(above). One might even imagine this structure to be formed by a prior inversion of the thiacyclohexanone starting material to a boat form. Attractive as this possibility might appear, it is not the path the molecule chooses. Rather it reacts in the same manner as the tetraphenyl compound studied by the Oklahoma group.[8] The thiacyclohexanone remains in the chair form; the steric compression in the chair-chair product is avoided by forming the nitrogen-containing ring as a boat; the product (except for the unlikely change to a double boat) is conformationally rigid.

Acknowledgment. We are indebted to the National Science Foundation (Grant CHE80-20388) for financial support.

Registry No. 2c (Ar = C_6H_5; R = B = H; A = OH), 82918-33-0.

Supplementary Material Available: Tables S1 (bond lengths involving hydrogen atoms) and S2 (anisotropic thermal parameters) (2 pages). Ordering information is given on any current masthead page.

A Novel Photochemical [3 + 2] Cycloaddition of 3-Cyano-5,5-dimethyl-2-cyclohexenone to Olefins[1]

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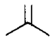
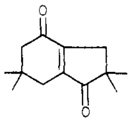
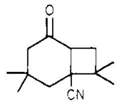
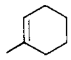
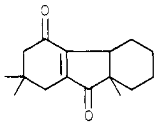
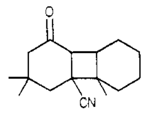
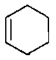
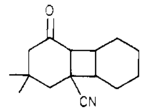
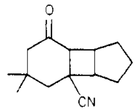
The inter- and intramolecular [2 + 2] photocycloaddition of cyclic enones to olefins has been the subject of synthetic and mechanistic investigations.[2] The intermediacy of enone triplet and subsequent 1,4-biradical formation are well-documented in many cases.[2,3] We have recently noted that cyano-substituted heterocycles such as 6-cyanouracils[4] and 2-cyanopyridine[5] undergo anomalous addition with olefins resulting in 1,4-transfer of cyano group or the formation of [3 + 2] adduct by interception of the intermediate biradicals by the cyano groups.[6] In further extending this study, we describe here a new temperature-dependent [3 + 2] photochemical cycloaddition of 3-cyanocylohexenone to olefins that competes with normal [2 + 2] cycloaddition.[7]

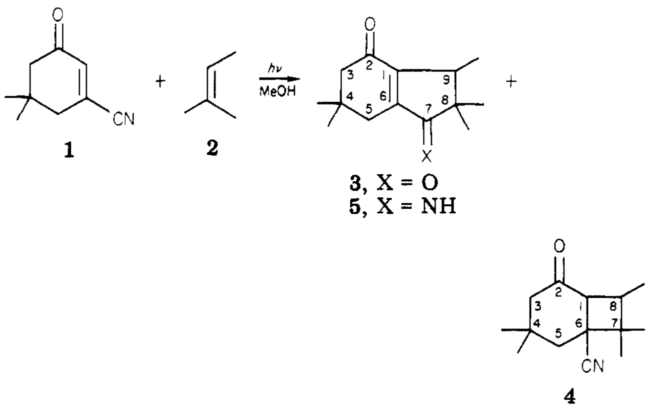
3-Cyano-5,5-dimethyl-2-cyclohexenone (**1**, 30 mM) was irradiated in methanol with a high-pressure mercury lamp (Pyrex filter) in the presence of 2-methyl-2-butene (**2**, 0.3 M) for 5 h at room temperature. Removal of the solvent followed by preparative TLC (silica gel, hexane-ethyl acetate) afforded two photoproducts **3** (35%) and **4** (30%).

Table I. Photoaddition of 3-Cyano-5,5-dimethyl-2-cyclohexenone (1) to Olefins[a]

no.	olefin	product (%)[b]	
1[c]		 **6** (38)	 **7** (46)
2		 **8** (35)	 **9** (30)
3		ND[d]	 **10** (80)
4		ND[d]	 **11** (75)

[a] Solutions of **1** (20 mM) and olefins (50 mM) in methanol were irradiated with a 100-W high-pressure mercury lamp (Pyrex filter) at room temperature under the standard conditions described in the Experimental Section. [b] Yields are for isolated pure products. [c] See the Experimental Section for reaction conditions. [d] Not detected.

