Table I. Solvolysis of 1-Methoxy-*endo*-2-norbornyl Brosylate (**6b**)

Solvent	[ROBs] × 10^2 *M*	[Salt] × 10^2 *M*	Temp, °C	Time, hr	Products, rel %[a] 9	10	5
HOAc	5.10	9.20[b]	105	22	88.4	7.4	4.2[c]
CF_3CO_2H	2.71	58.0[d]	115	13	95.0	5.0	
60% aq acetone	1.66	6.20[e]	125	3	82.4	8.8	8.8[f]

[a] No elimination products (<0.1%) were detected. [b] Potassium acetate. [c] *exo*-Acetate **5c**. [d] Sodium trifluoroacetate. [e] Sodium bicarbonate. [f] *exo*-Alcohol **5a**.

each was identified by direct spectroscopic comparison with authentic samples.[11]

Formation of norbornan-2-one (**9**) from the *exo*-brosylate (**5b**) is understandable since rearrangement of the C_1–C_6 bond produces a 2-methoxy-2-norbornyl cation, which, from earlier work, is expected to be favored.[6,12] The rearranged system (**7**) would provide ketone **9** on hydrolytic work-up.

In acetolysis of *endo*-brosylate **6b** the 1-methoxy-*exo*-2-norbornyl acetate **5c** is presumably derivable by direct nucleophilic attack on the covalent substrate or on an intermediate C-2 cation. Importantly, the formation of both norbornan-2-one (**9**) and bicyclo[3.1.1]heptan-2-one (**10**) indicates a competition between C-6 and C-7 migration at some stage. That no ring-contracted product is formed in solvolysis of the *exo*-brosylate **5b** (or in solvolysis of the parent *endo*-2-norbornyl brosylate[2]) suggests that at least for a fraction of molecules of **6b** the C-7 bridge migrates before the *endo* group has fully departed.[13]

Solvolysis rates for **5b** and **6b** in HOAc–excess KOAc were measured spectrophotometrically[14] and are summarized in Table II along with data for the parent norbornyl analogs determined under the same conditions. The last column in Table II lists relative *ionization* rates, which were obtained by correction for known internal return (k_α/k_t = 4.6[15]) in *exo*-2-norbornyl brosylate. No such corrections are made for the 1-methoxynorbornyl substrates because internal return after Wagner–Meerwein rearrangement would produce α-methoxy brosylates (**7** and **8**), which would be expected to ionize exceedingly more rapidly than the starting brosylates.

Table II. Rates of Solvolysis of Substituted Norbornyl Brosylates in HOAc–KOAc

Norbornyl brosylate	Temp, °C	*k* × 10^6, sec^{-1} [a]	Rel rates at 25° Solvolysis	Ionization
exo-2	(25.0)[b]	9.02	348	1600
exo-2	28.0	13.2 ± 0.2[c]		
exo-2	49.9	172 ± 1		
1-Methoxy-*exo*-2	(25.0)[b]	7.24	279	279
1-Methoxy-*exo*-2	28.0	10.8 ± 0.2[d]		
1-Methoxy-*exo*-2	49.9	160 ± 2		
endo-2	(25.0)[b]	0.0259	1.00	1.00
endo-2	80.0	27.5 ± 0.3[e]		
1-Methoxy-*endo*-2	(25.0)[b]	0.000737	0.0285	0.0285
1-Methoxy-*endo*-2	80.0	1.24 ± 0.01[f]		
1-Methoxy-*endo*-2	100.0	10.8 ± 0.2		

[a] Mean value from two or three runs. [b] Calculated. [c] $\Delta H^\ddagger$ = 22.1 kcal/mol; $\Delta S^\ddagger$ = −3.1 eu, in agreement with reported values (see ref 15b). [d] $\Delta H^\ddagger$ = 23.2 kcal/mol; $\Delta S^\ddagger$ = +0.25 eu. [e] Reported $\Delta H^\ddagger$ = 26.0 kcal/mol; $\Delta S^\ddagger$ = −1.5 eu for unbuffered acetic acid (ref 15b). [f] $\Delta H^\ddagger$ = 27.6 kcal/mol; $\Delta S^\ddagger$ = −3.1 eu.

