16.8 g (78 mmol) of pyridinium chlorochromate in 100 mL of CH_2Cl_2, and the mixture was stirred at 25 °C for 2 h. Ether (3 × 75 mL) was added and removed from the black residue and then filtered through a small column of Florosil. The filtrate was then washed with 100 mL of 0.1 N NaOH, dried over $MgSO_4$, filtered, evaporated, and distilled at 128–130 °C (0.8 mmHg), giving 7.67 g (79%) of **3**: IR 2940 (s), 1735 (s), 1320 (m), 1120 (m) cm^{-1}; ^1H NMR δ 0.95 (3 H, br t), 1.2–1.6 (6 H, m), 2.2–2.4 (4 H, m), 2.6 (2 H, br t), 3.05 (2 H, pentet, J = 1.5 Hz), 9.8 (1 H, br t).

6,9-Pentadecadiyn-1-en-3-ol (4). A solution of vinyl magnesium bromide (30 mL, 1 M in THF) was added with cooling to a solution of 4.68 g (24.6 mmol) of **3** in 20 mL of dry ether and the solution refluxed for 30 min. It was then poured into 80 mL of 1 N HCl and extracted with ether (3 × 100 mL), and the combined ether layers were washed with 100 mL of saturated $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated, leaving 5.33 g (98%) of **4** (after drying at 1 mmHg for 1 h). This was used in the next reaction without further purification: IR 3400 (br s), 2940 (s), 1430 (m), 1310 (s), 1050 (m) cm^{-1}; ^1H NMR δ 0.90 (3 H, br t), 1.2–1.6 (6 H, m), 2.2–2.4 (6 H, m), 3.05 (2 H, pentet, J = 1.5 Hz), 4.25 (1 H, q), 5.0–6.2 (3 H, m, typical of vinyl group).

Ethyl 8,11-Heptadecadiyn-4(*E*)-enoate (5). A solution of 5.33 g (24.4 mmol) of **4** and 0.13 mL of propionic acid (1.74 mmol) in 30 mL of triethyl orthoacetate (164 mmol) was heated to 138 °C for 1 h with distillative removal of ethanol. The solution was poured into 100 mL of ether, washed with 100 mL of saturated $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated. The excess triethyl orthoacetate was removed by distillation at 1 mmHg, and the residue was passed through a short column of silica gel. After removal of the solvent, the residue weighed 6.40 g (91%): IR 3050 (m), 2940 (s), 1740 (s), 1050 (s), 964 (s) cm^{-1}; ^1H NMR δ 0.97 (3 H, br t), 1.30 (3 H, t), 1.3–1.5 (6 H, m), 2.0–2.4 (8 H, m), 3.05 (2 H, pentet, J = 1.5 Hz), 4.15 (2 H, q), 5.46 (2 H, br s).

8,11-Heptadecadiyn-4(*E*)-en-1-ol (6). To a cooled solution of 6.40 g (22.2 mmol) of **5** in 50 mL of ether was added 1.01 g (26.6 mmol) of $LiAlH_4$ suspended in 20 mL of ether. The suspension was refluxed for 1 h and then the following were added in succession: 6 mL of ethyl acetate, 1 mL of methanol, and 100 mL of cold 1 N HCl. The material was extracted with ether (3 × 100 mL), and the combined ether layers were washed with 100 mL of saturated $NaHCO_3$, dried over $MgSO_4$, filtered, and evaporated. The crude product was filtered through a small column of silica gel and activated charcoal, leaving 5.03 g of **6** (92%): IR 3400 (br s), 2940 (s), 1050 (s), 965 (s) cm^{-1}; ^1H NMR δ 0.93 (3 H, br t), 1.2–1.8 (8 H, m), 2.0–2.4 (8 H, m), 3.05 (2 H, pentet, J = 1.5 Hz), 3.68 (2 H, t), 5.50 (2 H, br s).

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Registry No. **1**, 87681-28-5; **2**, 87681-29-6; **3**, 87681-30-9; **4**, 87681-31-0; **5**, 87681-32-1; **6**, 87681-33-2; **7**, 87681-34-3; **8**, 87681-35-4; **9**, 2441-53-4; 2-(4-pentynyloxy)tetrahydro-2*H*-pyran, 62992-46-5; 1-bromo-2-octyne, 18495-27-7; vinyl bromide, 593-60-2; triethyl orthoacetate, 78-39-7.

