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); ^{1}H 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$_2$O (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: ^{1}H 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$_3$CN) 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); ^{1}H 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); ^{1}H 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); ^{1}H 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; ^{1}H 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); ^{1}H 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); ^{1}H 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$_2$Cr$_2$O$_7$ 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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[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.

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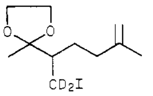
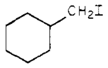
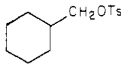
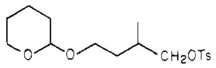
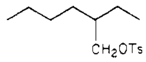
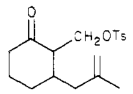
Table I. DBN- and DBU-Promoted Eliminations

no.	alkyl tosylate or iodide	procedure[a]	isolated yield of alkene, %
1		A (DBN in C_6H_6)	91
2		A (DBU in DMF)	~60
3		B	60
4		B	82
5		B	80
6	n-$C_8H_{17}OTs$	B	5
7		C	95

[a] A, iodide, 1.5 equiv of amidine, 80–90 °C, 3–4 h; B, tosylate, 2.5 equiv of NaI, DMF, 50 °C, 4–6 h, then 1.5 equiv of DBU, 80 °C, 3–4 h; C, tosylate, DBN, ether, 0 °C, 0.5 h.

sium *tert*-butoxide in dimethyl sulfoxide at 50 °C[5] yielded a 3:2 mixture of the terminal olefin and its rearranged trisubstituted isomer.

The failure of 1-octyl tosylate (**6**) to furnish a serviceable yield of 1-octene in procedure B is in agreement with the original report noted above. Treatment of cyclohexanemethyl tosylate (**3**) directly with DBU (as procedure B, but not sodium iodide) failed to give methylenecyclohexane. With suitable activation, however, the direct elimination of *p*-toluenesulfonic acid is feasible under mild conditions, as is shown by entry **7**. Procedure C consisted in reaction with DBN in ether at 0 °C for 0.5 h.

One additional observation is noteworthy. An equimolar mixture of 1-iodooctane and cyclohexanemethyl iodide (**2**) was treated in procedure B, but using only 0.5 equiv (total) of DBU. The water-insoluble material isolated consisted of four compounds in the indicated approximate yields: cyclohexanemethyl iodide (75%), 1-iodooctane (15%), methylenecyclohexane (10%), and 1-octene (5%). This distribution of products is consistent with selective reaction of DBU with the unbranched 1-iodooctane to form a water-soluble ammonium salt that does not undergo subsequent elimination. Branching at the β-carbon atom appears then to retard the substitution reaction between substrate and amidine leading to an ammonium salt but to accelerate the elimination to alkene. Earlier kinetic studies have demonstrated such an effect of β-alkyl substitution on displacement and elimination reactions at a primary carbon atom.[6]

Experimental Section

Materials and Equipment. General procedures have been described previously.[7] Preparation of **1**, **4**, and **7** is described in forthcoming publications.[8]

General Procedure for Elimination Reactions. A mixture of the tosylate and NaI (2.5 equiv) in DMF (2 mL/mmol) was heated at 50–55 °C for 5 h. This step was omitted for entries **1** and **2**. The mixture was cooled to room temperature, DBN or DBU (1.5 equiv) was added, and the reaction mixture was heated at 80–85 °C for 3 h. The mixture was cooled, poured into ice and water, and extracted with pentane (three times). The combined pentane extracts were washed with water, dilute HCl or oxalic acid, water, saturated $NaHCO_3$ solution, and brine and were dried. After removal of pentane by distillation through a 60-cm Vigreux column, the residue was distilled to afford the desired product. All products had spectra consistent with their assigned structures; NMR spectra indicated 2% or less double-bond isomerization.[9]

Registry No. 1, 82880-47-5; **2**, 5469-33-0; **3**, 3725-11-9; **4**, 82880-48-6; **5**, 78016-72-5; **6**, 3386-35-4; **7**, 82880-49-7; DBN, 3001-72-7; DBU, 6674-22-2; 2-methyl-2-(4-methyl-1-methylene-d_2-4-pentenyl)-1,3-dioxolane, 82890-86-6; methylenecyclohexane, 1192-37-6; 2-(4-methylene-1-oxapentyl)tetrahydropyran, 55975-11-6; 3-methyleneheptane, 1632-16-2; 1-octene, 111-66-0; 2-methylene-3-(2-methyl-2-propenyl)cyclohexanone, 82880-50-0.

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Crystal and Molecular Structure of 1,1,1,3,3,3-Hexaphenylpropane

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In connection with our studies of correlated rotation in systems containing two 9-triptycyl (Tp) groups attached to a common center,[1] we recently determined the X-ray structures of bis(9-triptycyl)carbinol (Tp_2CHOH),[1b] bis(9-triptycyl)methane (Tp_2CH_2),[1f] and bis(9-triptycyl) ketone (Tp_2CO).[1f] The most striking feature of these structures was found to be the greatly expanded central C–C–C bond angle which assumes the extraordinary value of 129° in all three compounds. Obviously, repulsive nonbonded interaction between the bulky Tp groups is to be held accountable for this phenomenon.

The observation of greatly expanded central bond angles in bis(triphenylmethyl) ether (127.9°)[2] and sulfide (119.8°)[3] suggests that the space-demanding properties of trityl (Tt) and Tp groups might be comparable in magnitude, and led to the prediction[1f] that the central bond angle in bis-

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