Interpretation of the rate data is not attempted here, however it is noteworthy that the 1-methoxy retards ionization of an *exo*-2-brosylate by a factor of 5.7 and of an *endo*-2-brosylate by a factor of 35. This retardation on the *exo*-2 system is less than the retardations that have been observed when a methoxy is located more remotely on the norbornane skeleton.[16] Evidently some factor is partially compensating for inductive withdrawal[17] by a 1-methoxy for an *exo* departing group.[18]

---

that the acetate product was entirely *exo* by reduction with $LiAlH_4$ to give *exo*-alcohol **5a** exclusively (<0.1% **6a**).

(11) We are grateful to Drs. W. Kirmse, H. Musso, and K. Grychtol for authentic bicyclo[3.1.1]heptan-2-one, whose ir and nmr were identical with those of our **10**.

(12) T. G. Traylor and C. L. Perrin, *J. Amer. Chem. Soc.*, **88**, 4934 (1966).

(13) In terms of bridged ions facile leakage from a C-7 σ-bridged ion to a C-6 σ-bridged ion would account for both skeletons. Reverse leakage is excluded by the results with the *exo*-brosylate **5b**.

(14) G. C. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

(15) (a) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, **87**, 376 (1965); (b) E. Clippinger, Ph.D. Thesis, University of California, Los Angeles, Calif., 1955.

(16) (a) P. J. Stang and P. von R. Schleyer, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts P 192; (b) the results of Professor Schleyer's kinetic studies are being separately submitted for publication.

(17) (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, p 113; (b) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

(18) Contrast the effects of a 1-cyano group in 2-apobornyl and 2-apoisobornyl systems. R. Muneyuki and T. Yano, *J. Amer. Chem. Soc.*, **92**, 747 (1970).

Yang-i Lin, Alex Nickon
Department of Chemistry, The Johns Hopkins University
Baltimore, Maryland 21218

Received February 24, 1970

Mechanisms of Photochemical Reactions in Solution. LXIII.[1] A 1,2- and 1,3-Benzyl Group Migration in Compounds Containing Phenyl and Conjugated Dienyl Chromophores

Sir:

As a continuation of our interest in the photochemistry of compounds containing two nonconjugated chromophoric units,[2] we wish to report the novel photochemical behavior of some 7-phenyl-2,4-heptadienes (**1**).

The dienes **1a–c** (Chart I) were synthesized by adding the Wittig reagent prepared from (2-methyl-2-butenyl)-triphenylphosphonium chloride to the appropriate aldehyde or ketone. Irradiation of *cis–trans* mixtures of the hydrocarbons in hexane solution with a low-pressure mercury lamp resulted in smooth conversion to a mixture containing 36–44% **2a–c** and 56–64% *cis*- and *trans*-**3a–c**.[3a] The 1,4-dienes, **2**, could be readily separated from the substituted vinylcyclopropanes **3** by preparative vapor chromatography.[3b] The structures of the 1,4-dienes are apparent from their spectra. Each contains a phenyl group and two olefinic units (nmr) which are not conjugated either to each other or to the phenyl group (ultraviolet). The 2-methyl-

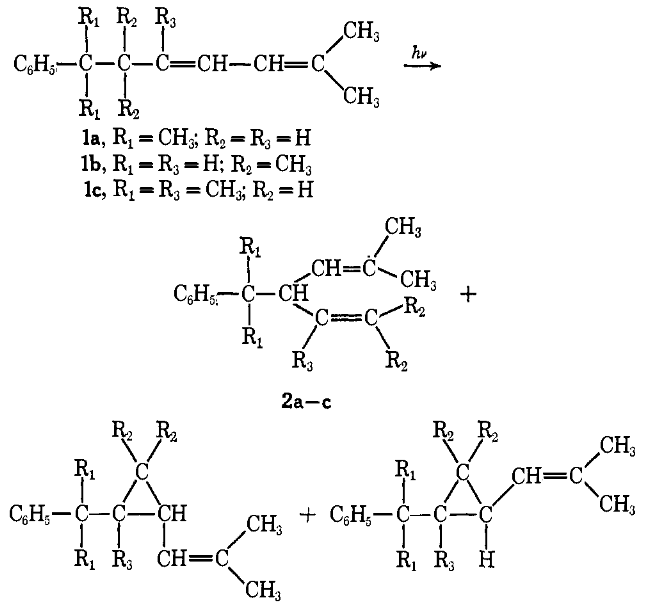
---

(1) Part LXII: R. S. Cooke and G. S. Hammond, *J. Amer. Chem. Soc.*, **92**, 2739 (1970).

