mg, 1.16 mmol) in C_6H_6 (40 mL) was treated with *p*-toluenesulfonic acid (100 mg, 0.58 mmol). The reaction mixture was refluxed during 1 h, removing H_2O by means of a Stark–Dean trap, concentrated to a small volume, diluted with H_2O, and extracted. The organic layer was washed with H_2O, dried, filtered, and evaporated giving **4a** (450 mg, 93%) as a colorless oil. Chromatography on silica (SiO_2) afforded the pure sample of **4a** as a colorless oil.

[1*R*-(1α,4β,4aβ,5α,6α,7β,8aβ)]-Octahydro-6,7-dihydroxy-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2-(1*H*)-one (4b). A solution of **4a** (3.8 g, 9.17 mmol) in CH_3OH (150 mL) was treated with KOH (4 g, 71.4 mmol) in H_2O (8 mL). The reaction mixture was refluxed during 2 h. Usual workup for hydrolysis[5] gave **4b** (400 mg) as white needles, mp 139–141 °C. Chromatography of the mother liquors through alumina (25 g) afforded **4b**, 300 mg, 31% overall yield. The analytical sample showed mp 142–143 °C. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86; O, 19.17. Found: C, 71.73; H, 8.72; O, 19.30.

[1*R*-(1α,4β,4aβ,5α,6α,7β,8aβ)]-Octahydro-7-hydroxy-4,8,8-trimethyl-9-methylene-6-[[(4-methylphenyl)sulfonyl]-oxy]-1,5-methanonaphthalen-2(1*H*)-one (4c). A solution of **4b** (1 g, 4.0 mmol) in pyridine (py, 12 mL) was treated with *p*-toluenesulfonyl chloride (2 g, 10.50 mmol) at 0 °C. The reaction mixture was stored at 4 °C during 24 h, poured over ice, and extracted. Usual workup for tosylations[5] afforded **4c** (1.2 g, 74%) as a white powder, mp 162–164 °C. The analytical sample showed mp 163–164 °C. Anal. Calcd for $C_{22}H_{28}O_5S$: C, 65.33; H, 6.98; O, 19.78; S, 7.91. Found: C, 65.17; H, 6.84; O, 19.88; S, 8.01.

[1*S*-(1β,2α,3α,4α,5β,7β,8α,11β)]-4,5-Bis(acetyloxy)-3-hydroxy-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undecan-9-one (1b). A solution of **1c**[5] (1 g, 3.73 mmol) in py (4 mL) was treated with $(CH_3CO)_2O$ (4 mL). The reaction mixture was stored at 4 °C during 4 h and worked up as usual for acetylations[5] to yield **1b** (850 mg, 65%) as white needles, mp 183–185 °C. The pure sample showed mp 199–201 °C. Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01; O, 27.24. Found: C, 64.57; H, 8.06; O, 27.09.

[1*S*-(1β,2α,3α,4α,5β,7β,8α,11α)]-3,4,5-Tris(acetyloxy)-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undecan-9-one (2b). A solution of **3b**[5] (1.90 g, 4.84 mmol) in EtOAc (160 mL) was stirred in the presence of prehydrogenated 10% Pd on activated charcoal (200 mg) under an H_2 atmosphere at room temperature and normal pressure until the uptake of the H_2 ceased. The catalyst was removed by filtration, and the solvent was evaporated to dryness. Crystallization from acetone–hexane gave **2b** (1.37 g, 72%) as white needles, mp 178–180 °C. The analytical sample, from acetone–hexane, showed mp 185–186 °C. Anal. Calcd for $C_{21}H_{30}O_7$: C, 63.94; H, 7.66; O, 28.39. Found: C, 64.01; H, 7.74; O, 28.72.