Thermal Reactions of Stereoisomeric 1-Phenyl-1,3,5-heptatrienes

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An electrocyclic reaction potentially can give two stereoisomeric products, one via an orbital symmetry allowed route and a second via either a forbidden route or a symmetry-independent route. The allowed route is well established, and the $\Delta\Delta H^{\ddagger}$ between it and the other routes has been estimated for the cyclobutene–butadiene[2] and octatetraene–cyclooctatriene[3] cases. No example of a suitable hexatriene–cyclohexadiene case giving sufficient nonallowed product has been found as yet, so no estimate of $\Delta\Delta H^{\ddagger}$ for this system is available. We have prepared and studied three hexatrienes with substitution intended to enhance the visibility of the nonallowed reaction.

The basis for this rests on the following facts: (a) this electrocyclization is essentially irreversible, (b) the allowed reaction rate is virtually independent of trans substituents on terminal carbons,[4] and (c) a phenyl group in that position should enhance the forbidden reaction rate,[5] and also any diradical process.[6] A rough calculation for the $\Delta H^{\ddagger}$ for formation of a pentadienyl–benzyl orthogonal diradical gives a value of 125–130 kJ/mol (263 − 84 for the pentadienyl radical[6] and −52 for the benzyl radical[6]). This suggests the diradical should be competitive with the allowed ring closure which has $\Delta H^{\ddagger} \approx 121$ kJ/mol. Since a phenyl in a cis rather than a trans position raises $\Delta H^{\ddagger}$ for the allowed reaction by ~20 kJ/mol, the diradical should be readily observed with that isomer.

Results and Discussion

Several attempts were made to prepare (*E*,*Z*,*E*)-1-phenyl-1,3,5-heptatriene (**2**) by semihydrogenation of (*E*)-1-phenyl-1-hepten-3-yn-6-ol or (*E*)-1-phenyl-5-hepten-3-yn-1-ol followed by an elimination. This basic scheme, used in many cases previously,[7] failed in this case. An alternative route to such stereoisomeric trienes was developed (Scheme I), and three isomeric 1-phenyl-1,3,5-

Scheme I

$$\mathrm{PhCH{=}CHBr + MeCH{=}CHC{\equiv}CH} \xrightarrow[\mathrm{CuI,\ Et_2NH}]{\mathrm{Pd(PPh_3)_2Cl_2}} \mathrm{PhCH{=}CHC{\equiv}CCH{=}CHMe} \xrightarrow{\mathrm{H_2/Pd}}$$

(1-*E*,5-*E*)-**1**
(1-*E*,5-*Z*)-**3**
(1-*Z*,5-*E*)-**5**

$$\mathrm{PhCH{=}CHCH{=}CHCH{=}CHMe}$$

(*E*,*Z*,*E*)-**2**
(*E*,*Z*,*E*)-**4**
(*Z*,*Z*,*E*)-**6**

heptatrienes were successfully prepared via this method. All the dienynes, **1**, **3**, and **5**, are stable compounds, unequivocally identifiable by NMR. As such, each represents a key point in the synthetic scheme since each was obtained in pure form, free from any isomeric impurity.

Semihydrogenation of such dienynes is not generally a clean reaction,[8] normally leading to mixtures including trienes whose central double bond can be of either *E* or *Z* configuration, overhydrogenation products, and possibly unreacted dienyne. No evidence for geometric isomerization of the initial double bonds has been noted. The pattern was followed in the present examples. Semihydrogenation of 1 gave 80% trienes and 20% overhy-

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drogenated material. Preparative separation led to some ring closure, but a triene having an ultraviolet spectrum with the usual three-peak pattern at 304, 317, and 327 nm was obtained. Kinetic analysis showed the presence of about 20–25% of a triene which did not undergo thermal ring closure. This is apparently the *E,E,E* isomer since its ultraviolet spectrum agrees with literature values.[9] Since this isomer is thermally stable, **2** was used with a significant amount of the *E,E,E* isomer present. Compound **2** has been reported to have an ultraviolet maximum at 307 nm (ϵ 8000).[9] It appears likely that that compound was really 1-phenyl-6-methyl-1,3-cyclohexadiene (see below) both from the spectral result and its mode of synthesis. Cyclic dienes are obtained by direct ring closure during a Wittig reaction.[10-12]