(2) H. Kristinsson and G. S. Hammond, *ibid.*, **89**, 5968 (1967).

(3) (a) Satisfactory elemental analysis was obtained for all new compounds. (b) The column used was a 10 ft × 3/8 in. Carbowax 20 M (15%) on 60–80 mesh Chromosorb W, at 150°.

Chart I



1a, $R_1 = CH_3$; $R_2 = R_3 = H$
1b, $R_1 = R_3 = H$; $R_2 = CH_3$
1c, $R_1 = R_3 = CH_3$; $R_2 = H$

2a–c

trans-**3a–c** *cis*-**3a–c**

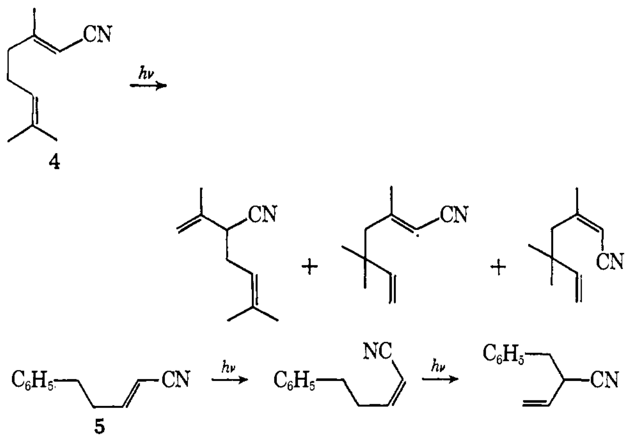
propenyl unit is evident in each compound (nmr). Other features of the nmr spectra are entirely consistent with the structures **2a–c**.

cis and *trans* isomers of **3b,c** were separated by preparative vapor chromatography. We were unable to separate stereoisomeric forms of **3a**. Compounds **3a–c** all contain the 2-methylpropenyl group (nmr) unconjugated with the phenyl ring (uv). The nmr spectra of both *cis*- and *trans*-**3b** contain methylene doublets, pairs of singlets for the ring methyl groups, and high-field multiplets for the ring hydrogen atoms. *cis*- and *trans*-**3c** and the mixture of *cis*- and *trans*-**3a** each show resonances due to the benzylic *gem*-dimethyl groups as well as high-field signals attributed to the ring hydrogens. In addition, *cis*- and *trans*-**3c** each show a high-field singlet due to the methyl substituents attached to the three-membered rings. The nmr spectral data have been deposited with the ASIS National Auxiliary Publications Service.[4]

Formation of **2** requires 1,3 migration of a benzylic group and stereoisomeric forms of **3** clearly come from 1,2 shifts of the same group. Indications are that both reactions occur from the lowest singlet excited state of the system because triplet sensitizers such as acetone and acetophenone do not effect the reaction. The rearrangements proceed smoothly in benzene solution under conditions such that the solvent absorbs nearly all of the light. This indicates that the reactions involve the lowest, benzene-like singlets, rather than higher diene-like states, since the former lie at sufficiently low energy to be produced by energy transfer from excited benzene singlets. Triplet energy transfer from benzene might occur, but is unlikely to be responsible for the skeletol rearrangement since other triplet sensitizers do not produce this change. The reactions are clearly reminiscent of the group of reactions referred to as "di-π-methane rearrangements," yet the formal requirements are not met, since the migrating group is attached to the unsaturated system across which it moves by a saturated center. Furthermore, the study of di-π-methanes has not yet produced examples of the 1,3 shift required to give **2a–c**.

Consideration of the reactions raises some interesting questions. Woodward and Hoffmann[5] suggested selection rules for concerted photochemical rearrangements of the lowest π,π* excited states of conjugated polyenes. According to those rules the 1,3 shift is an allowed, suprafacial process. The same rules do not, however, lead to the prediction that concerted 1,3 and 1,2 shifts should be competitive in the same system with the same stereochemistry. Since we have no stereochemical marker for the reactions observed we cannot comment on the possibility that the two reactions take independent paths. Similarly, the analysis of Zimmerman and Mariano,[6] based on the notion that the conversion of an excited state to a ground state transforms a Möbius system to a Hückel system, does not shed light on the competitive processes except to predict that they will be fundamentally different in character.