[1*S*-(1β,2α,3α,4α,5β,7β,8α,11α)]-3,4,5-Trihydroxy-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undecan-9-one (2c). As described for the preparation of **4b**, reaction of **2b** (900 mg, 2.28 mmol) in CH_3OH (50 mL) with KOH (900 mg, 16.07 mmol) in H_2O (4 mL) gave **2c** (520 mg, 85%) as white prisms. The pure sample showed mp 164–168 °C. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01; O, 23.85. Found: C, 67.09; H, 8.85; O, 23.90.

[1*S*-(1β,2α,3α,4α,5β,7β,8α,11α)]-4,5-Bis(acetyloxy)-3-hydroxy-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undecan-9-one (2a). As described for the preparation of **1b**, reaction of **2c** (460 mg, 1.71 mmol) in py (2 mL) with $(CH_3CO)_2O$ (2 mL) afforded **2a**, 320 mg, 53%. The pure sample, from EtOH–$CHCl_3$–hexane, showed mp 218–220 °C. Anal. Calcd for $C_{19}H_{28}O_6$: C, 64.75; H, 8.01; O, 27.24. Found: C, 64.87; H, 8.09; O, 27.18.

[1*R*-(1β,2α,3α,4α,5β,7β,8α)]-4,5-Bis(acetyloxy)-3-hydroxy-2,6,6,11-tetramethyltricyclo[5.4.0.0^{2,8}]undec-10-en-9-one (3a). As described for the preparation of **1b**, reaction of **3c**[5] (500 mg, 1.88 mmol) in py (2 mL) with $(CH_3CO)_2O$ (2 mL) gave **3a** (320 mg, 48%) as white needles. The analytical sample showed mp 183–184 °C. Anal. Calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48; O, 27.39. Found: C, 65.00; H, 7.54; O, 27.25.

[1*R*-(1α,4β,4aβ,5α,6α,7β,8aβ)]-6,7-Bis(acetyloxy)octahydro-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (4d). A solution of **1b** (1 g, 2.84 mmol) in CH_2Cl_2 (12 mL) was treated with $Et_2O{\cdot}BF_3$ (3 mL) at 0 °C. The reaction mixture was stored at room temperature during 24 h, poured over ice, and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried, filtered, and evaporated. The residue was chromatographed on SiO_2 to yield **4d** (850 mg, 89%) as a colorless oil.

[1*R*-(1α,4α,4aβ,5α,6α,7β,8aβ)]-6,7-Bis(acetyloxy)octahydro-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (5a). As described for the preparation of **4d**, reaction of **2a** (50 mg, 0.14 mmol) in CH_2Cl_2 (0.6 mL) with $Et_2O{\cdot}BF_3$ (0.15 mL) yielded **5a**, 30 mg, 64%. Chromatography on SiO_2 afforded **5a** as a colorless oil.

[1*R*-(1α,4α,4aβ,5α,6α,7β,8aβ)]-Octahydro-6,7-dihydroxy-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2-(1*H*)-one (5b). As described for the preparation of **4b**, reaction of **5a** (30 mg, 0.09 mmol) in CH_3OH (10 mL) with KOH (30 mg, 0.54 mmol) gave, from acetone–hexane, **5b** (20 mg, 89%) as white needles: mp 154–156 °C. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.96; H, 8.86; O, 19.17. Found: C, 72.12; H, 8.69; O, 19.14.

[1*R*-(1α,4aβ,5α,6α,7β,8aβ)]-6,7-Bis(acetyloxy)-4a,5,6,7,8,8a-hexahydro-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (6a). As described for the preparation of **4d**, reaction of **3a** (500 mg, 1.43 mmol) in CH_2Cl_2 (6 mL) with $Et_2O{\cdot}BF_3$ (1.5 mL) gave an oily residue which showed in the ^1H NMR spectrum to be a complex mixture. This mixture was chromatographed through SiO_2. The fraction eluted with C_6H_6–EtOAc (3:1) was rechromatographed to yield **6a**, 100 mg, 21%.

