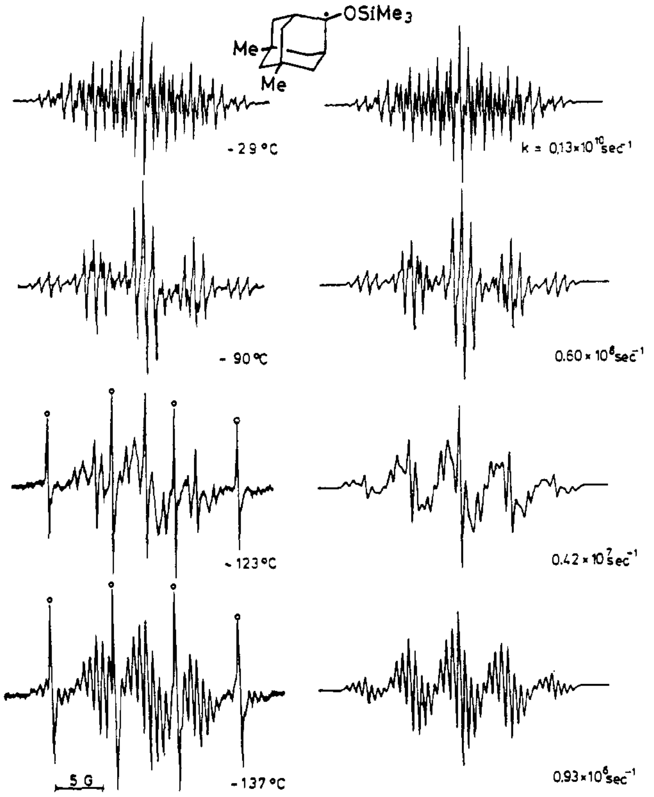

Figure 1. ESR spectra of **2b** at various temperatures: left, experimental; right, simulated with specified rate constants. Signals denoted with a small open circle in the experimental spectra are those of $Me_3Si\cdot$.

the half-occupied orbital on C_α due to hyperconjugation and steric hindrance.[10] The folded conformation B should be much higher in energy than A if the radical is pyramidal as inferred above. These two conformations are compatible with the equivalence of the β-hydrogen hfsc observed even at −137 °C and also with the temperature dependence of the spectrum. Since we have detected only one isomer of **2b** at the lowest temperature, the temperature-dependent behavior of the hfs pattern and the line-width alternation in the ESR spectrum (Figure 1) may be explained in terms of an exchange between the two equivalent structures A and A′[11] at rates of nearly the same order of magnitude as the difference in the hyperfine splittings for the two pairs of γ hydrogens expressed in frequency units.

The exchange rates were determined by comparing the experimental spectra with the simulated spectra obtained by solving the modified Bloch equations for the two-jump system[12] (Figure 1). From a plot of ln (k/T) vs. $1/T$, the following Eyring parameters for **2b** were obtained: $\Delta H^\ddagger = 4.2$ kcal/mol; $\Delta S^\ddagger = 1.2$ eu. A similar temperature dependence observed in the ESR spectrum of **2a** was complicated by an additional modulation due to the δ hydrogens.

Although the exchange should include two modes of motion, pyramidal inversion and silyl-group rotation, these motions are most probably strongly correlated and will avoid the high-energy conformation B. While the observed barrier to exchange should be taken as that for this rather complex motion,[11] it is noteworthy that the barrier is very similar to the inversion barrier (3.5 kcal/mol) for the 1-hydroxycyclohexyl radical calculated by ab initio methods.[13]

Registry No. 1a, 21517-94-2; **1b**, 81814-95-1; **2a**, 75890-76-5; **2b**, 81814-96-2; **3a**, 81814-97-3.

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[10] Edge, D. J.; Kochi, J. K. *J. Chem. Soc., Perkin Trans. 2* **1973**, 182.