Cookson, *et al.*,[7] have studied both thermal and photochemical rearrangements of biallylic systems. In the photoprocesses, 1,3 shifts have been observed although in compound **4** both inversion and retention of the structure of the migrating allyl group were observed.



4

5

An interesting feature of the systems that we have studied in this and earlier work[2] is the fact that the principal locus of electronic excitation in the state undergoing rearrangement is believed to be the migrating group. This feature is also shown by Zimmerman's examples and perhaps by compound **5**. In compound **4**, operational definition of migrating group is ambiguous. At first glance, it appears that analysis of the systems along the lines of ref 5 may be inappropriate since reference is explicitly made to excitation of the other part of the system. However, we doubt that the localized excitation model is valid. The absorption spectra of **1a–c**, as was the case with arenedienes earlier,[2] resemble those expected from addition of the contributions of individual chromophoric units but show evidence of weak interaction even in the absorption process. Furthermore, the fact that **1a–c** do not show measurable fluorescence, as would be expected

---

[4] Obtainable as document NAPS-00980 from CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. Advance payment (payable to CCMIC–NAPS) is required: $1.00 for microfiche; $3.00 for photocopies.

[5] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 87, 2511 (1965).

[6] H. E. Zimmerman and P. S. Mariano, *ibid.*, **91**, 1718 (1969), and references cited therein.

[7] (a) R. C. Cookson, U. N. Gogte, J. Hudec, and N. A. Mirza, *Tetrahedron Lett.*, 3955 (1965); (b) R. F. C. Brown, R. C. Cookson, and J. Hudec, *Tetrahedron*, 24, 3955 (1968); R. C. Cookson, *Quart. Rev. Chem. Soc.*, 22, 423 (1968).

of alkylbenzenes, indicates that decay of the arene-like excited state is considerably accelerated by the presence of the diene unit. We believe that the two chromophoric units are coupled in the lowest excited states and that molecular rearrangement is one of the paths by which electronic excitation is dissipated through the diene structure. We also suspect that the chemical reactions are related to the bimolecular quenching of fluorescence of aromatic compounds by dienes.[8]

Two other possibilities for the formation of **3** are immediately evident. Firstly, the divinylmethanes **2**, formed in a primary photochemical process, could rearrange through a secondary process to give vinylcyclopropanes.[6] This possibility was eliminated by our inability to effect any rearrangement of **3c**, either under direct irradiation in hexane or benzene solution, or with high-energy triplet sensitizers. Secondly, vinylcyclopropanes could conceivably arise from a 1,2-hydrogen atom migration. However, this process is impossible in **1b**, and the nmr spectrum of **1c**, which contains neither a methylene doublet nor a ring methyl doublet, clearly eliminates this pathway for **1c**.

The geometrical isomers of **1** are not easily separated by vapor chromatography.[9] Partial separation of the *cis–trans* isomers of **1c** has been achieved. In this case, isomerization of the diene unit proceeds more rapidly than rearrangement to **2c** and **3c**. As yet, we have neither determined quantum yields for the various processes, nor determined if **2** and **3** are formed with equal facility from both *cis* and *trans* isomers of **1**. *cis*-**3c** and *trans*-**3c** readily interconvert under reaction conditions or upon triplet sensitization. By starting with isomerically pure **1c** and carrying the reaction to low conversions, we hope to determine the stereospecificity of vinylcyclopropane formation.

Acknowledgment. This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Contract No. AF 49(638)-1479, and the National Research Council of Canada.

---

(8) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

(9) *cis–trans* isomers of **1a,b** are evident from the nmr spectra of the dienes.

Emerson C. Sanford, George S. Hammond
Contribution No. 4004, Gates and Crellin Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91109

Received January 22, 1970

Mechanisms of Excited State Deactivation. Quenching of Excited Singlets by Nucleophiles

Sir:

Excited states frequently have much shorter lifetimes in solution than in the gas phase or in rigid media. In addition to energy transfer and relaxation processes, several types of excited state solute and excited state solvent interactions including complex formation,[1] hydrogen abstraction,[2] reversible addition,[3] and electron transfer[4] have recently been reported. In the present communication we report the quenching of fluorescence of several electron-deficient compounds by a variety of nucleophiles. This quenching apparently is caused by addition of nucleophiles to excited singlet states; attack by nucleophiles may lead to addition products but in many cases addition followed by elimination simply provides a mechanism for radiationless deactivation.