[1*R*-(1α,4aβ,5α,6α,7β,8aβ)]-4a,5,6,7,8,8a-Hexahydro-6,7-dihydroxy-4,8,8-trimethyl-9-methylene-1,5-methanonaphthalen-2(1*H*)-one (6b). As described for the preparation of **4b**, reaction of **6a** (100 mg, 0.30 mmol) in CH_3OH (5 mL) with KOH (100 mg, 1.78 mmol) in H_2O (0.5 mL) gave, from acetone–hexane, **6b** (33 mg, 44%) as white prisms: mp 226–229 °C.

Hydrogenation of 6b. As described for the preparation of **2b**, reaction of **6b** (100 mg, 0.40 mmol) in AcOEt (50 mL) with H_2, catalyzed by prehydrogenated 10% Pd on activated charcoal (10 mg), gave a mixture of **4b** and **5b** in a ratio of ca. 4:1. Chromatography on SiO_2 afforded from the fractions eluted with C_6H_6–EtOAc (9:1) **4b**, 38 mg, 37%, and from the fractions eluted with C_6H_6–EtOAc (3:1) **5b**, 9 mg, 10%.

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Registry No. **1a**, 80388-43-8; **1b**, 131657-27-7; **1c**, 131724-23-7; **2a**, 131724-24-8; **2b**, 131724-25-9; **2c**, 131724-26-0; **3a**, 131657-28-8; **3b**, 112420-81-2; **3c**, 97280-00-7; **4a**, 131657-29-9; **4b**, 131724-98-6; **4c**, 131657-30-2; **4d**, 131657-31-3; **5a**, 131724-27-1; **5b**, 131657-32-4; **6a**, 131657-33-5; **6b**, 131657-34-6.

Supplementary Material Available: IR and optical activity for all substances. UV spectral data for **3a**, **4a**, **4c**, **6a**, and **6b**. Tables containing crystal data, collection and refinement parameters, atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, hydrogen atom coordinates, torsion angles, and labeled drawings of **4c** and **6b** (18 pages). Ordering information is given on any current masthead page.

Stereocontrolled Reductive Deoxygenation Using Low-Valent Titanium: Effects of Ultrasound Waves and Solvents

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Reductive deoxygenation of aldehydes and ketones with low-valent titanium is one of the most commonly used procedures for the preparation of alkenes and has been subjected to extensive synthetic and mechanistic investigations.[1] Occassional low yields and temperamental

(1) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255–3266.

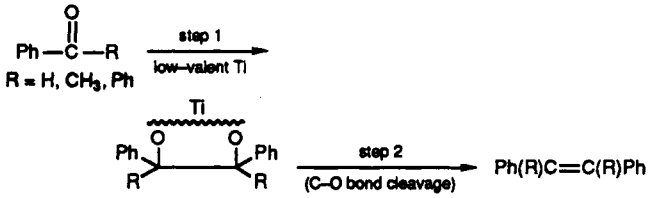
0022-3263/91/1956-1940$02.50/0

Table I. Ultrasonically Accelerated Reductive Deoxygenation and Hydrodimerization of Aromatic Carbonyl Compounds

				products[b]			
				alkenes[c] 2		pinacols[c] 3	
entry	substrate	solvent	conditions[a] (time)	E (%)	Z (%)	%	(dl/meso)
1	$C_6H_5COCH_3$	DME	reflux (16 h)	83	9	–	
2	$C_6H_5COCH_3$	THF	reflux (16 h)	25	64	–	
3	$C_6H_5COCH_3$	THF	sono (45 min)	21	66	–	
4	$C_6H_5COCH_3$	THF	stirring (45 min)	18	34	25	(12)
5	$C_6H_5COCH_3$	DME	sono (45 min)		–	75	(4.9)
6	$C_6H_5COCH_3$	DME	stirring (45 min)			38	(22)
7	C_6H_5CHO	THF	sono (45 min)		83	–	
8	$C_6H_5COC_6H_5$	THF	sono (60 min)		65	–	

[a] Reactions were run using 1:3.5:0.33 M ratios of $TiCl_3$:Li:aldehydes/ketones. Sonochemical/stirring reactions were carried out at 30 °C. [b] All the products showed the expected IR, MS, and ^1H NMR spectra. [c] Isolated yield after column chromatography.

