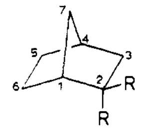


1 R = OBs, R' = D

2 R = D, R' = OBs

3 R = OAc R = H

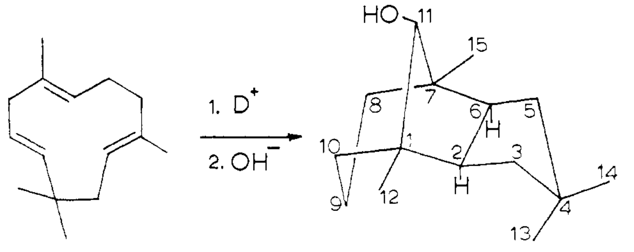
prepared from norborneol-*2-endo-d*[11] (0.99–1.0 *d* by combustion analysis), were solvolyzed (NaOAc buffer) under the conditions in Table I; the ^{13}C spectra of the norbornyl-*d* acetates clearly showed deuterium at C-1, C-2, and C-6 *only;* and integration gave the results in Table I. The *total* label scrambled to the remaining sites is known[10] to be <7% for **1** and <5% for **2**, and the amount at any *one* site would be below our limit of detectability (*ca.* 3%).[12]

Table I. ^{2}H Distribution by ^{13}C Nmr in **3** from Acetolysis of **1** and **2**

Substrate (mmol)	Temp, °C	Time, hr	—% D in **3** (±3%)— C-1	C-2	C-6
1[a] (2.25)	45	24	46	46	11
2[a] (4.24)	Reflux	20	38	38	22

[a] With tritiated analogs of **1** and **2**, average values for C-1, C-2, and C-6 of 40.1, 38.2, and 20.5 from **1**, and 36.0, 37.7, and 25.6 from **2** were obtained.[10a]

In studies on the mechanisms of polyene cyclizations we have treated humulene (**4**) with D_2SO_4 to produce apollanol (**5**).[13] The extent of deuterium incorporation depends on the experimental conditions, and a multilabeled product (**5**-d_n) from one such cyclization contained 13% d_0, 26% d_1, 34.5% d_2, 18% d_3, 6.5% d_4, 2% d_5 (total 1.85 *d*) by mass spectral analysis. Despite the complexity of the multideuteration, the ^{13}C spectra of the labeled and normal appollanol permitted identification of all labeled sites.



4 5

Owing to symmetry, the proton-decoupled ^{13}C spectrum of **5** contains only ten signals, which are readily assigned (ppm from TMS in C_6D_6) as 78.4 (C-11), 46.7 (C-2,6), 43.9 (C-3,5), 41.7 (C-1,7), 39.4 (C-4), 31.9 (C-8,10), 28.9 (C-14), 25.5 (C-13), 21.0 (C-12,15), 19.1 (C-9). Besides these signals, **5**-d_n exhibits triplets at 43.5, 31.4, and 20.6 ppm revealing deuterium at C-3(5), C-8(10), and C-12(15). Also, portions of the C-2(6), C-1(7), C-4, and C-9 absorptions show typical geminal isotope shifts of *ca.* 0.1 ppm; in fact, the major C-9 signal is shifted and there is a significant signal 0.2 ppm upfield from the normal peak signifying two geminal deuteriums. Further, the total intensity of the C-8(10) absorption shows that dideuteration occurs at this position. This fact, together with the shape of the C-9 absorption, confirms the methylene assignments. Intensity measurements revealed no detectable (<3%) deuterium at carbons 2(6), 9, 11, 13, 14, with the total content of 1.9 *d* distributed at the remaining sites as follows: CHD at C-3(5) (23%); CHD at C-8(10) (26%); CD_2 at C-8(10) (16%) and CH_2D at C-12(15) (16%); all values are ±3%.

Acknowledgments. We thank Professor E. W. Warnhoff and Dr. G. C. Joshi for the deuterated camphors. The work at the University of Western Ontario was supported by the National Research Council of Canada, and that at the Johns Hopkins University by the National Institutes of Health (GM 06304) and the National Science Foundation.

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Received June 19, 1972

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[11] B. L. Murr and J. A. Conkling, *J. Amer. Chem. Soc.*, **92**, 3462 (1970); J. A. Conkling, Ph.D. Dissertation, The Johns Hopkins University, 1969.

[12] We have similarly used ^{13}C nmr to study rearrangements in bridged polycyclic systems, and the results will be published elsewhere. (a) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Amer. Chem. Soc.*, **87**, 1613, 1615 (1965); (b) A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Lett.*, 2851 (1967); (c) A. Nickon and G. D. Pandit, *ibid.*, 3663 (1968).