Typical of compounds whose excited singlets react with nucleophiles are quaternary salts of nitrogen heterocycles such as acridine, the 1,2-bispyridylethylenes, and stilbazoles as well as polar, neutral molecules such as riboflavin. Representative data for quenching of fluorescence of methylacridinium fluoroborate (MAFB) (**1**), the dimethylfluoroborate of 1,2-bis(4-pyridyl)ethylene (4,4′-BPE-DMFB) (**2**), and riboflavin by nucleophiles are listed in Table I. Quenching rate constants are correlated fairly well (correlation coefficients 0.991 for **1** and 0.990 for **2**) with the two-parameter Edwards equation[5] for nucleophilicity

$$\log k_{\mathrm{N}}/k_{\mathrm{W}} = \alpha E_{\mathrm{n}} + \beta \mathrm{H}$$

Substrate parameters for **1** are $\alpha = 2.17 \pm 0.15$ and $\beta = -0.125 \pm 0.053$; those for **2** are $\alpha = 0.960 \pm 0.078$ and $\beta = -0.0150 \pm 0.017$. These are not very different from those for organic substrates in nucleophilic displacements.[6] Quenching constants for **2** and the dimethiodide of 1,2-bis(3-pyridyl)ethylene (**3**) increase in the series *t*-butyl alcohol, water, and ethanol; this is the predicted order of nucleophilicity. This result, together with the Edwards equation correlation, suggests that the present phenomena cannot be accounted for by electron transfer. Evidence that fluorescence quenching by chloride ion is a consequence of nucleophilicity and not a heavy atom effect comes from our finding that 1-chlorobutane does not quench

Table I. Quenching of Fluorescence by Nucleophiles[a]

	4,4′-BPE-DMFB[b]		MAFB[c]		Riboflavin[d]
Nucleophile	$k_q\tau$, M^{-1} [e]	k_q/k_w	$k_q\tau$, M^{-1}	k_q/k_w	$k_q\tau$, M^{-1}
H_2O	0.19	1.0	0.04	1.0	
SO_4^{2-}	0.39	2.0	0.08	2.0	0.01
C_2H_5OH	0.4	2.1	0.14	3.6	0.02
NO_3^-			0.15	3.7	0.03
$C_2H_5OC_2H_5$	0.21	1.1	0.30	7.5	
$CH_3CO_2^-$	1.8	9.5	0.39	9.7	0.08
$ClCH_2CO_2^-$			2.2	56	0.46
C_5H_5N	3.0	16			
Cl^-	3.4	18	67	1700	0.68
n-C_4H_9Cl	0.00	0.0	0.00	0.0	
SCN^-					104[f]

[a] Measured on a Hitachi Perkin-Elmer MPF-2A. Solutions degassed by bubbling with argon or by the freeze–pump–thaw method. Fluorescence of 4,4′-BPE-DMFB and MAFB was measured in acetonitrile or 90% water–10% acetonitrile by volume, and $k_q\tau$ values were corrected for competitive water quenching. [b] λ_{ex} = 313 nm. [c] λ_{ex} = 403 nm. [d] Measured in water; λ_{ex} = 468 nm. [e] The product, $k_q\tau$ (k_q is the rate constant for quenching and τ is the fluorescence lifetime), was obtained from the slope of a Stern–Volmer plot. [f] Slight ground-state reaction was observed. No new fluorescence was observed in the presence of any quencher studied.

---

(1) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).

(2) See, for example, P. J. Wagner and A. Kemppainen, *J. Amer. Chem. Soc.*, **90**, 5896 (1968).

(3) J. Saltiel, K. R. Neuberger, and M. Wrighton, *ibid.*, **91**, 3658 (1969); J. Saltiel, *et al.*, *ibid.*, **92**, 411 (1970).

(4) N. J. Turro and R. Engel, *ibid.*, **91**, 7113 (1969); *Mol. Photochem.*, **1**, 143 (1969).

(5) J. O. Edwards, *J. Amer. Chem. Soc.*, **76**, 1540 (1954); *ibid.*, **78**, 1819 (1956).

(6) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 254.