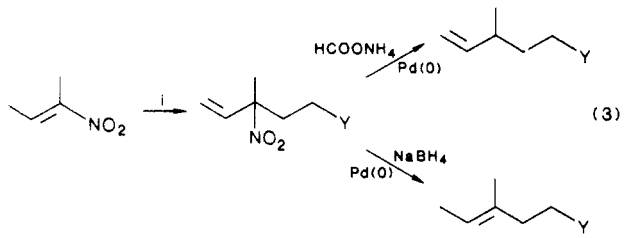
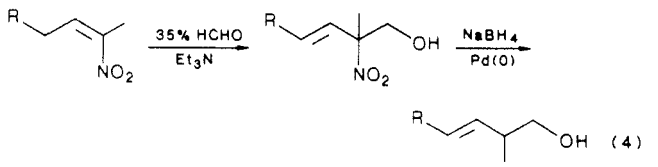
an activating group for carbon–carbon bond-forming reactions. Since the carbanions of allylic nitro compounds are produced from nitroolefins, the present denitration provides a useful synthetic methods. For example, 2-nitro-2-butene reacted with electron-deficient olefins in the presence of tetramethylguanidine (TMG, 0.1 equiv) to give the allylic nitro compounds, which were converted into 1-alkenes or 2-alkenes, respectively, as shown in entries 5–8.



Y = COOMe, CN, SO_2Ph
(i) CH_2=CHY, TMG (0.1 equiv), rt, 24 h

Base-catalyzed reaction of nitroolefins with aldehydes followed by denitration provides a new synthetic method of homoallyl alcohols (Table II). The reaction of nitroolefins with aldehydes was carried out by stirring a mixture of nitroolefins, 37% HCHO, and triethylamine (0.1 equiv) in acetonitrile at 20 °C for 15 h. Hydroxymethylated allylic nitro compounds were obtained in 80–90% yield by this procedure. Denitration was carried out by stirring a mixture of allylic nitro compounds, $NaBH_4$ (1.2 equiv), $Pd(PPh_3)_4$ (5 mol %), and PPh_3 (10 mol %) in THF–*i*-PrOH (1/1) at 0 °C for 5 h. When the reaction was carried out at 20 °C (entry 14) or dppe was used instead of PPh_3 (entry 13), the selectivity of the formation of homoallylic alcohols was poor. The results are summarized in Table II.



Registry No. 1, 83659-69-2; 2, 81769-17-7; 3, 103621-19-8; 4, 103621-20-1; 5, 103621-21-2; 6, 103621-22-3; 7, 103621-23-4; 8, 103621-24-5; 9, 103621-25-6; 10, 103621-26-7; $PhCH_2CH(CH_3)$-CH=CH_2, 1647-06-9; $PhCH_2C(CH_3)$=$CHCH_3$, 40296-93-3; H_2-C=$CHCH(CH_3)(CH_2)_2CO_2CH_3$, 90112-90-6; H_3CCH=$C(C$-$H_3)(CH_2)_2CO_2CH_3$, 97764-27-7; H_2C=$CHCH(CH_3)(CH_2)_2CN$, 100859-65-2; H_3CCH=$C(CH_3)(CH_2)_2CN$, 22117-92-6; H_2C=$CHCH(CH_3)(CH_2)_2SO_2Ph$, 103621-27-8; H_3CCH=$C(CH_3)$-$(CH_2)_2SO_2Ph$, 103621-28-9; (*E*)-$H_3CCH_2C(CH_3)$=$CHCO_2Et$, 13979-44-7; (*Z*)-$H_3CCH_2C(CH_3)$=$CHCO_2Et$, 13979-16-3; (*E*)-$EtO_2C(CH_2)_3C(CH_3)$=$CHCO_2Et$, 103621-29-0; (*Z*)-EtO_2-$(CH_2)_3C(CH_3)$=$CHCO_2Et$, 103621-30-3; H_2C=$C(CH_3)CH(C$-$H_2)_2CN(CH_2)_2COCH_3$, 103621-31-4; $H_3C(CH_2)_2CH$=$CHCH(C$-$H_3)CH_2OH$, 102877-67-8; $H_3C(CH_2)_3CH$=$C(CH_3)CH_2OH$, 37616-08-3; $H_3C(CH_2)_7CH$=$CHCH(CH_3)CH_2OH$, 103621-32-5; H_2C=$CHCH(CH_2OH)(CH_2)_3CH_3$, 53045-66-2; H_3CCH=$C(C$-$H_2OH)(CH_2)_3CH_3$, 21645-15-8; $H_3C(CH_2)_2CH$=$CHCH(NO_2)CH_3$, 103621-33-6; $H_3C(CH_2)_7CH$=$CHCH(NO_2)CH_3$, 103621-34-7; H_2C=$CHCH(NO_2)(CH_2)_3CH_3$, 103621-35-8.