[13] (a) A. Nickon, T. Iwadare, F. J. McGuire, J. R. Mahajan, S. A. Narang, and B. Umezawa, *J. Amer. Chem. Soc.*, **92**, 1688 (1970); (b) A. Nickon, F. Y. Edamura, T. Iwadare, K. Matsuo, F. J. McGuire, and J. S. Roberts, *ibid.*, **90**, 4196 (1968); (c) A. Nickon and F. Y. Edamura, *J. Org. Chem.*, **35**, 1509 (1970).

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^{13}C Nuclear Magnetic Resonance as a Monitor for Anionic Exchange Processes.[1] Remote Epimerization *via* Homoenolate Ions and Aryl D Exchange

Sir:

We wish to report the first example of epimerization *via* a homoenolate ion[2] at a center remote to a carbonyl group and to demonstrate how ^{13}C nmr greatly simplifies studies of anionic exchange.

In principle, *endo*-isocamphanone (**1**) and *exo*-isocamphanone (**2**)[3] should be interconvertible by alkali *via* the common homoenolate ion **3**, which could also lead to camphor (**4**).[4] Homoenolization in ketones **1**, **2**, and **4** is of added interest because each contains two enolizable protons, and the question arises whether their abstraction would preclude generation of higher energy homoenolate species. Demonstration of the compatibility of both processes within the same molecule would enhance the scope of homoenolization considerably.

Each of the ketones **1**, **2**, and **4** was heated at elevated temperatures in *t*-BuOK/*t*-BuOH, and the recovered ketone mixtures were analyzed by glpc. In addition

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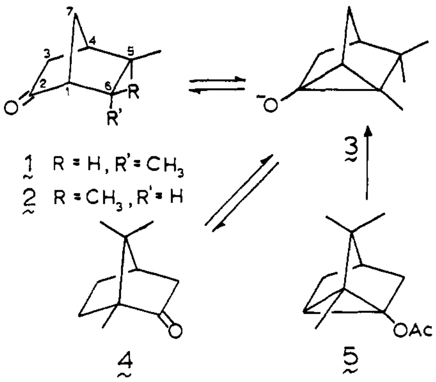
[1] Part XXV in the series ^{13}C Nuclear Magnetic Resonance Studies. Part XXIV: J. B. Stothers, C. T. Tan, A. Nickon, F. Huang, R. Sridhar, and R. Weglein, *J. Amer. Chem. Soc.*, **94**, 8581 (1972).

[2] (a) A. Nickon and J. L. Lambert, *ibid.*, **84**, 4604 (1962); **88**, 1905 (1966); (b) A. Nickon, J. L. Lambert, and J. E. Oliver, *ibid.*, **88**, 2787 (1966).

[3] E. Demole, *Helv. Chim. Acta*, **47**, 319 (1964).

[4] For examples of skeletal rearrangement *via* homoenolate ions, see (a) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Amer. Chem. Soc.*, **87**, 1615 (1965); (b) R. M. Coates and J. P. Chen, *Chem. Commun.*, 1481 (1970).



we subjected the related homoenol acetate **5**[5] to irreversible homoketonization at room temperature in *t*-BuOK/*t*-BuOH. The first two runs in Table I show that under the conditions used **1** experienced about 59.5% (58 + 1.5) homoenolization involving the H at C-6, and **2** experienced about 58% (22 + 36); these are minimum values since reversion to starting ketone would be undetected. The fact that **1** produced only 1.5% of its epimer **2** whereas **2** produced a substantial proportion of epimer **1** under comparable conditions is understandable on the basis that protonation of the homoenolate ion **3** in alkali is faster from the exo than the endo direction.[6]

Table I. Homoenolization and Homoketonization in the Isocamphanone–Camphor Series

Run	Substrate[a]	Temp, °C	Time, hr	Relative % after reaction 1	2	4
1	**1**	250	32	40.5	1.5	58
2	**2**	250	52	36	42	22
3	**2**	240	245	11	2	87
4	**4**	185	667[b]	0	1.5	97.5
		220	142			
5	Product of run 4	250	168	1	1.5	97.5
6	**5**	20	16	<0.1	<0.1	100

[a] Dr. E. Demole kindly provided the isocamphanones for these experiments. [b] After treatment at 185° the temperature was raised to 220° for 142 hr.

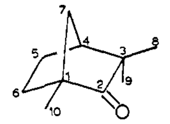
The results in Table I also qualitatively demonstrate an effect of temperature in homoenolate protonations. Whereas **3** generated at 20° from the homoenol acetate **5** produced camphor (**4**) exclusively (run 6), the same homoanion generated from **2** at 250° produced an appreciable fraction of **1** (run 2). Recognition of the temperature effect is important in planning stereoselective and site-selective deuterium incorporation *via* homoenolate ions.

Previously a combination of pmr, ir, and mass spectroscopy and separate synthesis of deuterated analogs was required to establish the course of D exchange in homoenolizations.[2,6] The same information can be obtained directly by ^{13}C nmr as we wish to show.