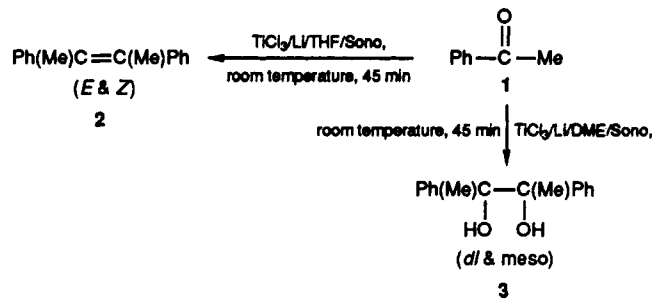
Scheme I



nature of some of these reactions have led to several improvements in the reagent systems.[2] Recent report of McMurry et al.[3] on the advantages of $TiCl_3(DME)_{1.5}$ complex for reductive deoxygenation prompts us to report our results on the marked influence of ultrasound and solvents on this reaction. In recent years, dramatic effects of ultrasonic waves on organic reactions have been observed.[4] We have recently reported marked enhancement in the rate of hydrodimerization of aromatic carbonyl compounds,[5] ortho-lithiation of aromatic ethers,[6] and other reactions[7] under the influence of ultrasonic irradiation. In continuation of this work, effects of ultrasound as well as of solvents on titanium-induced reductive duplication of aldehydes and ketones were explored by us. We have found that under the influence of ultrasound and use of appropriate solvents, hydrodimerization (in dimethoxyethane) or reductive deoxygenation (in tetrahydrofuran) of carbonyl compounds could be carried out at room temperature within 45–60 min. The stereochemistry of the products could also be controlled by the judicious use of solvents.

In the present investigation, acetophenone (1) was used as a model substrate. McMurry and his co-workers[1] have reported the formation of 2,3-diphenyl-2-butene (2) from 1 in 94% yield using $TiCl_3$/Li in dimethoxyethane (DME) under refluxing conditions (16 h). The *E*:*Z* ratio of the product as determined by NMR was 9:1. We also obtained similar results (Table I, entry 1) when the reaction was repeated in our laboratory under McMurry's conditions. However, when the same reaction was carried out in tetrahydrofuran (THF) (entry 2), an excellent yield (89%) of 2 was obtained but the product was predominantly the *Z* isomer (*E*/*Z*, 2/5). Thus it was clear that the solvent has a profound effect in the control of stereochemistry of the alkenes (see below).

Scheme II



Effects of ultrasonic irradiation on this reaction have also been studied. Low-valent titanium was conveniently generated by ultrasonic irradiation (1 h) of a mixture of $TiCl_3$ and Li in THF at ambient temperature (30 °C). Normally, this requires refluxing. During the reduction, the color of the reaction mixture changed from violet via blue and brown to black.[8] Addition of 1 followed by further ultrasonic irradiation (45 min) gave 2 in 87% yield with *Z* as the predominant isomer (entry 3). When a similar reaction was carried out with stirring at 30 °C but without sonication (entry 4), a mixture of 2 and 2,3-diphenylbutane-2,3-diol (3)[9] was obtained in 52% and 25% yields, respectively. Here also the *Z* isomer of 2 was the major product while 3 was obtained predominantly in the *dl* form (*dl*/meso = 12). Thus it is concluded that in THF ultrasound accelerates the deoxygenation by facilitating the cleavage of two carbon–oxygen bonds of the titanium pinacolates (Scheme I, Step 2), resulting in the formation of alkenes. It may be noted that the *Z* isomers are useful synthons for their facile photochemical transformation to phenanthrenes. Stilbene[1] and tetraphenylethylene[1] (entries 7 and 8) were obtained when benzaldehyde and benzophenone were used as substrates as shown in Table I.