The semihydrogenation of **3** and **5** gave mixtures containing **4** and **6**, respectively, along with overhydrogenated products. Both **4** and **6** are readily separated from overhydrogenated material. Kinetic analysis of either **4** or **6** indicated that neither was contaminated by identifiable amounts of the *E,E,Z* or *Z,E,E* isomer. No cross contamination of **2**, **4**, or **6** was observed, but it would be difficult to identify small amounts of one isomer in another by spectral means.

Thermal cyclization of **2** proceeds readily at 120–145 °C. The main product is *cis*-5-phenyl-6-methyl-1,3-cyclohexadiene (**7**) which has a typical homoannular diene band at 265 nm. For prevention of further thermal reactions which might occur during purification or analysis, the product was completely hydrogenated over platinum oxide. This material was analyzed by GLC and contained 1-phenylheptane, *cis*-1-phenyl-2-methylcyclohexane (**8**) and *trans*-1-phenyl-2-methylcyclohexane (**9**) identified by comparison with authentic samples. The ratio of **8** and **9** was 550:1, a value obtained from two independent runs. Rate of ring closure was followed by ultraviolet spectroscopy and good first-order rates were obtained to 2 or 3 half-lives. Results are given in the Experimental Section.

Both **4** and **6** rearrange thermally to produce 1-phenyl-6-methyl-1,3-cyclohexadiene (**10**) rather than the expected *trans*-5-phenyl-6-methyl-1,3-cyclohexadiene (**11**). Apparently the initial cyclization is followed by a 1,5 H shift. Both reactions are slower than the cyclization of **2** as is expected,[4] and **6** reacts 180 times slower than **2**. An attempt to find evidence for the presence of an intermediate in the rearrangement of **6** showed that the UV maximum at 297 nm converts smoothly to the product maximum at 304 nm. Assuming that the route to **10** is **6** $\xrightarrow{k_1}$ **11** $\xrightarrow{k_2}$ **10**, we can calculate[14] that if $k_2/k_1 = 5$, then the maximum concentration of **11** would be 13%.

Because the extinction coefficient of the homoannular diene **11** is about 16% of that for **6**, small amounts of **11** would be hard to identify. However, simulated curves indicate that ~10% of **11** could be found. Thus, we believe that k_2/k_1 must be greater than or equal to 5. If this is accepted, the hydrogen shift rate at 150 °C would be at least 2×10^{-5} s^{-1}. The hydrogen shift for *trans*-5,6-dimethyl-1,3-cyclohexadiene is 7.7×10^{-6} s^{-1} at 182 °C.[7] Thus the phenyl group has increased the rate of the hydrogen shift by a factor of ca. 100 times. This increase is to be expected, and the magnitude is quite reasonable. This shift rate would produce 2.6% of **10**, since the calculated rate of cyclization of **2** at 150 °C is 7.6×10^{-4} s^{-1}. The fortuitous agreement is clearly coincidental, but the result just as clearly illustrates that a large fraction of the **9** observed came from hydrogenation of **10**. This suggests that the $\Delta\Delta H^{\ddagger}$ between the allowed and the diradical routes could exceed 80 kJ/mol.

Experimental Section

(*E,E*)-1-Phenyl-1,5-heptadien-3-yne (1). The procedrue of Sonagashira, Tohda, and Hagihara[19] was used to prepare all the dienynes. To a solution containing 2.88 g (15.7 mmol) of (*E*)-β-bromostyrene[16,17] and 1.32 g (20.0 mmol) of (*E*)-3-penten-1-yne[15] in 50 mL of diethylamine were added 0.050 g (0.073 mmol) of bis(triphenylphosphine)dichloropalladium(II) and 0.028 g (0.153 mmol) of cuprous iodide. This reaction mixture was stirred under nitrogen for 6 h. The solution was mixed with 20 mL of water, and the organic materials were taken up in petroleum ether. The organic solution was washed with 10% hydrochloric acid, sodium bicarbonate solution, and, finally, water. The solution was dried ($MgSO_4$), and the solvent was removed by distillation.

