majority of the disadvantages of current procedures[13] and approaches the goal of a general synthesis. It is illustrated by the preparation of 2-methyl-4-(methylthio)-6-(4-methoxyphenyl)pyrylium tetrafluoroborate (**4**, R = 4-$CH_3OC_6H_4$; R^1 = CH_3; R^2 = SCH_3; X = $O^+BF_4^-$). Potassium *tert*-butoxide (5.04 g, 0.045 mol) was added to a stirred mixture of acetone (1.2 g, 0.02 mol) and the ketene dithioacetal **2** (R = 4-$CH_3OC_6H_4$; 5.0 g, 0.02 mol). An initial yellow suspension changed over a 16-h reaction period into a dense green precipitate of **3** (R = 4-$CH_3OC_6H_4$; R^1 = CH_3). This was collected and added to an ice-cold 4% HCl solution (200 mL), giving[10] the corresponding 1,5-diketone as a thick suspension which was collected and then stirred in dichloromethane (40 mL) with HBF_4 (20 mL of 48% solution) for 4 h at 50 °C. The yellow pyrylium salt separated during this period, and after addition of water (20 mL), the pyrylium salt was collected. It crystallized from acetic acid as light yellow needles (70%), mp 207–210 °C dec. Use of cyclohexanone as the ketonic component in the above reaction gave 2-(4-methoxyphenyl)-4-(methylthio)-5,6,7,8-tetrahydrobenzopyrylium tetrafluoroborate (**5**, X = $O^+BF_4^-$) as yellow-green needles (40%) from acetic acid, mp 246–250 °C dec. Aromatic substituents were readily introduced into the 2,6-positions; e.g., use of 4-methoxyacetophenone (**1**; R^1 = 4-$CH_3OC_6H_4$) in the above reaction gave 2,6-bis(4-methoxyphenyl)-4-(methylthio)pyrylium tetrafluoroborate (**4**, R = R^1 = 4-$CH_3OC_6H_4$; R^2 = SCH_3; X = $O^+BF_4^-$) as yellow prisms (53%) from acetic acid, mp 288–290 °C dec. In some cases the yield approaches quantitative as in the formation of 2,6-diphenyl-4-(methylthio)pyrylium tetrafluoroborate (**4**, R = R^1 = C_6H_5; R^2 = SCH_3; X = $O^+BF_4^-$) which was isolated as pale-green needles (93%) from 1,2-dichloroethane, mp 253–255 °C. The variety of aryl and heterocyclic ketones,[14] either as the α-ketoketene dithioacetal component or the ketonic component, which take part in this reaction allows the introduction of a wide variety of substituents in the 2 and 6 positions.

Alternatively, this synthesis may be accomplished in a one-pot reaction. In this case the 1,5-diketone is not isolated, and the tetrafluoroboric acid is merely added to the initial THF reaction mixture. The product is contaminated with KBF_4 which may be removed by washing with hot water, resulting in a reduced yield of the pyrylium salt. This procedure is best with aromatic substituents in the 2 and 6 positions. The 4-methylthio group in **4** (X = $O^+BF_4^-$), similar to the 4-chloro[15] and 4-methoxy groups,[16] is susceptible to displacement by nucleophiles such as secondary amines.

This synthesis offers many advantages over those currently used[17] for the preparation of the corresponding 4-(substituted-thio)pyrylium salts. As pyrylium salts of the corresponding 1,5-diketones are readily converted into thiopyrylium[18] and selenopyrylium[19] salts, these ring systems are now readily available with similarly diverse substitution patterns. Further extensions and applications of these syntheses are currently being studied in our laboratory.

(15) Föhlish, B.; Krockenberger, D. *Chem. Ber.* **1968**, *101*, 3990.
(16) Van Allan, J. A.; Reynolds, G. A., Petropoulos, C. C. *J. Heterocycl. Chem.* **1972**, *9*, 783. Van Allan, J. A.; Chie, C. S. *Ibid.* **1974**, *11*, 1065.
(17) King, L. C.; Ozog, F. J.; Moffat, J. *J. Am. Chem. Soc.* **1951**, *73*, 300.
(18) See, e.g.: Kharchenko, V. G.; Chalaya, S. N.; Naritsina, M. V.; Kulikov, L. K. *Khim. Farm. Zh.* **1976**, *10*, 80. *Chem. Abstr.* **1976**, *84*, 179975f. Reynolds, G. A. *Synthesis* **1975**, 638.
(19) Kudinova, M. A.; Krivun, S. V.; Tolmachev, A. I. *Khim. Geterotsikl. Soedin.* **1973**, 851. *Chem. Abstr.* **1973**, *79*, 105056q.