Interesting results were obtained when effects of solvents on the sonochemical reactions were studied (Scheme II). Ultrasonic irradiation of mixture of $TiCl_3$ and Li in nonpolar solvents like hexane or benzene did not bring about reduction of $TiCl_3$ as evidenced by the retention of violet color of titanium(III) chloride. Acetophenone was recovered unchanged under these conditions. Changing the solvent from nonpolar to polar aprotic solvents such as DME yielded 3 in 75% yield with the preponderence of *dl* isomer (*dl*/meso = 4.9) and 2 was not detected (entry 5). As mentioned above, use of THF under similar reaction conditions (entry 3) yielded 2 as the sole product. Therefore, by the choice of appropriate solvents, it is possible to restrict the reaction at the intermediate pinacol stage. Similar reaction with stirring but without sonication (entry 6) gave 3 in 38% yield (*dl*/meso = 22), and 56%

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of 1 was recovered. Cessation of the reaction at the pinacol stage in DME suggests that deoxygenation of the pinacols involving cleavage of C–O bonds does not take place in this solvent. This can be explained by the formation of a thermodynamically more stable 5-membered titanium complex with DME as compared to THF, resulting in the decrease in the oxophilicity of titanium thereby preventing the cleavage of C–O bonds of titanium pinacolates to form 2.

Thus, under ultrasonic irradiation, reduction of $TiCl_3$ to low-valent Ti, deoxygenation or hydrodimerization of aromatic carbonyl compounds can be carried out at an enhanced rates at ambient temperature. Further, the E/Z ratios can be altered by using appropriate solvents. Use of DME restricted the reactions to the hydrodimerization stage (step 1) only while in THF, deoxygenation to alkenes occurred. Though influence of solvents on the reactivities of low-valent titanium has been observed earlier,[10] this, to best of our knowledge, is the first report on the effects of solvents on the stereochemistry of the products.

Experimental Section

THF was distilled freshly from benzophenone–sodium ketyl. DME was distilled over CaH_2 prior to use. *n*-Hexane and benzene were dried over sodium. All manipulations were carried out under an atmosphere of argon. Ultrasonic irradiations were carried out using Ralsonic-R-200 ultrasonic cleaning bath.

Typical Example of an Intermolecular Coupling Using $TiCl_3$/Li under Ultrasound: 2,3-Diphenyl-2-butene (2). In a typical experiment, a dry argon-filled three-necked round-bottom flask was charged with 20 mL of dry THF, 2.3 g of titanium(III) chloride (15 mmol), and 365 mg of lithium (52 mmol). The flask was then immersed to the solvent (water) level in a sonicator (200 W, 40 KHz) and sonicated at 30 °C[11] for 1 h when the color of the reaction mixture changed from violet to black (few small pieces of Li remain unreacted). Acetophenone (600 mg, 5 mmol) in dry THF (5 mL) was then added to the reaction mixture and sonicated for additional 45 min. After the completion (45 min, monitored by TLC), the reaction mixture was diluted with petroleum ether and the slurry was passed through a small pad of Florisil on a sintered-glass filter to remove inorganic salts. Removal of solvent and subsequent column chromatography (SiO_2) yielded 2,3-diphenyl-2-butene (2) (oil, 452 mg, 87%) as 1:3 mixture of E and Z isomers. The E/Z ratio was determined by GLC (3% OV-17) an by comparison of peak heights of the methyl group resonances of the two isomers (Z δ 1.87, E δ 2.14) in PMR spectrum.[1]

In cases where pinacols (3) are the reaction products (entries 4, 5, and 6), hydrolysis of the reaction mixtures was carried out with 10% cold aqueous K_2CO_3 solution followed by extraction with ether.

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(11) The temperature of the cleaning bath was maintained at 30 °C throughout the reaction.