[11] If the radical is more planar than we have estimated with β-hydrogen hfsc's, the exchange between A and A′ (or between A and B) should represent essentially the hindered internal rotation about the C–O bond. However, if the rotational barrier of the Si–O bond would be very small, the experimental activation energy could represent a pyramidal inversion barrier. Thus, strictly speaking, the observed barrier should be considered as the upper limit of both pyramidal inversion and internal rotation. We thank a referee for useful comments on this point.

[12] Sullivan, P. D.; Bolton, J. R. *Adv. Magn. Reson.* **1970**, *4*, 39. The simulation program was modified for our specific spin system.

[13] Lloyd, R. V.; Causey, J. G.; Momany, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 2260.

Direct Observation of a Hydrocarbon Singlet 1,3-Biradical by Picosecond Fluorescence Spectroscopy

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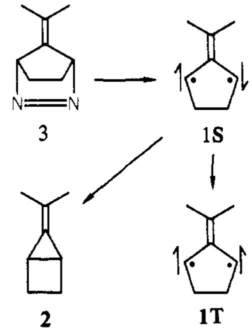
Recent experiments indicate that a finite energy barrier (2–3 kcal/mol) opposes the ring-closure of the planar singlet state of 2-isopropylidenecyclopentane-1,3-diyl (**1S**) to 5-isopropylidenebicyclo(2.1.0)pentane (**2**).[4-6] Moreover, the spin-retarded intersystem crossing (ISC) of **1S** to the more stable triplet biradical (**1T**) is only 10^{-5} times as fast as a molecular vibration.[6] These findings imply that **1S** is a local minimum on the reaction pathway, not a transition state. The present paper reports the direct spectroscopic observation of an excited state of **1S**.



The transients are generated by picosecond excitation[7] of the diazene **3**[6] in hexane solution and are monitored by their fluorescence. The radiative lifetime of the planar singlet **1S*** is expected[8] to be longer by at least 10^3–10^5 than the lifetimes observed in the present experiments, so that quenching of the fluorescence signal intensity strongly indicates the occurrence of some other chemical or physical process that consumes excited species.

Figure 1 shows the fluorescence decay beyond 310 and 380 nm. For both spectral ranges, the emission decay is found to be biphasic with two resolvable processes with lifetimes of 38 and 280 ps. The 280-ps component intensity is affected only slightly by restricting the observed fluorescence to longer than 380 nm. This restriction

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[1] Bell Laboratories, Murray Hill, NJ 07974.

[2] Yale University, Department of Chemistry, New Haven, CT 06511.

[3] Humphrey Chemical Co. Fellow, 1981.

[4] (a) Mazur, M. R.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 684. (b) *Ibid.* **1982**, *104*, 2217.

[5] (a) Rule, M.; Lazzara, M. G.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7091. (b) Rule, M.; Mondo, J. A.; Berson, J. A. *Ibid.* **1982**, *104*, 2209.

[6] (a) For reviews, see: Berson, J. A. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982. (b) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.

[7] Barbara, P. F.; Brus, L. E.; Rentzepis, P. M. *Chem. Phys. Lett.* **1980**, *64*, 447.

[8] The $^1A_1 \leftarrow {}^1E'$ transition for parent trimethylenemethane has been calculated[9] to occur at 289 nm with an oscillator strength $f \sim 0.1$. The Einstein probability of spontaneous emission for such a species gives rise to a lifetime of about 10 ns.[10]

[9] Davis, J. H.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, *99*, 4242.

[10] (a) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; p 174. (b) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Menlo Park, CA, 1978; pp 91 ff, 147.

