of excited *sec*-butyl radicals, as formed by recoil tritium addition to 1-butene or *cis*-2-butene. Evaluation of these changes indicates that about three-fourths of such additions to olefins are initiated by tritium atoms with kinetic energies in the range from 3 eV to thermal energies.

The reaction sequence is illustrated for *cis*-2-butene in eq 1–3; substitution of T for H in the parent molecule also occurs as in (4). The relative yields of $CH_3CH{=}CHT$ from (3) and the labeled parent molecule from (4)

$$T^* + CH_3CH{=}CHCH_3 \rightarrow CH_3CHCHTCH_3^* \qquad (1)$$

$$CH_3CHCHTCH_3^* + M \rightarrow CH_3CHCHTCH_3 + M \qquad (2)$$

$$CH_3CHCHTCH_3^* \rightarrow CH_3CH{=}CHT + CH_3 \qquad (3)$$

$$T^* + RH \rightarrow RT^* + H \qquad (4)$$

have been measured at 24 and 125° over a range of pressures from 3 to 76 cm. Similar observations were made concerning the terminal addition of T* to 1-butene, with the results shown in Figure 1. The ratio of the yield of propylene-*t* to that of the labeled parent molecule is higher at the higher temperature by 1.07 ± 0.02 at 5 cm, and 1.04 ± 0.01 at 76 cm for 1-butene experiments, with quite similar results for *cis*-2-butene. Decomposition by (3) accounts for 25–40% of the *sec*-butyl radicals from (1). At each temperature, the yield of propylene-*t* varies more than 30% with a 15-fold change in pressure.

Comparison of experimental results with the extensive data available from thermal H and D reactions with these olefins permits an estimate of the distribution of tritium atom energies involved in the addition reaction.[7-9] Approximately 50% of the tritium atoms adding to the olefins have less than 0.4 eV kinetic energy and are detected as n-C_4H_9T following the reaction of stabilized $CH_3\dot{C}HCHTCH_3$ with H_2S scavenger. Decomposition of radicals from thermal addition contributes to the observed temperature effect, but the major source of this variation lies with more highly excited radicals formed by reactions of above-thermal-energy tritium atoms. Approximately one-fourth of the addition reactions in (1) have sufficient excitation energy always to decompose in our experiments, corresponding to $\geqslant 3$ eV kinetic energy for the T atom. The tritium kinetic energies for addition reactions are generally much lower than for the substitution of T for H in c-C_4H_8, CH_4, or CH_3NC,[10-12] indicating that a large fraction of these addition reactions occur at energies below the energy threshold for the direct substitution reactions.

Detailed evaluation of the 1-butene system indicates that addition to the terminal position is favored by a factor of 2 or 3. Addition below 1 eV strongly favors the terminal position, as expected from thermal studies, while the higher energy addition proceeds at both positions more or less equally, as postulated by Urch and Wolfgang.[13]

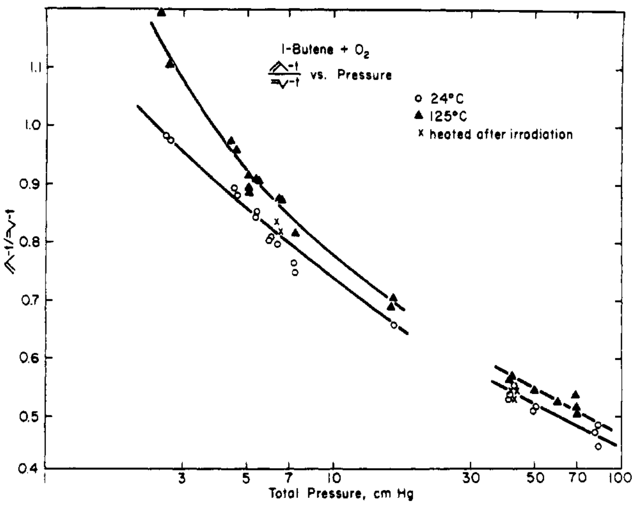

Figure 1.