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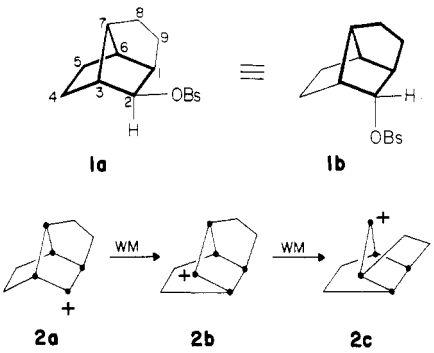
Ionization of 2-Brexyl Brosylate: An Exo-Like Rate without Symmetrical Bridging

Summary: 2-Brexyl brosylate and *exo*-norbornyl brosylate show similar ionization rates but differ markedly with respect to internal return, secondary isotope effect, and optical activity.

Sir: A central issue in norbornyl solvolyses is whether high exo/endo rate ratios stem largely from exalted exo or from suppressed endo rates.[1] Either view can be supported by judicious selection of reference standards.[1,2] In a brexane skeleton, a substituent at C-2 is simultaneously exo to one norbornyl unit and endo to another (note: **1a** is superposable on **1b**).[3] Therefore, whether **1** has the ionization character of an *exo*- or an *endo*-norbornyl derivative is of considerable interest. Like its norbornyl counterpart, a σ-bridged (i.e., nonclassical) 2-brexyl cation has a plane of symmetry and the localized (i.e., classical) structure (**2a**) is chiral. A degenerate Wagner-Meerwein (WM) rearrangement (**2a** ⇌ **2b**) converts the classical form to its mirror image. And repetitive WM (i.e., **2a** → **2b** → **2c** → etc.) alternates the chirality and can transfer the positive charge to every carbon of a core ring (shown by bold dots).



We recently developed an improved synthesis of brexan-2-one[4] and now report studies of buffered acetolysis of 2-brexyl brosylate (**1**), of its 2-deuterated analogue, and of its optically active form. The product acetates arise from two rearranged ions, viz. **3** and **4**. Consequently, it was essential to investigate also the exo and endo epimers of 4-brexyl brosylate (**5**) and of 2-brendyl brosylate (**6**).

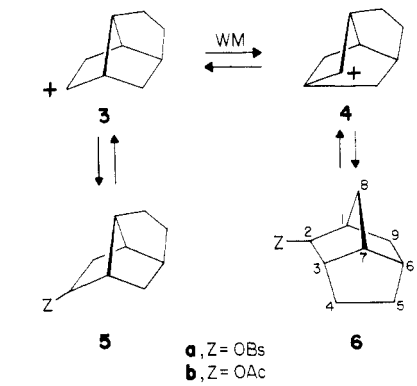


Table I summarizes our findings and also includes our own

(1) Recent reviews: (a) Barkhash, V. A. *Top. Curr. Chem.* **1984**, *116/117*, 1–265. (b) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426–431. (c) Brown, H. C. *Ibid.* **1983**, *16*, 432–440. (d) Olah, G. A.; Prakash, G. K. S.; Saunders, M. *Ibid.* **1983**, *16*, 440–448. (e) Walling, C. *Ibid.* **1983**, *16*, 448–454. (f) Kirmse, W. *Top. Curr. Chem.* **1979**, *80*, 125–331.

(2) Brown, H. C. *The Nonclassical Ion Problem*, with comments by Schleyer, P. v. R.; Plenum: New York, 1977; Chapter 8.

(3) Nickon, A.; Kwasnik, H. R.; Mathew, C. T.; Swartz, T. D.; Williams, R. O.; DiGiorgio, J. B. *J. Org. Chem.* **1978**, *43*, 3904–3916.

(4) Nickon, A.; Stern, A. G. *Tetrahedron Lett.* **1985**, *26*, 5915–5918.

