4-brexyl and 2-brendyl solvolysis products should be—and are—within experimental error, identical, and provide independent checks one on the other. In both Charts I and II, I have made the assumption—which appears fully justified by the data—that hydrogen migration is only affected by the counterion ($\overline{\text{OBs}}$) when the migrating hydrogen is on a carbon directly adjacent to it. Thus k_H' differs from k_H. We can safely assume[9] that the small variations in m_b–m_d are well within the limits of experimental error. It is important to note that *it is these small differences between m_b, m_c, and m_d which are the sole basis for the claim for nonclassical 2-brexyl cations.*

Chart I. Classical Scheme for Solvolysis of **1**-α-^{13}C

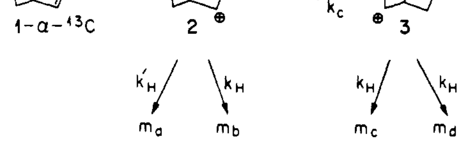

Chart II. Nonclassical Scheme for Solvolysis of **1**-α-^{13}C

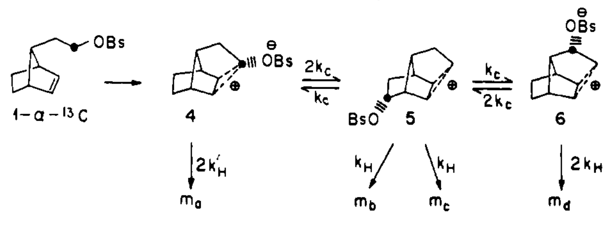

Table I. ^{13}C Distribution in Products of Acetolysis and Formolysis of β-(*syn*-7-Norbornenyl)ethyl-α-^{13}C Brosylate[a]

	m_a	m_b	m_c	m_d
acetolysis product				
2-brendyl	0.79 (C_1)	0.08 (C_5)	0.06 (C_4)	0.07 (C_8)
4-brexyl	0.77 (C_4)	0.08 (C_9)	0.06 (C_8)	0.08 (C_5)
av	0.78	0.08	0.06	0.075
formolysis product				
2-brendyl	0.58 (C_1)	0.14 (C_5)	0.13 (C_4)	0.15 (C_8)
4-brexyl	0.59 (C_4)	0.14 (C_9)	0.12 (C_8)	0.15 (C_5)
av	0.585	0.14	0.125	0.15

[a] Reference 3.

From Chart I, eq 1 can be derived easily,[10] and eq 2, 3, and 4 follow from Chart II. Equation 5 holds for both mechanisms. These equations are completely equivalent to the complicated kinetic treatment previously published.[2,3] From eq 1–5 it follows that $m_b = m_c = m_d$ for *both* classical and nonclassical mechanisms when $k_c \gg k_H'$ and k_H (in which case $2k_H'/k_c = 0$). Thus the 2-brexyl cation is degenerate and there is a counterion effect on product formation, the magnitude of which is given by k_H'/k_H.[11]

$$m_a/m_c = m_a/m_d = k_H'/k_H + 2k_H'/k_c \tag{1}$$

$$m_c/m_d = 1 + k_H/k_c \tag{2}$$

$$m_a + m_d(k_H'/k_H) = m_c[(2k_H'/k_H) + (2k_H'/k_c)] \tag{3}$$

$$m_b = m_c \tag{4}$$

$$\Sigma m_i = 1 \tag{5}$$

In summary, I agree that the Blys and co-workers have demonstrated complete degeneracy in the 2-brexyl cation and, in addition, a considerable counterion effect on product formation. It has been shown here, however, that, contrary to their statements,[3] their published data do not allow a distinction to be made between the two different kinds of intermediates.