Laser Flash Photolysis with NMR Detection. Submicrosecond Time-Resolved CIDNP: Kinetics of Triplet States and Biradicals

G. L. Closs* and R. J. Miller

*Department of Chemistry, The University of Chicago
Chicago, Illinois 60637*

Recently we described a time-resolved CIDNP investigation of the laser flash photolysis of benzyl phenyl ketone.[1] The time resolution of those experiments (1 × 10^{-6} s) was sufficient to discriminate between the geminate radical pair process and the much slower formation of random phase products on the time scale of diffusion-controlled encounters. The purpose of the present paper is to report attainment of a time resolution of 1 × 10^{-7} s by employing a high-power, broad-band pulse amplifier and active switching of the quality factor of the single coil probe circuitry.[2] This improvement makes NMR detection applicable to a greater diversity of dynamic phenomena. The results of experiments conducted on two ketones that react by Norrish type I cleavage shall serve as illustrative examples.

The investigation of benzyl phenyl ketone has been extended to the submicrosecond time domain. The results reported previously establish that any time dependency observable over the range of hundreds of nanoseconds must be attributable solely to the geminate recombination reaction (eq 1).[1] Singlet–triplet
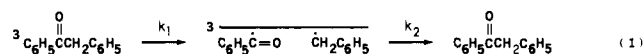
intersystem crossing in the n,π* state of the ketone is taken to be very fast, and parallel decay routes for the excited state ketone are neglected. Further, it is assumed that the dynamics describing the evolution of the spin states in the geminate radical pair and the chemical kinetics characterizing σ-bond formation to diamagnetic product can be consolidated into one phenomenological, first-order rate coefficient, k_2. The development of the signal from the emissively polarized benzyl protons of benzyl phenyl ketone is depicted in Figure 1. The large data scatter results from the poor signal-to-noise ratios obtained in this particular system. A

(1) Closs, G. L.; Miller, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 1639.
(2) A description of the instrumentation will be published elsewhere. Miller, R. J.; Closs, G. L. *Rev. Sci. Instrum.*, to be submitted for publication.
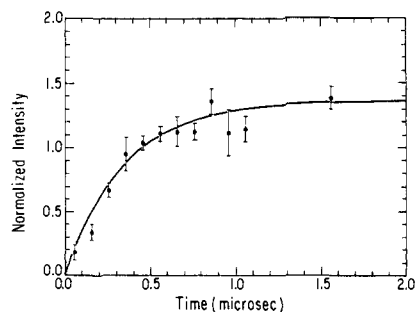
(13) For reviews, see: Perst, H. "Oxonium Ions in Organic Chemistry"; Verlag Chemie: Weinheim Bergstr., Germany, 1971. Balaban, A. T.; Schroth, W.; Fischer, G. *Adv. Heterocycl. Chem.* **1969**, *10*, 241.
(14) Rastogi, R. R.; Kumar, A.; Ila, H.; Junjappa, H. *J. Chem. Soc., Perkin Trans. 1* **1978**, 549. Thuillier, A.; Vialle, J. *Bull. Soc. Chim. Fr.* **1962**, 2182, 2187, 2194.

Figure 1. Time-dependent generation of the emissively polarized benzyl proton singlet of benzyl phenyl ketone during laser flash photolysis of 2.0 $\times$ 10^{-3} M benzyl phenyl ketone in C_6D_6 containing C_6H_6 (2% v/v) at 30 °C. Intensities are normalized to the C_6H_6 internal reference signal.[1] Error bars on the individual datum points indicate the reproducibility of the experiment. The solid line illustrates the computed best fit of an expression of the form $A[1 - \exp(-kt)]$ to the experimental data.[3]

Scheme I
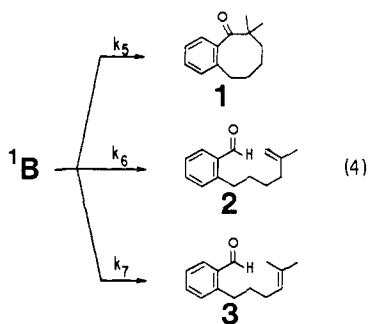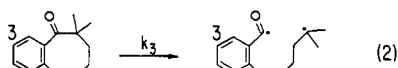
fit of an exponential generation function to the data yields a rate coefficient of 2.9 ± 0.4 $\times$ 10^6 s^{-1} in benzene-d_6 at 30 °C.[3] We assign this to k_1. This assignment is corroborated by literature values of k_1: 4.2 ± 1.3 $\times$ 10^6 s^{-1} in benzene as measured by laser flash photolysis with optical detection[4] and 2.4 ± 0.8 $\times$ 10^6 s^{-1} in benzene at 22 °C as obtained from Stern–Volmer-type quenching experiments.[5] Thus in this case the rate of formation of the geminate product is limited by the rate of decay of the triplet state ketone precursor.