0022-3263/86/1951-3736$01.50/0

Table I. Acetolysis of *p*-Bromobenzenesulfonates in HOAc/5 × 10^{-3} M KOAc at 24.9 °C[a]

brosylate	exo acetate ratio[b] **6b**/**5b**	k × 10^3 (min^{-1}) solvolysis	k × 10^3 (min^{-1}) ionization	ratio k_{ioniz}/k_{solv}	relative k_{ioniz} entire series	relative k_{ioniz} exo/endo epimers	relative k_{ioniz} exo series only	relative k_{ioniz} endo series only
2-brexyl (**1**)	1.17[c]	3.75[d]	9.40	2.5	566		0.37	566
exo-4-brexyl (*exo*-**5a**)	1.19	50.2[d]	178[e]	3.5[e]	10 720[e]	28 200[e]	6.9	
endo-4-brexyl (*endo*-**5a**)	1.07	6.27 × 10^{-3}[f]	6.27 × 10^{-3}[f]	1	0.38			0.38
exo-2-brendyl (*exo*-**6a**)	1.18	1.15[g]	1.15	1	69.2	1870	0.045	
endo-2-brendyl (*endo*-**6a**)	1.25	6.15 × 10^{-4}[f]	6.15 × 10^{-4}[f]	1	0.037			0.037
exo-norbornyl		5.59	25.7[h]	4.6[i]	1550	1550	1	
endo-norbornyl		1.66 × 10^{-2}[f]	1.66 × 10^{-2}[f]	1	1			1

[a] Measured spectrophotometrically (Swain, G. C.; Morgan, C. R. *J. Org. Chem.* **1964**, *29*, 2097–2098 and ref 19a). [b] The hydrocarbon deltacyclane (ref 3) was a minor product (0.5–6.4%) in all cases. [c] Also, 2-brexyl acetate was detected in minute amount (ca. 0.35%). [d] *Initial* solvolysis by analysis of the curved plot (ref 8). [e] This is a minimum value. It would increase by a factor of 1.6 if we presumed that internal return produces the rearranged brosylate (*exo*-**6a**) and the starting brosylate in the same capture ratio (1.19) as for the two acetates. Such "hidden" return to *exo*-**5a** has no observable kinetic effect. [f] Calculated from rates we measured at higher temperatures. [g] See ref 6 for an independent titrimetric measurement. [h] Computed from our k_{solv} and the factor 4.6 reported for k_{polar}/k_{solv} (ref 18). [i] Reference 18.

data for *exo*- and *endo*-norbornyl brosylates measured by the same experimental method.

Each tricyclic brosylate produced two acetate products, *exo*-**6b** and *exo*-**5b**, in virtually the same ratio (ca. 1.18, respectively).[5,6] On this basis, the ion (or ions) that capture solvent are the same from the five presursors.[7]

All brosylates obeyed first-order kinetics except **1** and *exo*-**5a**. Both of these gave curved plots corresponding to a rapid initial solvolysis and a final slower rate (identical with that of *exo*-**6a**) indicating ion-pair return. Analysis of the curved plots by an established method[8] permitted evaluation of the initial rate of acetate formation (k_{solv}), the total rate of disappearance of starting brosylate (k_{ioniz}), and the rate of skeletal isomerization to *exo*-6a (k_{isom}). Thus, for **1**, the tabulated k_{ioniz}/k_{solv} ratio of 2.5 means that 40% of the molecules proceed directly to acetates and 60% first rearrange to brosylate *exo*-**6a** before ultimately producing acetates.

We resolved brexan-2-ol[3] (α_D −164.5°) via the 3β-acetoxy-Δ^5-etienate ester[9] and converted the alcohol to its brosylate ((−)-**1**; α_D −88.5°) and to (−)-brexan-2-one (α_D −320°).[10] This ketone was rearranged via its homoenolate anion to (−)-brendan-2-one (α_D −51.5°), a route that preserves enantiomeric purity.[3,11,12] Solvolysis of (−)-**1** gave the two acetates, each with appreciable optical activity! The brendyl acetate (*exo*-**6b**) was transformed to (+)-brendan-2-one having 18.9% enantiomeric excess (i.e., 81.1% racemized). The sign of rotation (+) corresponds to preservation of absolute configuration[10,12] within the sequence **2a** → **3** → **4** → *exo*-**6b**.