The assigned structures are based on their spectral data. Support for the enedione structure of **3** is furnished by the low-field ^{13}C NMR signals (149.0, 159.9, 199.3, and 214.8 ppm), two carbonyl stretching bands (1710 and 1680 cm^{-1}) in the IR, and a UV absorption at 258 nm. The ^{1}H NMR showed a long-range coupling (J = 2.5 Hz) attributable to homoallylic coupling between the C-5 methylene group and the C-9 methine proton, indicating the orientation of the adduct **3**. The enedione **3** was formed from bicyclic imine **5** during workup. In fact, **5** was isolated by careful preparative high-performance liquid chromatography. Treatment of hydrolytically sensitive **5** with a catalyic amount of HCl immediately produced **3**. The orientation of the [2 + 2] cycloadduct **4** is apparent from the vicinal coupling (J = 10.5 Hz) between the C-1 and C-8 methine protons in the ^{1}H NMR spectrum. However, we were not confident in assigning the stereochemistry of **4**, although no change in the ^{1}H NMR resulted upon treatment of **4** with basic alumina, suggestive of the cis ring junction of **4**.[8]



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(1) Photoinduced Reactions. 140.

(2) (a) Eaton, P. E. *Acc. Chem. Res.* **1971**, *2*, 41. (b) Bauslaugh, P. G. *Synthesis* **1970**, 287. (c) de Mayo, P. *Acc. Chem. Res.* **1971**, *4*, 41. (d) Dilling, W. L. *Photochem. Photobiol.* **1977**, *25*, 605.

(3) For a recent example, see: Loutfy, R. O.; de Mayo, P. *J. Am. Chem. Soc.* **1977**, *99*, 3559 and references therein.

(4) (a) Saito, I.; Shimozono, K.; Matsuura, T. *J. Am. Chem. Soc.* **1980**, *102*, 3948. (b) Saito, I.; Shimozono, K.; Miyazaki, S.; Matsuura, T.; Fukuyama, T.; Katsube, Y. *Tetrahedron Lett.* **1980**, *21*, 2317.

(5) Saito, I.; Kanehira, K.; Shimozono, K.; Matsuura, T. *Tetrahedron Lett.* **1980**, *21*, 2737.

(6) Several recent examples for anomalous photoadditions involving rearrangement of 1,4-biradicals include the following: (a) Wolff, S.; Barany, F.; Agosta, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 2378. (b) Wagner, P. J.; Lin, K-C; Noguchi, Y. *Ibid.* **1981**, *103*, 3837. (c) Hussain, S.; Agosta, W. C. *Tetrahedron* **1981**, *37*, 3301.

(7) Photoaddition of 3-cyano-2-cyclohexenones with olefins and *tert*-butyl alcohol has previously been reported. (a) Agosta, W. C.; Lawrance, W. W., Jr. *J. Org. Chem.* **1970**, *35*, 3851. (b) Cantrell, T. S. *Tetrahedron* **1971**, *27*, 1227. (c) Kuemmerle, E. W., Jr.; Rettig, T. A.; Still, J. K. *J. Org. Chem.* **1975**, *40*, 3665.

(8) Corey, E. J.; Le Mahieu, R.; Bass, J. D.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

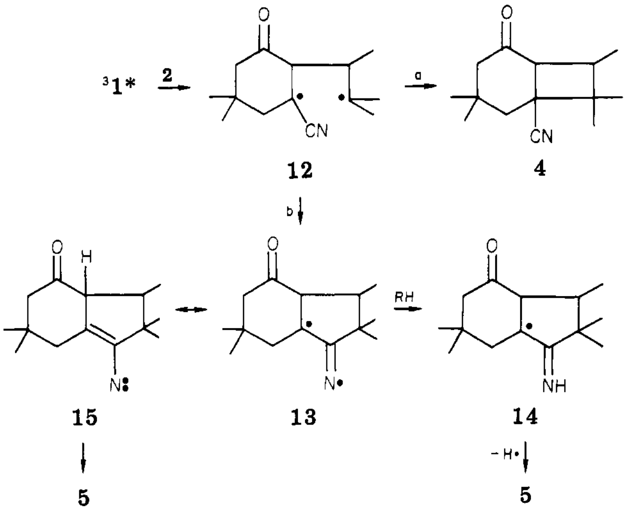
0022-3263/82/1947-4356$01.25/0

Table II. Photoaddition of 1 to 1-Methylcyclohexene at Various Temperatures[a]