Stereochemical Investigations: Reduction of *syn*-8-Chloro- and Cleavage of *anti*-8-*tert*-Butoxy-*endo*-3,3-diphenyltricyclo-[3.2.1.$0^{2,4}$]oct-6-enes

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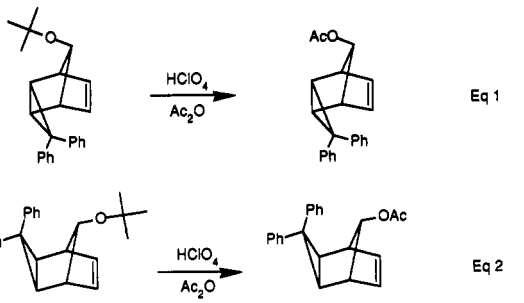
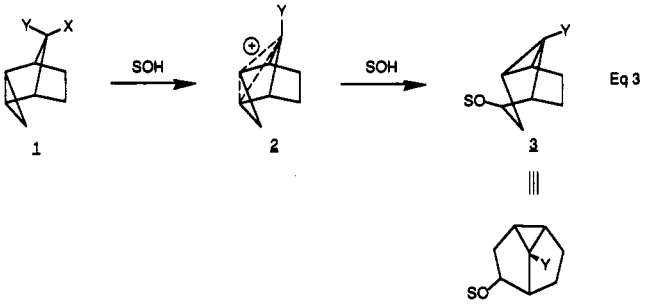
The perchloric acid/acetic anhydride cleavage of the endo-syn and exo-anti isomers of 8-*tert*-butoxy-3,3-diphenyltricyclo[3.2.1.$0^{2,4}$]oct-6-ene lead to the corresponding acetates (eqs 1 and 2), while the exo-syn and endo-anti isomers produced complex product mixtures which were not completely characterized.[1a] *endo*-Tricyclo-[3.2.1.$0^{2,4}$]octan-*anti*-8-yl derivatives (1) are known[2] to readily[3a] undergo carbocation rearrangements to tricyclo-[3.3.0.$0^{4,6}$]octan-3-yls[3b] (3) (eq 3). *p*-Toluenesulfonic acid





catalyzed rearrangement of the *endo*-tricyclo[3.2.1.$0^{2,4}$]-octan-*anti*-8-ol (1, X = OH) in acetic acid gave 3-acetoxytricyclo[3.3.0.$0^{4,6}$]octane[2a] (3, SO = AcO) and the corresponding *anti*-8-*p*-nitrobenzoate (1, X = OPNB) gave tricyclo[3.3.0.$0^{4,6}$]octan-2-ol (3, SO = HO) in dioxane–water.[2a-c] Rearrangement of an 8-aryl-substituted *anti*-8-*p*-nitrobenzoate 1 (X = OPNB, Y = *p*-$C_6H_4OCH_3$) to 3 (SO = HO, Y = *p*-$C_6H_4OCH_3$) has also been reported.[2d] Other endo-anti derivatives have given similar products under solvolytic conditions.[4]

Since the norbornene bridgetop proton syn to the double bond is between the shielding and deshielding regions of the double bond, small structural changes in derivatives of this rigid system result in considerable ^{1}H NMR chemical shift changes.[5] Such changes make chemical shift comparisons unreliable for stereochemical assignments.

Results and Discussion

While exploring synthetic approaches that ultimately led to 8-keto and 8-methylene[6] tricyclic systems, the endo-anti ether 4[1a] was reduced with diimide[7] to 5 which

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(3) (a) The parent 1 (X = OPNB) is reported[2a-c] to solvolyze 10^{14} faster than bicyclo[2.2.1]heptan-7-yl-*p*-nitrobenzoate. (b) The current IUPAC name. See footnote 22b of ref 2a for other names such as tricyclo-[5.1.0.$0^{4,8}$]- or -[3.2.1.0.$0^{4,8}$]octyl that have also been used.
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(7) LAH did not reduce 9 at room temperature or at THF reflux, though LAH reduction of a norbornene with a bridgetop *tert*-butoxy[8] group over the double bond is reported.

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0022-3263/91/1956-1942$02.50/0