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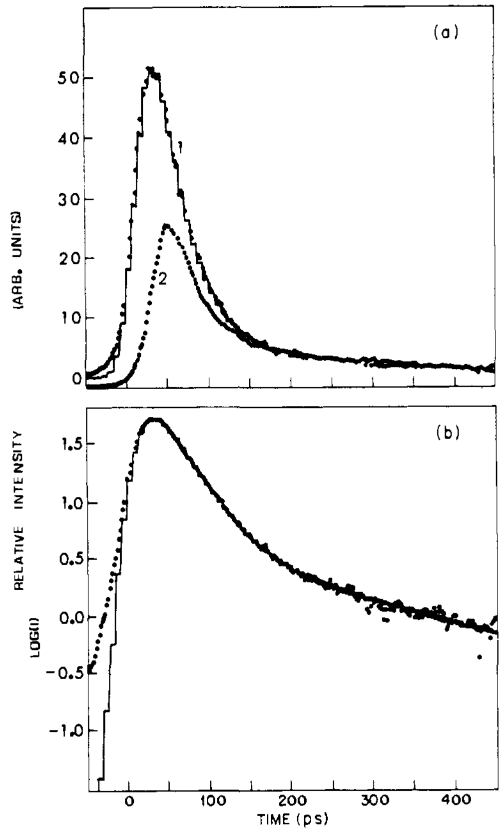

Figure 1. Fluorescence decay of diazene after excitation with a 266-nm 25-ps pulse: (a) emission wavelength greater than 310 nm (a1) and greater than 380 nm (a2). The solid line (a1) is calculated on the basis of the known excitation pulse length assuming $\tau_1 = 38$ ps and $\tau_2 = 280$ ps. (b) The 310^+-nm fluorescence (a1) plotted in the form of log *I* vs. *t*. The solid line is the log plot of the calculated curve of Figure 1a.

substantially decreases the intensity of the 38-ps component, implying that the fluorescence of the long-lived component is significantly red-shifted compared to the short-lived one. This conclusion is supported by comparison of the total laser-induced transient emission spectrum with the continuous-wave (CW) irradiation spectrum of **3** (Figure 2). Several features distinguish the transient from the static spectrum. The laser-induced and static spectra maxima occur at 430 and 400 nm, respectively. Also, the shoulder at 445 nm and the maximum at 625 nm in the laser-induced spectrum do not appear in the static spectrum. These differences rule out the possibility that the 280-ps component is due to impurities.[11]

We assign the 38-ps lifetime to the predissociation of an excited singlet state of diazene **3**. Loss of nitrogen leads to the biradical **1S** in its lowest planar singlet state ($^1E'$ for substituted trimethylene–methane, TMM),[9] which must absorb another laser photon to fluoresce from **1S*** ($^1A_1$ state).[12-14] This fluorescence is associated with the 280-ps lifetime and dominates the laser-induced total-emission spectra.[15] Comparison of the two spectra in the 360–420-nm region shows that the diazene fluorescence (Figure 2b) must be weak compared to the biradical fluorescence if these two are to give the observed total spectrum (Figure 2a). This is expected on the basis of oscillator strengths[8,16] and observed lifetimes.

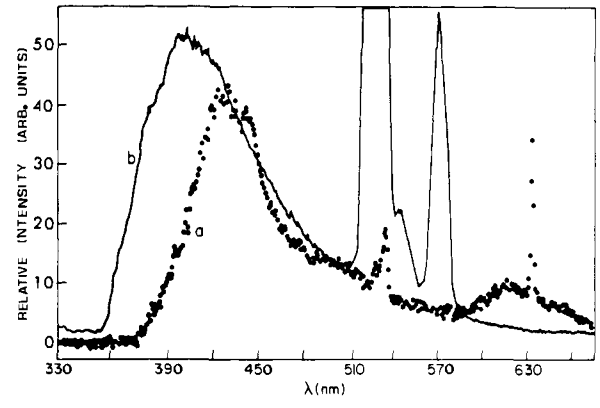

Figure 2. (a) Total transient emission recorded by a $^1/_4$ M spectrometer–vidicon system following 266-nm 25-ps excitation. The sharp feature at 532 nm is due to scattered second harmonic laser light (the peak ~538 is green light entering the spectrometer slit after several reflections through the apparatus). The peak at 632.8 nm is a wavelength reference. (b) Static fluorescence spectrum of diazene **3** recorded by a Perkin-Elmer fluorimeter, also excited at 266 nm. The maxima at 532 and ~575 nm are due to second-order grating reflections and Raman scattered light. The 625-nm peak is a function of the history of the sample.