Deuterium incorporation in fenchone (**6**) is readily monitored[1] since separate ^{13}C signals arise from each carbon.[7] Treatment of **6** with *t*-BuOK/*t*-BuOD at 185° led to sequential deuteration at C-6 and C-8 (*exo*-methyl). After 400 hr there is still no detectable deuterium at any other carbon. Data for deuterium incorporation in **6** as a function of time are listed in Table II together with the mass spectral results to show the agreement obtained. The ^{13}C spectra clearly establish that of the possible homoenolate species involving methyl groups, the one involving C-8 forms preferentially. In earlier studies,[2,6] the symmetry of homoenolate species precluded detection of stereoselectivity for homoenolate formation at methyl carbons. Homoenolization at C-6 not only accounts for exchange at that site but could permit rearrangement to the skeleton **7**, and indeed we found that the alkaline treatment produced *ca.* 6% of a mixture of **7a** and **7b** in a 3:1 ratio.

Table II. Deuterium Incorporation in **6** by Treatment with *t*-BuOK/*t*-BuOD at 185°

Time, hr	% D by ^{13}C nmr, C-6 CHD	C-6 CD$_2$	C-8 CH$_2$D	Atom % D by ^{13}C	Atom % D by mass spectrometry
60	42	7	0	0.56	0.57
140	59	19	7	1.04	1.01
272	44	42	17	1.45	1.53
400	36	50	26	1.62	1.67



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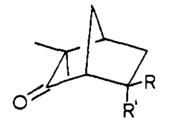
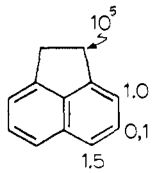


7a R = H, R' = CH$_3$

7b R = CH$_3$, R' = H

Many aromatic hydrocarbons are also amenable to quantitative deuterium analysis by ^{13}C nmr. Although assignments have been made for several cases,[8] definitive or corroborative evidence is provided by the spectra of ^{2}H-labeled materials because $J_{CCCD} > 1$ Hz and $J_{CCD} \sim 0.15$ Hz.[9] Thus, signals for carbons geminal to C–D exhibit readily resolved isotope shifts (~0.1 ppm), whereas those for vicinal carbons are appreciably broadened. Utilizing these features we examined H/D exchange of acenaphthene and found a unique reactivity pattern for aryl exchange.

Acenaphthene (**8**) was treated with 0.24 *N* *t*-BuOK/*t*-BuOD in sealed, degassed tubes. For exchange at the bridge positions (C-1,2), proton spectra yielded a



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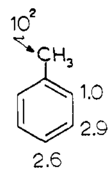

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(5) G. C. Joshi, W. D. Chambers, and E. W. Warnhoff, *Tetrahedron Lett.*, 3613 (1967). We thank Professor Warnhoff who kindly provided experimental details in advance of publication.

(6) (a) A. Nickon, J. H. Hammons, J. L. Lambert, and R. O. Williams, *J. Amer. Chem. Soc.*, **85**, 3713 (1963); (b) A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstuik, *ibid.*, **88**, 3354 (1966).

(7) E. Lippmaa, T. Pehk, J. Paasivirta, N. Belikova, and A. Plate, *Org. Magn. Resonance*, **2**, 581 (1970).

(8) A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Amer. Chem. Soc.*, **92**, 2386 (1970), and references therein.

(9) F. J. Weigert and J. D. Roberts, *ibid.*, **89**, 2967 (1967).

pseudo-first-order rate constant per hydrogen of 1.9×10^{-5} sec^{-1} at 120.4°; ring exchange required much higher temperatures. The ^{13}C spectrum of deuterated **8** obtained after 185 hr at 185° revealed extensive exchange at the ortho (C-3,8) and para (C-5,6) positions. The isotope-shifted components of the meta (C-4,7) signal showed zero, one, and two deuterium atoms on geminal carbons. The relative exchange rates at 204° (see **8**) may be compared with those for toluene[10,11] shown in **9**; although toluene exchange has been interpreted in terms of phenyl anions, the preferential ortho/para exchange in **8** suggests a different mechanism.

Acknowledgments. The work at the University of Western Ontario was supported by the National Research Council of Canada, and that at the Johns Hopkins University by the National Institutes of Health (GM 06304) and the National Science Foundation.

(10) A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 155 (1963).

(11) A. Streitwieser, R. A. Caldwell, R. G. Lawler, and G. R. Ziegler, *J. Amer. Chem. Soc.*, **87**, 5399 (1965).

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Received June 19, 1972

A Direct Method for Determining Light Intensity Dependent Rates. Triplet–Triplet Annihilation in Benzophenone

Sir:

We wish to report a novel technique for the evaluation of triplet–triplet annihilation rate constants based on the interrogation of either the integrated phosphorescence emission, or integrated absorption decay, monitored 180° from the axis of excitation. This technique avoids the necessity of making corrections for variations in light intensity along the excitation pathway.[1] The mathematical treatment of the emission or absorption observations is summarized here, and an example of the method is provided.