A localized 2-brexyl cation (**2a**) has two opportunities to racemize, viz., by one (or more) WM rearrangements *prior* to the 4,2-H shift (**2a** → **3**) and again later by a symmetrizing 9,2-H shift in the 2-brendyl cation (**4**). To correct for racemization at the brendyl stage, we synthesized and solvolyzed *endo*-2d,*exo*-2-brendyl brosylate. The derived 2-brendyl acetate was separated and converted to brendan-2-one that contained 13% of the original deuterium, an amount that persists as a result of H shift[13] in the "brendyl" cation. This approximate correction to the solvolysis of (−)-**1** gives 25.5% as the minimum[14] proportion of 2-brexyl cations that manage to be diverted before a competing WM event can racemize them.

We also determined the rate of loss of optical activity for (−)-**1** and for its 2-deutero analogue. The respective first-order rate constants (k_{polar}) ((9.82 ± 0.03) × 10^{-3} and (8.02 ± 0.02) × 10^{-3} min^{-1}) correspond to a secondary isotope effect k_H/k_D of 1.22.[15]

Several important relationships emerge: (1) Kinetically, 2-brexyl brosylate (**1**) is clearly in the *exo*- and not in the *endo*-norbornyl category in terms of k_{ioniz}.[16] (2) The 25.5% residual optical activity demonstrates that for this σ-route to the 2-brexyl cation, at least one-fourth of the initially formed 2-brexyl cations undergo the chirality-preserving H shift before the skeleton achieves effective planar symmetry.[17] In the norbornyl series, where exo brosylate loses all optical activity, such a hydride shift does not preserve chirality but provides an additional path for racemization.[1f,18] (3) The close agreement between k_{polar} and k_{ioniz} for (−)-**1** establishes that little (if any) of the substrate undergoes ionization, WM, and return to starting brosylate. Contrast *exo*-norbornyl brosylate, where 78% of the R^+-OBs^- ion pairs return and thus scramble labels before the eventual journey to racemic acetate.[1f,18] (4) The isotope effect (1.22) for (−)-**1** is close to that reported for *endo*-norbornyl brosylate (1.20) but not for *exo*-norbornyl bro-

(5) See table footnote c.

(6) The π-route to the 2-brexyl cation likewise gives the same ratio of these acetates. Bly, R. S.; Bly, R. K.; Bedenbaugh, A. O.; Vail, O. R. *J. Am. Chem. Soc.* **1967**, *89*, 880–893.

(7) The slightly higher ratio from *endo*-**6a** and the slightly lower ratio from *endo*-**5a** are understandable in terms of a minor contribution by an S_N2- like component. Banert, K.; Kirmse, W. *J. Am. Chem. Soc.* **1982**, *104*, 3766–3767.

(8) Young, W. G.; Winstein, S.; Goering, H. L. *J. Am. Chem. Soc.* **1951**, *73*, 1958–1963.

(9) Djerassi, C.; Burakevich, J.; Chamberlin, J. W.; Elad, D.; Toda, T.; Stork, G. *J. Am. Chem. Soc.* **1964**, *86*, 465–471.

(10) Nakazaki et al. obtained (−)-brexan-2-one and (−)-brexan-2-ol by other routes and reported α_D −201° and −158°, respectively. Nakazaki, M.; Naemura, K.; Kadowaki, H. *J. Org. Chem.* **1976**, *41*, 3725–3730. A subsequent publication implied that the rotation of the ketone is 283°. Nakazaki, M.; Chikamatsu, H.; Naemura, K.; Nishino, M.; Murakami, H.; Asao, M. *J. Chem. Soc., Chem. Commun.* **1978**, 667–668.

(11) Nickon, A.; Kwasnik, H.; Swartz, T.; Williams, R. O.; DiGiorgio, J. B. *J. Am. Chem. Soc.* **1965**, *87*, 1615–1616.

(12) Prepared differently, (+)-brendan-2-one had α_D +31.3°. Nakazaki, M.; Naemura, K.; Kondo, Y. *J. Org. Chem.* **1979**, *44*, 16–20.

(13) In studies of the 2-brexyl cation generated by the π-route, Bly and co-workers concluded that no H shifts take place after the 2-brexyl ion has rearranged to the "brendyl" ion. Bly, R. S.; Bly, R. K.; Hamilton, J. B.: Jindal, S. P. *J. Am. Chem. Soc.* **1975**, *99*, 204–216. Bly, R. S.; Bly, R. K.; Hamilton, J. B.; Hsu, J. N. C.; Lillis, P. K. *Ibid.* **1975**, *99*, 216–223.