Assignment of the 280-ps lifetime to an excited triplet state, **1T*** ($^3A_2$), is unlikely on the basis of reactive quenching data. In 1.9 M acrylonitrile, the lifetimes of the short- and long-lived transients decrease. The short lifetime (τ_1) decreases from 38 to 19 ps, whereas the long-lived (τ_2) decreases from 280 to 200 ps. In 3.7 M acrylonitrile, the values are 19 and 130 ps, respectively. If these quenching effects were due to chemical reactions between acrylonitrile and the biradical, the bimolecular rate constant would be 7–10 × 10^8 M^{-1} s^{-1}, which approaches the diffusion-limited encounter frequency. The reaction with **1T***, like that of **1T**,[16b] would be expected to be orders of magnitude slower because the concerted reaction is spin-forbidden, and as previous studies show,[16b] the stepwise reaction is 10^4 times slower than the diffusion-controlled encounter frequency. The very fast rate observed here is consistent with the formation of a charge-transfer complex between the diazene **3** and acrylonitrile, which is indicated in the static absorption spectrum by the diminution in intensity of the n → π* band at 343 nm and the appearance of a new band near 380 nm.

Of the several conceivable pathways that might deplete the **1S*** species in the absence of trapping agents, we consider one of the most likely contributors to be ISC to **1T***, analogous to the previously observed[4,6] ground state ISC (**1S** → **1T**). From the previous experiments[4,17] which indicate an Arrhenius preexponential term of $10^{9.6}$ s^{-1} and an activation energy near zero for ground-state ISC, a lifetime for the **1S** → **1T** reaction of about 250 ps may be estimated. If the 280-ps lifetime of **1S*** consists mainly of the reaction **1S*** → **1T***, the near correspondence in **1S** → **1T** and **1S*** → **1T*** lifetimes would be in agreement with theoretical considerations,[9] which suggest that the ground-state and excited-state singlet–triplet energy separations and vibronic couplings are similar.

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(11) Control experiments show that the transient fluorescence does not arise from the solvent. However, the peak at 625 nm (Figure 2) was found to be a function of the history of the sample. This emission peak was not detected by the streak camera and is not included in the kinetic data.

(12) Although barely feasible on energetic grounds, single-photon production of **1S*** from **3** is improbable. This would lead to identical emission spectra under laser and CW conditions. Also, it would be expected to result in different products from pyrolysis and photolysis of **3**, which would involve intermediates **1S** and **1S***, respectively. These requirements are at variance with experiment (see Figure 2 and ref 4 and 13).

(13) Corwin, L. R.; McDaniel, D. M.; Bushby, R. J.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 276.

(14) In the limit of low laser flux, the fluorescence intensity would be proportional to the square of the laser intensity, but the low extinction coefficient of **3**, in combination with the high extinction coefficient of **1S**, makes it likely that the **1S** → **1S*** transition will be saturated at the flux levels involved (~4 GW/cm^2). This would produce an approximately linear response, as is observed experimentally.

(15) It must be noted that, although the laser-induced spectrum is wavelength normalized, the streak camera is much more sensitive in the UV than in the visible range. This explains the relative intensities observed in the kinetic measurements. The spectral response of the fluorimeter is fairly flat from 350 to about 450–500 nm, after which the sensitivity drops off significantly.

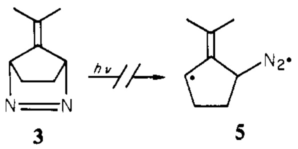
(16) (a) Turro, N. J.; Mirbach, M. J.; Harrit, N.; Berson, J. A.; Platz, M. S. *J. Am. Chem. Soc.* **1978**, *100*, 7653. (b) Platz, M. S.; Berson, J. A. *Ibid.* **1980**, *102*, 2358.

(17) Pinhas, A.; Schmidt, S. P.; Platz, M. S.; Mazur, M. R.; Hammons, J. H.; Berson, J. A., unpublished results.