The photochemistry of 6,6-dimethyl-7,8,9,10-tetrahydro-5-(6H)-benzocyclooctenone (1) has been studied. The results can be rationalized in terms of Scheme I (eq 2–4). The photophysics of generation and possible decay of the triplet state ketone are again neglected. The singlet state of the biradical, ^{1}B, is considered explicitly: this is reasonable for products formed directly in their ground states via intramolecular disproportionation and recombination reactions (eq 4). Furthermore, a common reaction intermediate provides a convenient description of the observed distribution of products by means of relative reaction rates. The presumptions are made therefore that k_4 may be a composite rate coefficient reflecting rotational equilibration of the biradical as well as intersystem crossing, and consequentially that $(k_5 + k_6 + k_7) \gg k_4$. These hypotheses are supported by typical lifetimes of the order of 100 ns measured for 1-ketyl-4-alkyl biradicals in
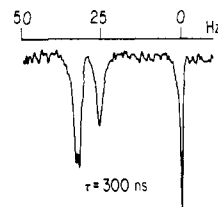
(3) Rate coefficients were calculated by χ^2 minimization using the STEPIT routine of the STEPT package. Error estimates were computed by the FIDO routine of STEPT. Chandler, J. P. *QCPE* **1976**, *12*, 307.

(4) Fouassier, J.-P.; Merlin, A. *Can. J. Chem.* **1979**, *57*, 2812.

(5) Heine, H.-G.; Hartmann, W.; Kory, D. R.; Magyar, J. G.; Hoyle, C. E.; McVey, J. K.; Lewis, F. D. *J. Org. Chem.* **1974**, *39*, 691.

Figure 2. High-field portion of a representative 60-MHz ^{1}H NMR spectrum obtained during laser flash photolysis of 1.6 $\times$ 10^{-2} M **1** in $(CD_3)_2SO/D_2O$ (4:1 w/w)[7] at 30 °C. This particular spectrum was taken 300 ns after the laser flash by signal averaging 500 times (total acquisition time ca. 15 min). The methyl groups of **1** are assigned a chemical shift of 0 Hz. The signal at 25 Hz arises from one of the two methyl groups of **3**. The feature at 33 Hz is composed of overlapping signals corresponding to the second methyl group of **3** and that of **2**. Spectral assignments for **2** and **3** are based upon 2-methyl-1-hexene and 2-methyl-2-hexene, respectively.
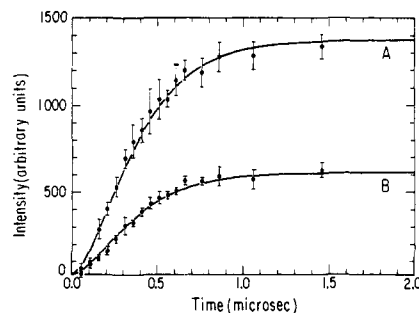

Figure 3. Time-dependent generation of the nuclear spin polarized methyl protons of **1** (A, 0 Hz) and **3** (B, 25 Hz) during laser flash photolysis of **1**. The experimental conditions and spectral assignments are given in the legend of Figure 2. Error bars on the individual datum points indicate the reproducibility of the experiment. Data points at infinite time are not shown. The solid lines illustrate the computed best fits of an expression of the form $A(1 + [1/(k_4 - k_3)][k_3 \exp(-k_4 t) - k_4 \exp(-k_3 t)])$ to the sets of experimental signal intensities.[3]

polar media and the reported conclusion that these lifetimes are determined by irreversible intersystem crossing from the triplet to the singlet biradical.[6]

Figure 2 shows the high-field portion of a spectrum obtained 300 ns after flash photolysis of **1** in $(CD_3)_2SO/D_2O$ (4:1 w/w)[7] at 30 °C. Figure 3 illustrates the evolution of two of those signals as a function of time. The pronounced sigmoidal character of the plots is observed for all lines in the spectrum; it is highly reproducible and independent of substrate concentration. Within the framework of the model developed above, these facts justify a kinetic analysis in terms of two consecutive, first-order reactions. Fits of an expression of the requisite form to the data yield the following rate coefficients: k_3 = 5.3 ± 1.0 $\times$ 10^6 and k_4 = 5.3 ± 1.0 $\times$ 10^6 s^{-1}.[3,8] The distribution of products is evaluated by integration of selected signals and application of appropriate statistical corrections and provides relative rates for the reactions of ^{1}B: k_6/k_5 = 1.56 ± 0.05 and k_7/k_5 = 1.60 ± 0.05. The kinetics of formation of the various products therefore furnish information regarding the dynamics of the triplet state ketone as well as the triplet and singlet states of the biradical.