(14) It could be higher if (a) the brendyl cation **4** from (−)-**1** has any chance for 9,2-H shift before as well as after return to *exo*-**6a** or (b) favorable counterion location[6] enhances H-shift aptitude for that fraction (0.40) of **4** that goes directly to products.

(15) The small fraction of *optically active exo*-**6a** formed by internal return (0.60 × 25.5%) and its slower ionization relative to **1** (by a factor of ca. 8, see table) ensured first-order kinetics in k_{polar} through 3 half-lives.

(16) Under the same conditions in CCl_4, brexan-2-one, brexan-4-one, and norbornan-2-one all show ν(C=O) at 1751 ± 1 cm^{-1}; brendan-2-one is 1747 cm^{-1}.

(17) For conclusions about the nature of the 2-brexyl cation from the π-route, see ref 6, 13, and Collins, C. J. *J. Am. Chem. Soc.* **1979**, *101*, 1878–1880.

(18) Winstein, S.; Clippinger, E.; Howe, R.; Vogelfanger, E. *J. Am. Chem. Soc.* **1965**, *87*, 376–377.

sylate (1.12)[19] Our polarimetric value for (-)-1 is not plagued by label scrambling[20] and closely parallels the value (~1.22) usually ascribed to a "limiting" solvolysis.[1f,21]

Our optical activity results preclude symmetrical bridging as the primary basis for the exo-like rate. Nonbonded interactions and precise trajectories in U-shaped regions deserve close attention, as proposed by H. C. Brown.[22]

Acknowledgment. This research was supported by the National Science Foundation and the National Institutes of Health.

Registry No. (±)-1, 103478-21-3; (-)-1, 103478-22-4; (±)-*exo*-**5a**, 103531-56-2; (±-*endo*-**5a**, 103531-57-3; (±)-*exo*-**6a**, 103531-58-4; (±)-*endo*-**6a**, 103531-59-5; *exo*-**6b**, 61800-14-4; D_2, 7782-39-0; *endo*-2-norbornyl brosylate, 840-89-1.

Supplementary Material Available: Physical constants and spectral and analytical data for brosylates 1, *exo*-**5a**, *endo*-**5a**, *exo*-**6a**, and *endo*-**6a** (2 pages). Ordering information is given on any currrent masthead page.

(19) (a) Murr, B. L.; Conkling, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 3462-3464. (b) Lee, C. C.; Wong, E. W. C. *Can. J. Chem.* **1965**, *43*, 2254-2258.

(20) (a) Sunko, D. E.; Borčić, S. *Isotope Effects in Chemical Reactions*; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: New York, 1970; Chapter 3. (b) Scheppele, S. E. *Chem. Rev.* **1972**, *72*, 511-532.

(21) (a) Harris, J. M.; Hall, R. E.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 2551-2553. (b) Shiner, V. J., Jr.; Fisher, R. D. *Ibid.* **1971**, *93*, 2553-2554.

(22) Brown, H. C.; Rothberg, I.; Chandrasekharan, J. *J. Org. Chem.* **1985**, *50*, 5574-5577.

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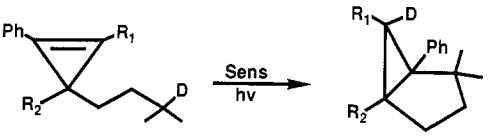
Deuterium Isotope Effects in the Intramolecular Hydrogen-Transfer Reactions of Some 1-Alkyl-Substituted Cyclopropenes

Summary: The photochemical behavior and deuterium isotope effect of a number of 1-alkyl-substituted cyclopropenes which contain a hydrogen atom in the γ-position of the side chain have been studied. The results are consistent with the Kwart proposal wherein nonlinear hydrogen-transfer reactions show temperature-independent isotope effects.