While we are here reporting a temperature dependence of yield for recoil tritium reaction products, we wish to emphasize that our explanation of this observed effect has been made entirely in terms of the temperature effect on the *secondary* decomposition reaction, and not upon the primary reaction itself. Indeed, our treatment implicitly assumes that the primary process occurs in essentially identical manner with groups of molecules at 24 and 125°, with an energy contribution from the hot reaction that is independent of the detailed internal energy of the struck molecule.

The experimental procedures are quite routine,[1,2] with the exception of irradiation in thermostated temperature baths at the two temperatures. Samples irradiated at 24°, and subsequently heated to 125° for a time equivalent to that of the irradiation, gave identical results to the standard 24° samples, thereby eliminating the possibility of some temperature-catalyzed alteration of the product distribution.

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[7] Our most detailed quantitative calculations have assumed that a small part of the temperature dependence is contributed by the slightly greater decomposition of RT* at higher temperatures.

[8] B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, **30**, 735 (1959).

[9] B. S. Rabinovitch, R. F. Kubin, and R. E. Harrington, *ibid.*, **38**, 1692 (1963).

[10] E. K. C. Lee and F. S. Rowland, *J. Am. Chem. Soc.*, **85**, 897 (1963).

[11] Y. N. Tang and F. S. Rowland, *J. Phys. Chem.*, **72**, 707 (1968).

[12] C. T. Ting and F. S. Rowland, *ibid.*, **72**, 763 (1968).

[13] D. Urch and R. Wolfgang, "Chemical Effects of Nuclear Transformations," Vol. 2, International Atomic Energy Agency, Vienna, 1961, p 99.

[14] This research was supported by AEC Contract No. AT-(11-1)-34, Agreement No. 126.

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Kinetic Evidence for the Existence of Free Bis(phenylthio)methylene in Solution

Sir:

From a variety of preparative results[1] we concluded[2] some time ago that carbenoid A[3] is in equilibrium with bis(phenylthio)methylene (B) in THF solution. Since the classical work of Hine,[4] who proved that in aqueous

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[1] D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **6**, 443 (1967).

[2] Independently Professor Arens and his coworkers made the same proposal from some observations of the alkylation of A: G. A. Wildschut, H. J. T. Bos, L. Brandsma, and J. F. Arens, *Monatsh. Chem.*, **98**, 1043 (1967).

[3] D. Seebach, *Angew. Chem. Intern. Ed. Engl.*, **6**, 442 (1967).

[4] J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.

Table I. Rate Constants for the Thermal Decomposition of Tris(phenylthio)methyllithium[a]

A_0, 0.175 M				A_0, 0.023 M; LiClO$_4$, 0.156 M	A_0, 0.06 M; C_0, 0.05 M
$k_{p1} \times 10^5$ sec^{-1} [b]	$k_{p2} \times 10^4$ l./mole sec[c]	$k_1k_3/k_2 \times 10^5$ sec^{-1}	A_0, 0.108 M		
8.6	6.4	2.62 (81%)	2.99 (80%)	2.8 (82%)	2.6
7.0	5.6	2.81	3.44	3.1	2.5
6.0	5.0	2.76	3.49	3.0	2.9
4.9	4.4	2.49	3.04	2.5	2.8
3.6	3.6	2.70	3.05	2.9	2.9
3.2	3.4	2.71	3.01	2.3	2.8
2.7	3.0	2.56	3.13	2.4	2.7
2.5	2.9	2.57	3.00	2.0	2.5
1.6	2.3	2.42	3.05	2.3 (30%)	2.2
1.5	2.2	2.32	2.79		
1.4		2.62	2.64		
1.3		3.05 (15%)	2.43 (14%)		
1.2					
		Mean: 2.6	3.0	2.7	2.6

[a] Solvent: THF–10% *n*-hexane; temperature +40 ± 0.1°. [b] $k_{p1} = [\ln (A/A_0)]/t$; pseudo first order. [c] $k_{p2} = [(1/A) - (1/A_0)]/t$; pseudo second order.