temp, °C	product yield,[b] % 8	9
−78	10	40
−20	22	35
20	35	30
65	45	22

[a] All reactions were carried out in methanol containing 1 (20 mM) and 1-methylcyclohexenone (50 mM).
[b] Yields for isolated products.

Scheme I



Irradiation of 1 with other olefins under similar conditions gave the corresponding enediones in competition with cyclobutane formation as summarized in Table I. Irradiation of 1 with cyclopentene or cyclohexene gave the corresponding [2 + 2] cycloadduct exclusively, whereas the photoreaction with isobutene or 1-methylcyclohexene afforded a mixture of [2 + 2] and [3 + 2] cycloadducts at ambient temperature. These results indicate that 1,1-disubstituted olefins giving sterically hindered tertiary radicals are favorable for the [3 + 2] cycloaddition with 1.

Acetophenone and benzophenone can sensitize the photoaddition of 1 to 2 giving 3 and 4 in approximately the same ratio (ca. 1:1) as in the case of direct irradiation, whereas Michler's ketone cannot sensitize the photoaddition. The most interesting feature of this photoreaction is the remarkable temperature effect. For example, the yield of [3 + 2] adduct 8 was increased at the expense of cyclobutane 9 as the reaction temperature was raised in the photoreaction of 1 with 1-methylcyclohexene as indicated in Table II. A similar temperature effect has also been observed in the photoreaction of 6-cyanouracil with olefins.[4a] In contrast, there was little solvent effect on the product ratio. The ratio 3/4 was not changed signifcantly in benzene (1.1), 2-propanol (1.4), ethanol (1.2), acetonitrile (1.2), THF (1.1), and methanol (1.2), although a cleaner formation of 3 has been observed in alcoholic solvents.

The simplest mechanism that readily accounts for all of these observations is given in Scheme I, using as an example of the reaction of 1 with 2. This involves as a first step formation of 1,4-biradical 12 originated from the interaction of triplet state of 1 with 2. The biradical intermediate 12 may close to cyclobutane 4 after spin inversion in the usual way (path a). Alternatively, 12 could cyclize at the carbon of the cyano group and furnish five-membered-ring iminyl radical 13 (path b).[4,9] In case of more congested bis-tertiary biradicals derived from 1,1-disubstituted olefins, both processes can occur competitively because of the reluctance of two tertiary radicals to couple, leading to 4 on steric grounds. As the reaction temperature is raised, more activation energy for the formation of the bicyclic iminium species 13 is provided to result in the increased yield of 5 (path b). A similar temperature-dependent photochemical transformation that can compete with [2 + 2] cycloaddition has previously been observed by Agosta and Wolff in the photorearrangements of citral and geranonitrile at elevated temperatures.[6a,10] Subsequent hydrogen reorganization of the biradical 13, leading to 5, may occur via 14 by hydrogen abstraction most probably from allylic hydrogens of 2 (Scheme I). In fact, formation of a considerable amount of polymeric products derived from olefins has been observed, in all cases. Alternatively, a contributing resonance form (15) of the iminyl radical 13 would undergo tautomerization directly to 5.[11]

In summary, the present work has demonstrated an additional example of novel type of [3 + 2] photocycloaddition of α,β-unsaturated nitrile to olefins. We feel that this type of photochemical [3 + 2] cycloaddition can occur generally between α,β-unsaturated nitriles and olefins, if congested bis-tertiary biradicals are produced as intermediates and sufficient thermal activation is available. Preliminary results indicate that 2-cyanochromone undergoes such a [3 + 2] cycloaddition to 1,1-disubstituted olefins efficiently.