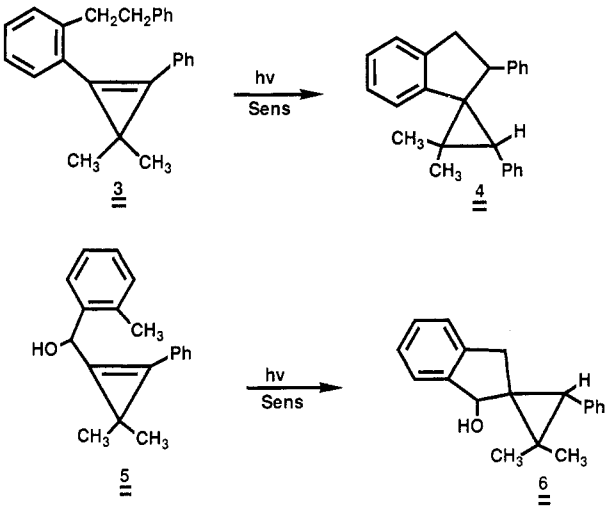
Sir: Triplet-sensitized irradiation of 3-alkyl-substituted cyclopropenes which possess γ-hydrogen leads to products involving intramolecular transfer from the side chain to the $\pi-\pi^*$ excited state of the alkene.[1-4] A mechanism involving a short-lived triplet biradical has been proposed,[2-4] having some relation to the n,π^* triplet process in the type II reaction of aralkyl ketones.[5] The magnitude of the primary isotope effect in the hydrogen-transfer reaction was found to be markedly dependent on the nature of the substituent groups attached to the double bond.[4] The symmetrically substituted diaryl isomer exhibited an isotope effect significantly larger than any previously reported value for hydrogen transfer to an excited state.[6]



1; R_1=Ph; R_2=CH_3 (k_H/k_D~20/1)
2; R_1=CH_3; R_2=Ph (k_H/k_D~3.5/1)

The present contribution addresses additional details of the hydrogen-transfer reaction with structurally related cyclopropenes. The hydrogen-transfer reaction is thought to proceed by way of a nonlinear six-membered transition state.

The triplet-sensitized photobehavior of **3** in benzene (thioxanthone) produced spirobenzocyclopentane **4** in 81% isolated yield (Φ = 0.26). The structure of **4** was based on its characteristic spectral data and was further supported by a single-crystal X-ray structure analysis.[7] With carbonyl compounds, efficient intramolecular abstraction of hydrogen requires that the C-H-bond axis be directed toward the half-vacant n orbital of the carbonyl oxygen atom.[8] With alkenes, 1,5-hydrogen shifts generally take place only when γ-hydrogen atoms are absent.[9] In the above case, however, photocyclization proceeds via a seven-membered transition state. Similar behavior was encountered with cyclopropene **5**. When the sensitized irradiation of **5** was carried out in benzene (thioxanthone), spirobenzocyclopentane **6** was obtained as the exclusive photoproduct in 85% isolated yield (Φ = 0.24) [NMR ($CDCl_3$, 360 MHz) δ 0.82 (s, 3 H), 0.87 (s, 3 H), 1.57 (s, 1 H), 1.90 (br s, 1 H), 3.19 (d, 1 H, J = 15.0 Hz), 3.25 (d, 1 H, J = 15.0 Hz), 4.95 (s, 1 H), 6.95-7.35 (m, 9 H)].



We have also studied the triplet-induced photobehavior of cyclopropenes **7** and **8**. The sensitized irradition of **7** produced the 2-methylpentenyl trans-substituted cyclopropane **9** in high yield (85%, Φ = 0.21) [NMR ($CDCl_3$,

(1) van Tamelen, E. E.; Whitesides, T. H. *J. Am. Chem. Soc.* **1971**, *93*, 6129.

(2) Padwa, A.; Chiacchio, U.; Hatanaka, N. *J. Am. Chem. Soc.* **1978**, *100*, 3928.

(3) Padwa, A.; Blacklock, T. J.; Chou, C. S.; Hatanaka, N. *J. Am. Chem. Soc.* **1979**, *101*, 5743.

(4) Padwa, A.; Chou, C. S.; Rosenthal, R. J.; Rubin, B. *J. Am. Chem. Soc.* **1981**, *103*, 3057.

(5) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(6) Coulson, D. R.; Yang, N. C. *J. Am. Chem. Soc.* **1966**, *88*, 4511.

(7) Compound 4 crystallizes in the monoclinic space group $P21/n$ with eight molecules per unit cell. The cell constants are a = 14.558 Å, b = 8.689 Å, c = 29.709 Å, and β = 90.86°. The unit cell is nearly orthorhombic. Further details will be reported in our full paper.

(8) Turro, N. J.; Weiss, D. S. *J. Am. Chem. Soc.* **1968**, *90*, 2185.

(9) Aoyama, H.; Inoue, Y.; Omote, Y. *J. Org. Chem.* **1981**, *46*, 1965; *J. Chem. Soc., Chem. Commun.* **1985**, 1381.

0022-3263/86/1951-3738$01.50/0