dioxane haloforms are hydrolyzed by alkali through dihalocarbenes, the work of many investigators[5] has furnished "overwhelming evidence against the intermediacy of free carbenes in α-eliminations"[6] in less polar media. Furthermore, since Scheibler's "struggling"[7] for an organic derivative of carbon monoxide, it was tried many times to find evidence for or even isolate stable carbenes of type $:CX_2$ ($X_2 = (NR_2)_2$; NR_2,SR; $(SR)_2$; $(OR)_2$).[8] For these reasons we were not surprised when our report[1] met serious doubts. We currently undertake kinetic measurements, preliminary results of which are presented here. They are fully consistent with our previous suggestion.

$$\underset{\text{A}}{(C_6H_5S)_3CLi} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{B}}{(C_6H_5S)_2C:} + \underset{\text{C}}{C_6H_5SLi} \qquad \text{(1a)}$$

$$\text{A} + \text{B} \xrightarrow{k_3} \underset{\text{D}}{(C_6H_5S)_2C{=}C(SC_6H_5)_2} + \text{C} \qquad \text{(1b)}$$

The decomposition at +40° of A to form D[9a] was followed by hydrolysis of samples and automatic potentiometric titration of LiOH (from A) and C_6H_5SLi (pH 10.3 and 5.8, respectively).[9b] The most interesting feature of this reaction is the fact that its rate increases with decreasing starting concentration, A_0;[10] the effect of concentration is, however, rather small, and the curves obtained at A_0 = 0.18 and 0.11 M are superimposable (Figure 1, I).

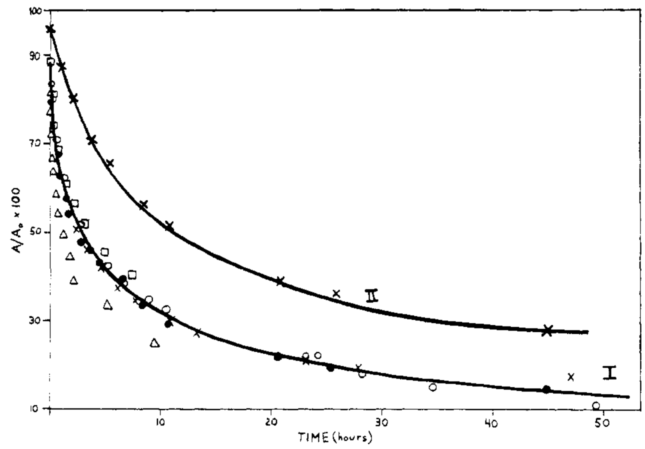

Figure 1. Decrease of carbenoid A at +40 ± 0.1° in THF-*n*-hexane 9:1. □, ○, ●, and △ refer to starting concentrations, A_0, of 0.26, 0.18, 0.11, and 0.019 M, respectively; × shows the reaction at A_0 = 0.06 M in the presence of 0.05 M C_6H_5SLi (C_0).

This would suggest a first-order reaction, but calculation shows that it is even "slower" than second order (Table I, columns 1, 2). A kinetic description matching its behavior can be derived making the assumption that the rate-determining step is given by eq 1b;[11] this implies that carbene B reacts much faster with lithium thiophenolate (C)[12] than with tris(phenylthio)methyllithium (A) ($k_2 > k_3$), and that the presumable[1] intermediate of reaction 1b, pentakis(phenylthio)ethyllithium, is going to D very rapidly.

By combining (2) (rate-determining step), (3) (given by the stoichiometry), and (4) (equilibrium constant of process 1a), and by integrating we obtain the rate law 5. This equation [13] indeed describes a decrease of A with time, independent of the starting concentration A_0.

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(5) Reviews: W. Kirmse, *Angew. Chem. Intern. Ed. Engl.*, **4**, 1 (1965), and G. Köbrich, *ibid.*, **6**, 41 (1967); but: D. Seyferth, *et al.*, *J. Am. Chem. Soc.*, **90**, 6182 (1968), and earlier work cited therein.

(6) R. M. Magid and J. G. Welch, *ibid.*, **90**, 5211 (1968), ref 6.