Experimental Section

All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were measured on Varian HA-100 and FT-80A spectrometers, respectively, using Me_4Si as an internal standard. Ultraviolet spectra were obtained on a Shimadzu UV-200 spectrophotometer. Infrared spectra were measured on a JASCO IRA-1 spectrophotometer. VPC analyses were performed on a Shimadzu GC-2C (column, silicon DC 550; 1.5-m length). All irradiations were performed with a 100-W high-pressure mercury lamp surrounded by a Pyrex water cooling jacket under a nitrogen atmosphere unless otherwise noted. For irradiation at high temperature, the reaction vessel fitted with a reflux condenser was wrapped with a heating jacket. In the case of low-temperature irradiation the reaction vessel was cooled in a dry ice–methanol bath (−78 °C) or ice–ethanol bath (−20 °C).

Photoaddition of 3-Cyano-5,5-dimethyl-2-cyclohexenone (1) to 2-Methyl-2-butene (2). A solution of 1[12] (450 mg, 3 mmol) and 2 (2.10 g, 30 mmol) in 100 mL of methanol was irradiated at room temperature for 5 h under the standard condition. VPC and TLC analyses of the reaction mixture indicated complete disappearance of the starting material and the formation of three major products. One of them was decomposed upon addition of trace of dilute HCl. After removal of the solvent, the oily residue was purified by silica gel column chromatography and successive preparative TLC (hexane–ethyl acetate, 3:1) to give 230 mg (35%) of 3 and 198 mg (30%) of 4 together with polymeric products derived from 2. Analytically pure 3 was obtained by vacuum distillation. 3: bp 121–123 °C (7 mmHg); ^{1}H NMR ($CDCl_3$) δ 1.05 (s, 6 H), 1.08 (s, 3 H), 1.11 (s, 3 H), 1.15 (d, 3 H, $J = 7.5$ Hz), 2.30 (d, 2 H, $J = 2.5$ Hz), 2.41 (s, 2 H), 2.82 (tq, 1. H, $J = 2.5$,

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[9] Addition of alkyl radicals to cyano group has precedent in free-radical reactions. See, for example, (a) Kalvoda, J.; Botta, L. *Helv. Chim. Acta* **1972**, *55*, 356. (b) Freeksen, R. W.; Pabat, W. E.; Raggio, M. C.; Sherman, S. A.; Wroble, R. R.; Watt, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 1536. (c) Roberts, B. P.; Winter, J. N. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1353. The temperature-dependent cyclization of the 4-cyanobutyl radical to the cyclopentaniminyl radical has also been demonstrated: Griller, D.; Schimid, P.; Ingold, K. U. *Can. J. Chem.* **1979**, *57*, 831.

[10] (a) Barany, F.; Wolff, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1946. (b) Wolff, S.; Agosta, W. C. *J. Org. Chem.* **1978**, *43*, 3627.

[11] We thank a reviewer for suggesting this possibility.

[12] This compound was prepared from dimedone by the known procedure: Benson, W. R.; Pohland, A. E. *J. Org. Chem.* **1964**, *29*, 385.

7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 15.0, 19.3 26.8, 27.8, 28.1, 34.1, 34.8, 43.1, 48.4, 53.3, 149.0, 159.9, 199.3, 214.8; IR (neat) 1710, 1680 cm^{-1}; UV (EtOH) 258 nm (log ε 4.16).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.20; H, 9.10.

4: mp 129–130 °C (from ether–hexane); ^1H NMR ($CDCl_3$) δ 1.00 (d, 3 H, *J* = 6.5 Hz), 1.12 (s, 6 H), 1.14 (s, 3 H), 1.30 (s, 3 H), 1.95–2.05 (m, 2 H), 2.20–2.50 (m, 3 H), 2.76 (d, 1 H, *J* = 10.5 Hz); ^{13}C NMR ($CDCl_3$) δ 12.8, 21.3, 22.3, 25.6, 31.1, 34.5, 38.8, 39.5, 41.4, 42.2, 50.2, 51.1, 121.9, 207.5; IR (Nujol) 2230, 1705 cm^{-1}.

Anal. Calcd for $C_{14}H_{21}NO$: C, 76.66; H, 9.65; N, 6.39. Found: C, 76.46; H, 9.90; N, 6.42.