References and Notes

(1) Research sponsored in part by the Division of Chemical Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

(2) R. S. Bly, R. K. Bly, J. B. Hamilton, and S. P. Jindal, *J. Am. Chem. Soc.*, **99**, 204 (1977).
(3) R. S. Bly, R. K. Bly, J. B. Hamilton, J. N. C. Hsu, and P. K. Lillis, *J. Am. Chem. Soc.*, **99**, 216 (1977).
(4) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1613, 1615 (1965).
(5) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, **89**, 880 (1967).
(6) A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Lett.*, 2851 (1967).
(7) R. E. Leone, J. C. Barborak, and P. v. R. Schleyer, "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, Chapter 33, pp 1921–1923, 1973.
(8) Although the counterion has been shown (C. J. Collins, *Rev. Chem. Soc.*, **4**, 251 (1975); C. J. Collins and B. M. Benjamin, *J. Am. Chem. Soc.*, **92**, 3182 (1970); B. M. Benjamin and C. J. Collins, *ibid.*, **92**, 3183 (1970); C. J. Collins and B. M. Benjamin, *J. Org. Chem.*, **37**, 4358 (1972)) to control product formation during aliphatic deaminations, the Blys' [2,3] results are

the first clear-cut evidence for counterion control during nondeaminative solvolyses.

(9) There is some doubt (Table II and note 9 of ref 3) as to which of two signals represent C_4 and C_8 (m_c and m_d) in 2-brendyl formate and acetate; further, the C_5 and C_8 signals (m_c and m_d) for 4-brexyl formate were poorly resolved.

(10) The method used involved use of the "area thorem" of J. E. Hearon, and was described by B. M. Benjamin and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 4332 (1956).

(11) Calculation of the isotope effects using Charts I and II and eq 1–4 from the data (ref 2, Table I) for the solvolysis of β-*syn*-7-norbornenyl-α-d_2 and -β-d_2 brosylates gives additional confidence in the validity of the schemes presented here. For the formolysis of **1**-α,α-d_2, $m_a = 0.45$, $m_b + m_c = 0.36$, and $m_d = 0.19$. Assuming $m_b = m_c$ and knowing that $k_H'/k_H = 4.18$ from the ^{13}C data, $k_H'/k_D' = 1.67$. In like manner, for the formolysis of **1**-β,β-d_2, $m_a = 0.56$, $m_b + m_c = 0.17$, and $m_d = 0.10$, from which $k_H/k_D = 1.7$, and $k_H'/k_H = 4.1$. Similar consistent results can be obtained from the data for acetolyses.

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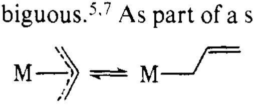
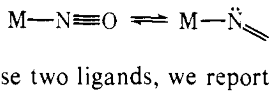
Ligand Dynamics of $Ir(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2^+$. A Facile Linear–Bent Nitrosyl Equilibrium

Sir:

A key proposal for catalytically active complexes containing allyl and nitrosyl ligands involves a change in bonding mode of the ligands from 3e⁻ to 1e⁻ donors as a means of generating coordinative unsaturation.[1-5] While $\eta^3 \rightleftharpoons \eta^1$ (π–σ) allyl conversion (eq 1) is well documented,[6] evidence for the linear ⇌ bent equilibrium of metal nitrosyls (eq 2) is sparse and, where it exists, ambiguous.[5,7] As part of a study of the relative dynamics of these two ligands, we report the synthesis and solution behavior of $[Ir(NO)(\eta^3\text{-}C_3H_5)L_2]^+$ (L = PPh_3) which exhibits a facile, well-defined linear ⇌ bent nitrosyl equilibrium. The complex also shows allyl fluxionality in a separate process. The X-ray structural characterization of one isomeric form of this cation shows it to be the first example of an η^3-allyl complex containing a bent nitrosyl.


(1)


(2)

The complex $[Ir(NO)(C_3H_5)L_2]^+$ is prepared as its PF_6^- salt (**1**) by reaction of $[IrCl(NO)L_2](PF_6)$[8] with tetraallyltin at 0 °C in THF, followed by precipitation with Et_2O and recrystallization from CH_2Cl_2/Et_2O, to give light-brown needles in 60–70% yield.[9] Repetition of the synthesis using $[IrCl(NO)L_2](BF_4)$, followed by similar isolation techniques, affords the BF_4^- salt hemihydrate (**2**) as red-brown crystals.[10] Both **1** and **2** are air stable as solids and moderately air stable in solution.