It is our opinion that NMR detection in flash photolysis can offer real advantages over more conventional, optical detection methods because of the greater information content inherent in the NMR spectrum.[9] Laser flash photolysis experiments on **1**

(6) Small, R. D., Jr.; Scaiano, J. C. *J. Phys. Chem.* **1977**, *81*, 2126. Scaiano, J. C.; Lissi, E. A.; Encina, M. V. *Rev. Chem. Intermed.* **1978**, *2*, 139.

(7) The protio analogue of this mixed solvent system has the following physical properties at 25 °C: viscosity, 3.45 cP; dielectric constant, 65.3. Covington, A. K.; Dickerson, T. "Physical Chemistry of Organic Solvent Systems"; Plenum: New York, 1973; p 19.

(8) The reported values represent the average of rate coefficients calculated on the basis of each of the five signals observed in the spectrum. All individual values fall well within the quoted error estimates.

(9) For example, see: Closs, G. L.; Sitzmann, E. *J. Am. Chem. Soc.*, in press.

have been carried out in this laboratory by employing optical detection. The results of this study were unfortunately completely ambiguous: it was not possible to distinguish definitively between transient absorptions resulting from the triplet state ketone and the biradical. While NMR detection monitors only the kinetics of formation of the final diamagnetic products, at least one feature of the NMR spectrum of each product molecule is totally resolved, and assignments are readily made. It is obvious, however, that the time resolution of NMR detection will never approach that available with modern optical detection, and it is doubtful that further improvements will exceed a few tens of nanoseconds.
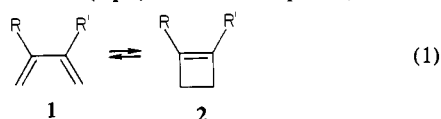
Selective Isomerization of Butadiene–Cyclobutene Systems via Infrared Multiphoton Excitation

James L. Buechele, Eric Weitz,* and Frederick D. Lewis*

*Department of Chemistry, Northwestern University
Evanston, Illinois 60201*
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It is now a well-established fact that polyatomic molecules can undergo chemical change as a result of the absorption of many infrared photons from an intense laser field. By selective excitation of one isotopic compound in a mixture, it has been shown possible to preferentially dissociate that component of the mixture and thus achieve an anomalous isotope ratio in the system. This procedure has resulted in isotopic enrichment of a number of chemically and technologically important isotopes.[1] Frequency selective vibrational excitation of one isomer in a mixture of isomers is also often possible because of the finite vibrational frequency shifts that occur due to the change in energy of normal modes of different isomers.[2,3]

By selective excitation of isomers in the 2,4-hexadiene system, we have shown it possible to drive this system away from the thermodynamically most favored isomer.[3] However, in the hexadiene system, the ΔH's involved in the isomerization step were small, of the order of 1 kcal.[4] In this communication we report the achievement of efficient and selective isomerization of 2,3-dimethyl-1,3-butadiene (**1a**) and 2-methyl-1,3-butadiene (**1b**) to the cyclobutenes **2a** and **2b** (eq 1). For these species, ΔH and

$$\text{(1)}$$

	kcal/mol	ΔS, eu
a, R = R′ = CH$_3$	+9.6[5a,d]	−3.6[5d]
b, R = CH$_3$, R′ = H	+10.6[5c,d]	−3.9[5c,d] (1.9 eu)[5d]
c, R = R′ = H	+11.4[5a,b]	−3.6[5b,c]

ΔS are from ref 5a and as indicated. Where more than one

Table I. Isomerization Yields

parent[e]	fluence, J/cm^2	helium pressure, torr	10^6 × yield/pulse cm^{-2}
methylbutadiene[a]	1.0	0	1.0
	2.0	0	2.9
	3.0	0	19.0
	4.0	0	35.0
	4.0	1	27.1
	4.0	2	25.6
	4.0	5	21.4
	4.0	10	17.8
methylcyclobutene[b]	2.7	0	0.85
	2.7	2	0.45
	2.7	5	0.0
	3.3	0	20.7
	3.3	5	16.0
	3.3	10	12.5
dimethylbutadiene[c]	1.7	0	2.0
	2.1	0	2.6
	2.7	0	3.5
	2.7	0.5	2.7
	2.7	1.0	1.8
	2.7	2.5	0.2
	4.7	0	140
	5.0	0	462
dimethylcyclobutene[d]	2.7	0	4.1
	3.0	0	8.0
	3.0	1.3	4.8
	3.0	5.5	3.5
	3.0	15	2.2
	3.8	0	20.0