A second possibility is internal conversion to the lowest singlet state. However, the 280-ps lifetime increases to ~900 ps at 77 K. Since the rate of internal conversion is expected to be approximately temperature independent, this process probably makes only a small contribution to the total quenching rate.

Other possible pathways that cannot yet be ruled out include direct ring-closure, **1S*** → *ground-state* **2**, and ring-opening, **1S*** → 3-isopropylidenepenta-1,4-diene.

Although an excited diazenyl biradical **5***, derived by cleavage of only one bond of **3**, might be compatible with the 280-ps lifetime, independent chemical evidence[18] opposes such an intermediate in the photolysis of **3**.



3 **5**

Because of the methyl and methylene substituents in **1S**, the main *absorption* maximum should lie slightly to the red of 289 nm, predicted theoretically[8] for the $S \rightarrow S^*$ (${}^1E' \rightarrow {}^1A_1$) transition of the parent trimethylenemethane singlet. Although we have not yet observed the absorption spectrum of **1S** directly, the observed fluorescence maximum at 430 nm, ~60 nm beyond the onset of the band progression (Figure 2), and the assumption of the absorption and fluorescence spectra[9b] mirror-image relationship are in agreement with theoretical predictions[8] of an absorption band near 300 nm.

Registry No. 1, 32553-01-8; **2**, 72447-89-3; **3**, 31689-32-4.

Supplementary Material Available: Experimental details (1 page). Ordering information is given on any current masthead page.

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[18] (a) Cichra, D. A.; Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 8507. (b) Cichra, D. A.; Duncan, C. D.; Berson, J. A. *Ibid.* **1980**, *102*, 6527.

S_N2 Displacements at 2-Norbornyl Brosylates

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Inverting nucleophile displacements at 2-norbonyl derivatives are rare,[1] and none of the recorded examples has been studied kinetically. The reluctance of *exo*-2-norbornyl derivaties to undergo S_N2 displacements[2,3] has been discussed in terms of steric hindrance to endo attack by nucleophiles[1c,2,5] but is also explicable by the high rate of unimolecular ionization. Quantitative data are required to solve this problem. We report that S_N2 displacements by azide ion at *exo*- and *endo*-2-norbornyl brosylates proceed at similar rates which indicate substantial (though not excessive) steric hindrance.

Scheme I

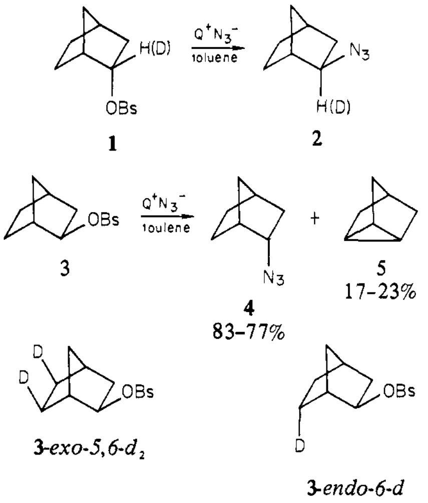

Table I. Second-Order Rate Constants for Alkyl Azide Formation from Alkyl Brosylates and Tributylhexadecylphosphonium Azide ($Q^+N_3^-$) in Toluene

ROBs	run no.	temp., °C	$[ROBs]_0$, M	$[Q^+N_3^-]_0$, M	elim, %	10^3k, M s^{-1}
1	1	65	0.02	0.025		2.17 ± 0.08[c]
	2	65	0.04	0.025		2.10 ± 0.06
	3	65	0.02	0.05		1.54 ± 0.06
	4	65	0.02	0.025[a]		1.50 ± 0.04
	5	65	0.02	0.0125		2.67 ± 0.13
	6	40	0.02	0.025		0.151 ± 0.007
		27.5[b]	0.02	0.025		0.034
2	7	65	0.02	0.025	17	1.90 ± 0.05
	8	65	0.02	0.05	10	1.50 ± 0.04
	9	40	0.02	0.025	23	0.101 ± 0.002
		27.5[b]	0.02	0.025		0.019
6	10	40	0.02	0.025	5	5.75 ± 0.15
	11	27.5	0.02	0.025	7	1.33 ± 0.05
7	12	27.5	0.02	0.025		74.6 ± 1.7
8	13	27.5	0.02	0.025		3.46 ± 0.07
9	14	27.5	0.02	0.025	6	16.3 ± 0.6

[a] Q^+OTs^- (0.025 M) added. [b] Calculated from data at higher temperatures. [c] Errors are standard deviations from a least-squares treatment. The results of duplicate runs agreed within these limits.