The decay of the excited triplet state can be expressed by the general equation

$$d[T_1]/dt = -k_1[T_1] - mk_2[T_1]^2 \qquad (1)$$

where k_1 is the summation of all radiative and unimolecular and pseudo-unimolecular nonradiative deactivation processes, and k_2 is the overall rate constant for the spin-allowed process

$$T_1 + T_1 \xrightarrow{k_2} S_n + S_0 \qquad (2)$$

This so-called triplet–triplet annihilation process yields a ground-state singlet, S_0, and one excited state singlet, S_n, with two possible resulting situations as follows.

(a) Internal conversion and intersystem crossing result in very efficient repopulation of the triplet state by $S_n \rightarrow T_1$, as occurs in benzophenone, so that $m = 1$ (eq 1), or (b) chemical reactions, as in biacetyl,[2] and/or other deactivation pathways, dominate with S_n so as to preclude repopulation of T_1 and $m = 2$. In the following derivation, we are assuming condition a holds.

In a pulsed experiment, the density of triplets in an incremental volume about the position x is given by the solution to eq 1 which is

$$n(t,x) = n(0,x)/[e^{k_1 t} + (k_2/k_1)n(0,x)(e^{k_1 t} - 1)] \qquad (3)$$

where $n(0,x)$ is the initial triplet concentration at $t = 0$. Under conditions where the second term in the denominator of eq 3 approaches or exceeds $e^{k_1 t}$, the phosphorescence decay becomes nonexponential. Because of the variation in $n(0, x)$, however, along the excitation path, it is difficult[1] to evaluate k_2 in conventional[3,4] flash-emission and -absorption experiments, and almost prohibitive for situations where the concentration of absorbing species is high.

From Beer's law, the initial triplet concentration with respect to path length, x, along the incident line of excitation through the sample cell is

$$n(0,x) = \alpha I(0,0)e^{-\beta x} \qquad (4)$$

where $I(0,0)$ is the incident intensity of pulsed radiation at $t = 0$ and $x = 0$,[5] β is the optical density of the material being excited, and α is a constant which converts $I(0,0)$ into units of concentration.

The integrated triplet concentration, $n(t,x)$, as a function of time along the path of the penetrating exciting pulse is thus

$$\int_0^l n(t,x)dx = \{[\alpha I(0,0)e^{-k_1 t}]/\beta\} \times$$

$$\int_0^{\beta l} [e^{-\beta x}d(\beta x)]/[1 + (k_2/k_1)\alpha I(0,0)(1 - e^{-k_1 t})e^{-\beta x}] \qquad (5)$$

The exponential theory for first-order decay processes follows directly, *i.e.*, when $[k_2\alpha I(0,0)] \ll k_1$

$$n(t) \equiv n(t,x)dx = [\alpha I(0,0)e^{-k_1 t}(1 - e^{-\beta l})]/\beta \qquad (6)$$

which, for total light absorption, *i.e.*, $e^{-\beta l} \rightarrow 0$, reduces to

$$n(t) = [\alpha I(0,0)e^{-k_1 t}]/\beta \equiv n_e(t) \qquad (7)$$

For the case in which the second-order process is important

$$n(t) = [n_e(t)/c(t)] \ln \{[1 + c(t)]/[1 + c(t)e^{-\beta l}]\} \qquad (8)$$

where $c(t) = (k_2/k_1)[\alpha I(0,0)(1 - e^{-k_1 t})]$. Note that for complete light absorption

$$n(t) = [n_e(t)/c(t)] \ln [1 + c(t)] \qquad (9)$$

The number of photons emitted, n_ν, is obtained as follows.[6]

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(1) (a) F. C. Henriques, Jr., and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **62**, 1038 (1940); (b) W. A. Noyes, Jr., and F. C. Henriques, Jr., *J. Chem. Phys.*, **7**, 767 (1939).

(2) (a) H. W. Sidebottom, C. C. Badcock, J. G. Calvert, B. R. Rabe, and E. K. Damon, *J. Amer. Chem. Soc.*, **94**, 13 (1972); (b) C. C. Badcock, H. W. Sidebottom, J. G. Calvert, B. R. Rabe, and E. K. Damon, *ibid.*, **94**, 19 (1972).

(3) C. A. Parker, "Photoluminescence of Solutions," Elsevier, New York, N. Y., 1968.

(4) J. B. Birks, "Photophysics of Aromatic Molecules," Wiley-Interscience, New York, N. Y., 1970.

(5) We assume for this analysis that the radiation pulse duration is gaussian and short compared to the duration of the emission. These assumptions simplify our treatment but can easily be generalized for different excitation conditions.