[a] Irradiated with P(42) 10.6 μm. [b] Irradiated with P(20) 10.6 μm. [c] Irradiated with P(38) 10.6 μm. [d] Irradiated with P(22) 9.6 μm. [e] All experiments were done at a parent pressure of 100 mtorr.

reference is indicated, the appropriate values were calculated by using data from both sources. Parameters are reported for the reaction progressing left to right. This report constitutes the first example of infrared-laser-induced reactions which are substantially endoentropic and endoenthalpic.[6] By shifting irradiation frequency, the cyclobutenes can be efficiently and cleanly ring opened. The yield of cyclobutene product is highly dependent upon methyl substitution, laser fluence, and added rare gas pressure.

Irradiation of dienes **1a**–**c**[7] and cyclobutenes **2a,b**[8,9] was performed by using the output of a Lumonics K203-2 TEA laser. All irradiation studies were performed in an unfocused geometry, with variations of fluence being achieved by collimation of the beam with a Galilean telescope. For accurate definition of the beam area, beams were spatially filtered with a glass iris. Irradiation of the various isomers took place on the laser lines and over the fluence range indicated in Table I. Yields are reported as yield pulse^{-1} cm^{-2} of irradiated area. Laser energies were measured with a Scientech calorimeter and irradiation frequencies were determined with an Optical Engineering CO$_2$ laser spectrum analyzer. Irradiation was typically performed in a 10-cm Pyrex cell with NaCl windows. Product analysis was by gas chromatography using a 10-ft × $^1/_8$-in. column of 20% dimethylsulfolane on 80–100 mesh Chromosorb P. For each isomer system, product assignments were checked at least once via GC/MS. In the case of 1,3-butadiene (**1c**) laser irradiation produces a mixture of two unidentified isomers of mass 54, one of which is most likely cyclobutene (**2c**).

(1) (a) Letokhov, V. S.; Moore, C. B. In "Chemical and Biochemical Applications of Lasers", Moore, C. B., Ed.; Academic Press: New York, 1977; Vol. 3, Chapter 1. (b) Ambartzumian, R. V.; Letokhov, V. S. *Acc. Chem. Res.* **1977**, *10*, 61–67. (c) Bloembergen, N.; Yablonovitch, E., *Physics Today* **1978**, May 23–30.

(2) (a) Glatt, I.; Yogev, A. *J. Am. Chem. Soc.* **1976**, *98*, 7087–7088. (b) Yogev, A.; Lowenstein-Benmair, R. M. J. *Ibid.* **1973**, *95*, 8487–8489. (c) Ambartzumian, R. V.; Chekalin, N. V.; Dolzhikov, V. S.; Letokhov, V. S.; Lokman, V. N. *Opt. Commun.* **1976**, *18*, 400–402. (d) Ambartzumian, R. V.; Chekalin, N. V.; Dolzhikov, V. S.; Letokhov, V. S.; Lokhman, V. N., *J. Photochem.*, **1976**, *6*, 55–57. (e) Danen, W. C. *Opt. Eng.* **1980**, *19*, 21.

(3) Buechele, J. L.; Weitz, E.; Lewis, F. D. *J. Am. Chem. Soc.* **1979**, *101*, 3700–3701.

(4) Doering, V. C. E.; Hauthal, H. G. *J. Prakt. Chem.* **1964**, *24*, 27–37.

(5) (a) Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: New York, 1970. (b) Danti, A. *J. Chem. Phys.* **1957**, *27*, 1227. (c) Research Project 44, American Petroleum Institute, Table 11, College Station, TX, 1972. (d) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(6) A study has been performed where the reaction was driven in a counterenthalpic direction, but this direction was entropically favorable. See: Yogev, A.; Benmair, R. M. J. *Chem. Phys. Lett.* **1977**, *46*, 490.

(7) Dienes **1a**, **1b** (Aldrich Chemical Co.), and **1c** (Matheson Chemical Co.) contained <1% impurities by gas chromatographic analysis.

(8) Cyclobutenes **2a** and **2b** were prepared by the method of Srinivasan. Purification was achieved by spinning band distillation followed by preparative gas chromatography (15 ft × $^1/_4$ in.—20% dimethylsulfolane on 60–80 mesh NAW Chromosorb P). Products were identified by NMR, FTIR, and GC/MS.

(9) Srinivasan, R. *J. Am. Chem. Soc.* **1962**, *84*, 4141–4145.