(7) H. Scheibler, *et al.*, *J. Prakt. Chem.*, (2) **133**, 131 (1932); *Chem. Ber.*, **66**, 501 (1933); **67**, 1507, 1514 (1934); **69**, 12 (1936).

(8) Reviews: H.-W. Wanzlick, *Angew. Chem. Intern. Ed. Engl.*, **1**, 75 (1962); R. W. Hoffmann, *ibid.*, **7**, 754 (1968); N. Wiberg, *ibid.*, **7**, 766 (1968).

(9) (a) In preparative runs hydrolysis after several days at room temperature gave a mixture of tris(phenylthio)methane, thiophenol, and tetrakis(phenylthio)ethylene (D), amounting to >90% of the material balance. (b) The reliability of this analysis was assured by blank tests.

(10) The rate of the more complex decomposition of carbenoid Cl_2CHLi was measured qualitatively to become larger at higher concentrations: G. Kobrich and H. R. Merkle, *Chem. Ber.*, **99**, 1782 (1966).

(11) Assuming a steady state, $dB/dt = 0$, leads to essentially the same kinetic equation.

(12) Indeed, it was shown that the highly nucleophilic anion of C is a most effective scavenger for carbenes: J. Hine, *J. Am. Chem. Soc.*, **72**, 2438 (1950); *cf.* L. H. Slaugh and E. Bergman, *J. Org. Chem.*, **26**, 3158 (1961).

(13) We were not able to find an example of such a kinetic equation in the literature.

$$-\frac{dA}{dt} = k_3AB \qquad (2)$$

$$A_0 = A + C \qquad (3)$$

$$K = \frac{k_1}{k_2} = \frac{BC}{A} \qquad (4)$$

$$A_0\left(\frac{1}{A} - \frac{1}{A_0}\right) + \ln\frac{A}{A_0} = \frac{k_1k_3}{k_2}t \qquad (5)$$

The experimental data fit the equation satisfactorily (Table I, columns 3, 4). The rate enhancement observed when going to lower concentrations, A_0, was shown to be due to a "salt effect";[14] adding lithium perchlorate to a run starting with $A_0 = 0.02\ M$ to bring the total lithium concentration to 0.18 M ($A_0/(\text{LiClO}_4) = {}^1/_7$) reduces the value of k_1k_3/k_2 to that of the 0.18 M run (Table I, column 5).

Adding lithium thiophenolate (C) must decrease the rate by shifting equilibrium 1a to the left side ("common ion effect"). As demonstrated for $A_0 = 0.06$ and $C_0 = 0.05\ M$ by curve II in Figure 1, this is the case. If, as anticipated, no rate-determining species other than A, B, and C are present or accumulate during the reaction, this run must correspond to an approximately half-reacted run having started with $A_0 = 0.11\ M$ and with no C_0 added. In fact, II falls exactly on I if plotting is started at 50% (Figure 1, I, crosses). This is also verified mathematically by using eq 5, modified for this situation to $(A_0 + C_0)\cdot[(1/A) - (1/A_0)] + \ln(A/A_0) = (k_1k_3/k_2)t$ (Table I, column 6).

The results described here are the first example of a kinetic measurement of carbenoid decomposition.[10] The unusual kinetic behavior found is described by a simple equation, in accordance with the existence of a free methylene[15] formed by α elimination in THF solution and with the reaction of this carbene with its carbenoid precursor to form the "dimer." Previously, this mode of dimer formation has been postulated to be most likely.[4,16] Further measurements with the aim of determining the equilibrium constant K are in progress.

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[14] Or the dissociation of A to $(C_6H_5S)_3C^-$ and Li^+ prior to formation of the carbene.

[15] Calling a spade a spade, we would rather name it "carbon monoxide bis(phenylthio)acetal," according to its low electrophilic carbene reactivity.[1]

[16] J. Hine, R. P. Bayer, and G. G. Hammer, *J. Am. Chem. Soc.*, **84**, 1751 (1962).