The reactions of *endo*-2-norbornyl brosylate (**1**) (Scheme I) with tributylhexadecylphosphonium azide[7] ($Q^+N_3^-$) in toluene at 40–65 °C afforded >97% of *exo*-2-norbornyl azide (**2**).[8] The analogous treatment of the deuterated brosylate **1**-d_2 did not lead to scrambling of the label (${}^2H$ NMR), thus excluding the intervention of 2-norbornyl cations. Rates were measured by quantitative IR analysis of the 2-norbornyl azide **2**.[9] Second-order kinetics, rate = $k[\mathbf{1}][Q^+N_3^-]$, were followed beyond 80% conversion. The rate constants (Table I) were independent of the initial concentration of **1** (runs 1 and 2) but decreased with increasing concentration of $Q^+N_3^-$ (runs 1, 3, and 5). Addition of

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[1] (a) Cristol, S. J.; Brindell, G. D. *J. Am. Chem. Soc.* **1954**, *76*, 5699. (b) Nickon, A.; Hammons, J. H. *Ibid.* **1964**, *86*, 3322. (c) Schaefer, J. P.; Weinberg, D. S. *J. Org. Chem.* **1965**, *30*, 2635, 2639. (d) Tanigawa, Y.; Kanamaru, H.; Murahashi, S. I. *Tetrahedron Lett.* **1975**, 4655. (e) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669. *Tetrahedron* **1979**, *35*, 5671. (f) Fischer, W.; Grob, C. A.; von Sprecher, G. *Helv. Chim. Acta* **1980**, *63*, 806.

[2] Grob, C. A.; Lutz, E. *Helv. Chim. Acta* **1981**, *64*, 153.

[3] *endo*-2-Norbornyl derivaties are more susceptible to inverting displacement;[1b,c,f] even the solvolyses of *endo*-2-norbornyl tosylate appear to be weakly solvent assisted.[4]

[4] (a) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1952**, *74*, 1147, 1154. (b) Harris, J. M.; Mount, D. L.; Raber, D. J. *Ibid.* **1978**, *100*, 3139. (c) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5466.

[5] Steric hindrance to ionization has been invoked to explain the high solvolytic exo:endo rate ratios of 2-norbornyl derivatives.[6]

[6] Brown, H. C. "The Nonclassical Ion Problem", with comments by P. v. R. Schleyer; Plenum, New York, 1977; Chapter 8.

[7] Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796. *Nouv. J. Chim.* **1979**, *3*, 575. We obtained $Q^+N_3^-$ by repeated exchange of Q^+Br^- in ether with 4 M NaN_3 in water. The residual Q^+Br^- was <1%.

[8] We have not been able to separate *exo*- and *endo*-2-norbornyl azide by VPC. Configurations were assigned by NMR (2-H of **2**: br t, J = 4–6 Hz, at δ 3.44; 2-H of **4**: dt, J = 10 and 4 Hz, at δ 3.89) and by catalytic hydrogenation (PtO_2 toluene). The azide obtained from **1** gave 97.8% of *exo*- and 2.2% of *endo*-2-norbornylamine. With the azide obtained from **3**, the exo:endo ratio of the amines was 2.6:97.4.

[9] The absorption of alkyl azides at 2100 cm^{-1} was sufficiently resolved from the absorption of $Q^+N_3^-$ at 2000 cm^{-1}. Calibration curves of the pure alkyl azides were established in the presence of the appropriate concentration of $Q^+N_3^-$ to account for an eventual overlap of the absorption bands.

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