A portion of the crude reaction mixture was subjected to preparative HPLC [Waters ALC/GPC 204, Nucleosil 7 C_{18} column, $MeOH-H_2O$ (4:1)]. Two main fractions (retention time 5 and 7 min) were collected, the former being **3**. Another fraction, after removal of solvent, gave **5** as a colorless oil: ^1H NMR ($CDCl_3$) δ 1.06 (s, 3 H), 1.08 (s, 6 H), 1.10 (s, 3 H), 1.12 (d, 3 H, partially obscured), 2.31 (m, 2 H), 2.38–2.41 (m, 2 H), 2.70–2.90 (m, 1 H); UV (CH_3CN) 263 nm (log ε 4.00). Upon treatment of **5** in methanol with dilute HCl, **5** was converted to **3**. Attempts to obtain an analytically pure **5** were unsuccessful because of its extremely high sensitivity to hydrolysis.

Photoaddition of 1 to Isobutene. The reaction vessel was charged with a solution of 1.14 g (7.65 mmol) of **1** and 100 mL of methanol. Isobutene was condensed into the solution until the volume was increased by 3 mL. After 7 h of irradiation at ambient temperature under a nitrogen atmosphere, VPC analyses showed the formation of two photoproducts. After removal of the solvent, the viscous oil residue (1.50 g) was purified by silica gel column chromatography (benzene as eluent) to give **6** (596 mg, 38%) and **7** (791 mg, 46%). Analytically pure **6** was obtained by vacuum distillation. **6**: bp 115–118 °C (5 mmHg); ^1H NMR ($CDCl_3$) δ 1.08 (s, 6 H), 1.16 (s, 6 H), 2.32 (dd, 2 H, *J* = 3.1, 3.7 Hz), 2.44 (s, 2 H), 2.54 (dd, 2 H, *J* = 3.1, 3.7 Hz); IR (neat) 1715, 1695 cm^{-1}.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.40; H, 8.80.

7: mp 71.5–88 °C (from ether); ^1H NMR ($CDCl_3$) δ 1.13 (s, 9 H), 1.45 (s, 3 H), 1.92–2.09 (m, 4 H), 2.27 (m, 2 H), 3.21 (m, 1 H); IR (Nujol) 2225, 1710 cm^{-1}.

Anal. Calcd for $C_{13}H_{19}NO$; C, 76.05; H, 9.33; N, 6.82. Found: C, 76.16; H, 9.50; N, 6.86.

Photoaddition of 1 to Other Olefins. Photoaddition of **1** to other olefins was performed in a similar manner under the conditions described in Table I. Spectral data of the photoproducts are as follows. **8**: mp 50–56 °C (from ether); ^1H NMR ($CDCl_3$) δ 1.07 (s, 6 H), 1.09 (s, 3 H), 1.25–2.10 (m, 8 H), 2.32 (d, 2 H, *J* = 2.2 Hz), 2.41 (s, 3 H), 2.70–2.87 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 19.4, 19.5, 25.0, 25.7, 27.9, 28.3, 30.2, 34.2, 34.8, 44.7, 48.9, 53.3, 150.2, 159.5, 199.3, 214.8; IR (Nujol) 1715, 1690 cm^{-1}; UV (EtOH) 263 nm (log ε 4.23).

Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.5; H, 9.07.

9: mp 149–155 °C (from ether–hexane; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.14 (s, 6 H), 1.43–2.45 (m, 13 H), 3.10 (d, 1 H, *J* = 10.5 Hz); IR (Nujol) 2220, 1695 cm^{-1}.

Anal. Calcd for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 78.04; H, 9.61; N, 5.79.

10: mp 105–106 °C (from benzene); ^1H NMR ($CDCl_3$) δ 1.10 (s, 6 H), 1.40–3.00 (m, 14 H), 3.12 (d, 1 H, *J* = 11 Hz); IR (Nujol) 2220, 1695 cm^{-1}.

Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 77.73; H, 9.37; N, 5.98.