Infrared spectra of **1** and **2** in the solid state (KBr pellet) exhibit single nitrosyl stretches but with values differing by 130 cm⁻¹ (ν_{NO} 1763 and 1631 cm⁻¹, respectively). Solutions of either compound in CH_2Cl_2 or CH_3CN at 30 °C show both stretches at equal intensity, however. Cooling of these solutions causes an increase in the intensity of the 1763-cm⁻¹ band with a simultaneous decrease in the 1631-cm⁻¹ stretch. This spectral change is reversible; repeated cooling and warming of the same sample give identical results. The sum of the absorbances for these two bands is constant as a function of temperature within experimental error.

The existence of two nitrosyl stretches in solutions of $Ir(NO)(C_3H_5)L_2^+$, together with our ability to isolate two separate species, each containing only one ν_{NO} in the solid state, leads to the conclusion that two isomeric forms of the cation exist which are in equilibrium in solution. The constancy of the sum of the ν_{NO} absorbances over the temperature range ~−50 to +30 °C lends support to this notion.

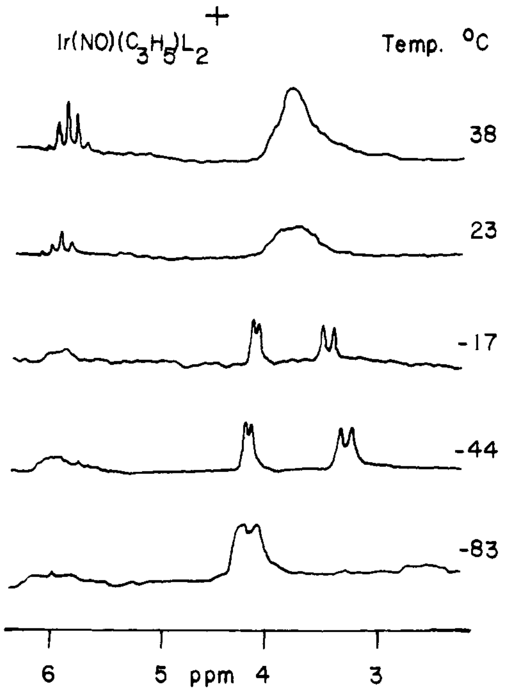
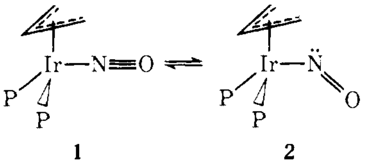


Figure 1. Allyl ¹H NMR spectra of $[Ir(NO)(C_3H_5)(PPh_3)_2]^+$ as a function of temperature in acetone-d_6.

The ¹H NMR spectra of **1** and **2** in acetone-d_6 are identical and also provide evidence of dynamic behavior as the temperature is varied. Representative spectra are shown in Figure 1. At 37 °C the spectrum consists of a quintet at δ 5.8 whose spacing is 9 Hz and a broad resonance at 3.8 (integrated ratio 1:4). Cooling of the sample to −44 °C leads to a single allyl pattern which unambiguously characterizes the allyl bonding mode as trihapto: central proton (A), δ 6.0 (m); syn protons (B), 4.24 (d); anti protons (C), 3.36 (d); integrated ratio A:B:C, 1:2:2; $J_{AB} = 7$, $J_{AC} = 11$ Hz. At even lower temperatures (−83 °C), a new pattern emerges which is not readily interpretable. It does indicate that an additional dynamic process is occurring at lower temperatures, but, in light of the spectra at −44 and −17 °C, syn-anti exchange can not be involved.

From both the IR and NMR spectra of $Ir(NO)(C_3H_5)L_2^+$ it is clear that several dynamic processes are occurring in solution. The most intriguing of these is the facile interconversion of the two nitrosyls. The fact that both nitrosyl stretches are observed in the temperature range −50–0 °C in which only η^3 coordination of the allyl exists leads to the conclusion that the two isomers are not related by $\eta^3 \rightleftharpoons \eta^1$ allyl fluxionality. The equilibration of the isomers is, however, rapid on the NMR time scale. We therefore propose the interconversion of the two isomers to be a simple bending and straightening of the Ir–NO unit as shown in eq 3.


(3)

1 **2**

The higher value of ν_{NO} for isomer **1** is consistent only with a linearly coordinated nitrosyl, and the structure of **1** is thus assigned as shown in eq 3 in analogy to the X-ray-determined structure of the 18e⁻ complex $Ru(NO)(\eta^3\text{-}C_3H_5)L_2$ reported

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