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Nuclear Magnetic Resonance Spectroscopy. Studies of Fluorine-19 Chemical Shifts in Norbornane Derivatives[1]

Sir:

The use of fluorine-19 nuclear magnetic resonance (fmr) spectroscopy for investigation of conformational analysis has achieved considerable popularity in recent years.[2-7] However, little attention has been paid to a detailed structural interpretation of the wide variation in the fluorine chemical shifts which are observed, although it has been pointed out that chemical-shift differences in a related series of fluorides may reflect conformational subtleties.[8,9]

We have initiated research on substituent effects on fluorine shielding in relatively rigid systems, taking as a starting point norbornyl compounds, which have proven to be so interesting and useful in studies of other kinds. We present here some preliminary results on fmr chemical shifts in variously methylated 2,2-difluoronorbornanes.

Nine 2,2-difluoronorbornanes were prepared by treatment of the corresponding ketones with sulfur tetrafluoride,[10,11] and their fluorine shifts were obtained at 56.4 MHz with a Varian A56/60 spectrometer (see Table I). The spectra were basically of the AB type with varying amounts of resolvable fine structure caused by proton–fluorine coupling. The broadness of the signals often made it impossible to determine the coupling constants and chemical shifts to better than 5–10 Hz.

The work of Anet[12] plus the demonstration by Williamson[13] that a Karplus-type curve is a good description of vicinal proton–fluorine coupling permitted in each case the reasonable assignment of the upfield resonances as being due to the *endo* fluorines. The data clearly show the extreme sensitivity of fluorine shielding to the molecular environment in closely related compounds. Examination of the data for the first four entries in Table I reveals an important vicinal orientation effect on fluorine shielding. A large upfield shift occurs at a methyl–fluorine dihedral angle of 0°; the effect is much smaller at 60° and essentially absent at 120°. The data for *trans*-decalin derivatives indicate that a large upfield shift should also occur at a dihedral angle of 180°.[14] Approximate molecular orbital calculations employing extended Hückel wave functions[15] and the magnetic shielding formalism of Pople[16] provide some quantitative support for the effect of a vicinal methyl group on fluorine shielding as a function of dihedral angle.[14] The computed effects are, however, so much smaller than those actually observed

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[1] Supported by the National Science Foundation.

[2] J. B. Lambert and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 3884 (1965).

[3] J. Jonás, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 3396 (1965).

[4] (a) J. T. Gerig and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 2791 (1966); (b) S. L. Spassov, D. L. Griffith, E. S. Glazer, K. Nagarajan, and J. D. Roberts, *ibid.*, **89**, 88 (1967); (c) R. Knorr, C. Ganter, and J. D. Roberts, *Angew. Chem.*, **79**, 577 (1967).

[5] E. L. Eliel and R. J. L. Martin, *J. Amer. Chem. Soc.*, **90**, 682, 689 (1968).

[6] A. A. Bothner-by and D. F. Koster, *ibid.*, **90**, 2351 (1968).

[7] (a) R. E. Lack and J. D. Roberts, *ibid.*, **90**, 6997 (1968); (b) R. E. Lack, C. Ganter, and J. D. Roberts, *ibid.*, **90**, 7001 (1968); (c) G. A. Yousif and J. D. Roberts, *ibid.*, **90**, 6428 (1968); (d) R. D. Stolow, T. W. Giants, and J. D. Roberts, *Tetrahedron Lett.*, 5777 (1968).

[8] J. D. Roberts, *Chem. Brit.*, 529 (1966).

[9] M. J. S. Dewar and T. G. Squires, *J. Amer. Chem. Soc.*, **90**, 210 (1968).

[10] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *ibid.*, **82**, 543 (1960); see also F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *ibid.*, **84**, 4275 (1962).

[11] Satisfactory elementary analyses have been obtained for new compounds.

[12] F. A. L. Anet, H. H. Lee, and J. L. Sudmeier, *J. Amer. Chem. Soc.*, **89**, 4431 (1967).

[13] K. L. Williamson, Y.-F. Li, F. H. Hall, and S. Swager, *ibid.*, **88**, 5678 (1966).

[14] For details see the Ph.D. thesis of J. B. Dence, California Institute of Technology, 1968.

[15] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[16] J. A. Pople, *ibid.*, **37**, 53, 60 (1962).