11: mp 92–96 °C (from benzene); ^1H NMR ($CDCl_3$) δ 1.10 (s, 6 H), 1.15–2.20 (m, 8 H), 2.28 (m, 2 H), 2.52–2.72 (m, 2 H), 2.95 (m, 1 H); IR (Nujol) 2220, 1760 cm^{-1}.

Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.16; H, 8.88; N, 6.21.

Sensitized Photoaddition of 1 to 2. Solutions containing **1** (100 mg), **2** (200 mg), and appropriate sensitizer in 5 mL of acetonitrile in quartz tubes were prepared. Concentrations of sensitizers were adjusted so that more than 90% of the incident light was absorbed by the sensitizers. The solutions were irradiated in a merry-go-round apparatus with a 400-W high-pressure mercury lamp. The 313-nm light was isolated by using a $K_2Cr_2O_7$ filter solution. After 43 h of irradiation, 1 mL of acetic acid (50%) was added to each solution, which were warmed on a water bath (60 °C) for 1 h to ensure the conversion of **5** to **4**. VPC analyses of the solutions using 1-methoxynaphthalene as an internal standard indicated that acetophenone-sensitized irradiation produced **3** (30%) and **4** (32%). Benzophenone-sensitized irradiation gave a similar result (38% of **3** and 30% of **4**), whereas Michler's ketone sensitized irradiation did not give any appreciable amount of products.

Registry No. 1, 65115-71-1; **2**, 513-35-9; **3**, 82902-18-9; **4**, 82890-93-5; **5**, 82890-94-6; **6**, 82890-95-7; **7**, 82890-96-8; **8**, 82890-97-9; **9**, 82890-98-0; **10**, 82890-99-1; **11**, 82891-00-7; isobutene, 115-11-7; 1-methylcyclohexene, 591-49-1; cyclohexene, 110-83-8; cyclopentene, 142-29-0.

Convenient Preparation of 1,1-Disubstituted Olefins from Primary Tosylates and Iodides

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Since their introduction in the mid-1960s 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and its higher homologue, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), have enjoyed wide use as convenient and efficacious reagents for formation of alkenes through elimination from alkyl halides and sulfonates.[1,2] A variety of structural types is generally reactive, down to and including saturated secondary bromides. The original investigators noted that 1-bromooctane yielded an ammonium salt but no 1-octene with DBN,[1] and presumably for this reason, there are virtually no subsequent reports of attempts to apply these reagents to primary halides or sulfonates lacking an activating substituent of some sort.[3] We have now found that DBN and DBU are useful in effecting elimination of hydrogen iodide from primary alkyl iodides in which the β-carbon atom is disubstituted. From this observation we have evolved a procedure for conversion of β-disubstituted primary tosylates to the related iodide and then, without isolation, elimination to the 1,1-disubstituted olefin. This is a convenient and inexpensive alternative to conversion of the alcohol to a selenate ester and subsequent oxidative elimination.[4] Examples of these transformations are gathered in the table.

In procedure A, a solution of the preformed iodide was heated at 80–90 °C with 1.5 equiv of the indicated amidine for 3–4 h. In procedure B, the tosylate and 2.5 equiv of sodium iodide were warmed at 50 °C in dimethylformamide for 4–6 h, the solution was cooled, 1.5 equiv of DBU was added, and the mixture was heated at 80 °C for 3–4 h. In each procedure a simple water and pentane workup was employed. Products were identified through their spectroscopic properties. No isomerization of the double bond occurred in any case within the limits of detection of 60-MHz NMR spectroscopy. In contrast, conversion of the tetrahydropyranyl-protected tosylate **4** to the corresponding bromide and subsequent treatment with potas-

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[1] Oediger, H.; Kabbe, H. J.; Möller, F.; Eiter, K. *Chem. Ber.* **1966**, *99*, 2012.

[2] For a review, see Oediger, H.; Möller, F.; Eiter, K. *Synthesis* **1972**, 591.

[3] For an example in which activation is provided only by a β-alkoxy group, see Rhoads, S. J.; Watson, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 5813.

[4] Sharpless, K. B.; Young, M. W. *J. Org. Chem.* **1975**, *40*, 947. Grieco, P. A.; Gilman, S.; Nishizawa, M. *Ibid.* **1976**, *41*, 1485.

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