The concentrate was chromatographed on alumina with petroleum ether as the eluant, giving 2.20 g of light yellow oil after removal of the solvent. A small sample was distilled, giving an oil: NMR (CCl_4) δ 1.85 (d of d, 3 H, J = 7, 1.5 Hz), 5.61 (d of m, 1 H, J = 16 Hz), 6.12 (d of q, 1 H, J = 16, 1.5 Hz), 6.21 (d of d, 1 H, J = 16, 2 Hz), 6.96 (d, 1 H, J = 16 Hz), 7.2–7.4 (m, 5 H); IR (CCl_4) 2270, 945 cm^{-1}; UV max (cyclohexane) 305 (sh), 311 nm (ϵ 37 000), 338 (sh). Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.66; H, 7.12.

(*Z,E*)-1-Phenyl-1,5-heptadien-3-yne (5). This dienyne was prepared from (*Z*)-β-bromostyrene[18] (recrystallized from pentane at −78 °C) and (*E*-3-penten-1-yne according to the directions above. The product obtained after concentration of the washed and dried petroleum ether solution was separated by GLC (9% SE-30 on 45/60 Chromosorb W, $^1/_4$ in. × 8 ft column at 160 °C into unreacted halide and the desired dienyne: NMR (CCl_4) δ 1.78 (d, 3 H, J = 6 Hz), 5.66 (d of m, 1 H, J = 16 Hz), 5.72 (d of d, 1 H, J = 12, 2 Hz), 6.13 (d of q, 1 H, J = 16, 6 Hz), 6.48 (d, 1 H, J = 12 Hz) 7.15 (m, 3 H), 7.78 (m, 2 H); irradiation at the methyl frequency reduced the olefinic spectrum to δ 5.66 (d of d, J = 16, 2 Hz), 6.13 (d, J = 16 Hz). IR (neat) 2175, 950, 780, 690 cm^{-1}; UV max (cyclohexane) 232 nm (ϵ 34 000), 310 (44 000), 328 (31 000). Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.70; H, 7.25.

(*E,Z*)-1-Phenyl-1,5-heptadien-3-yne (3). A modification of the above procedure was employed to prepare this dienyne. A solution containing 1.2 g (18.2 mmol) of (*Z*)-3-penten-1-yne[15] in 2.5 mL of ether was mixed with a suspension of 2.75 g (15 mmol) of (*E*)-β-bromostyrene, 0.040 g (0.057 mmol) of bis(triphenylphosphine)dichloropalladium(II), and 0.022 g (0.114) mmol) of cuprous iodide in 30 mL of diethylamine. The mixture was stirred under nitrogen for 10 h, and the product was isolated as described above: NMR δ 1.96 (d of d, 3 H, J = 6, 1 Hz), 5.64 (d of m, J = 10 Hz), 6.00 (d of q, 1 H, J = 10, 6 Hz), 6.18 (d of d, 1 H, J = 16, 2 Hz), 6.90 (d, 1 H, J = 16 Hz), 7.3 (m, 5 H); IR (neat) 2255, 945, 740, 705, 680 cm^{-1}; UV max (cyclohexane) 311 nm (ϵ 30 000). Anal. Calcd for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.71; H, 7.19.

(*E,Z,E*)-1-Phenyl-1,3,5-heptatriene (2). A freshly purified sample (1.10 g, 6.55 mol) of **1** was hydrogenated over Lindlar catalyst (0.40 g) in 30 mL of cyclohexane containing 5 μL of synthetic quinoline. Hydrogen uptake was monitored by GLC ($^1/_8$ in. × 6 ft column, 3% XF-1150) until no **1** remained. The major product, ca. 80%, was separated from overhydrogenated products by GLC ($^1/_4$ in. × 8 ft column, 9% SE-30 at 115 °C),

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though some ring closure during this separation was noted. Samples were stored under nitrogen in the freezer but rapidly absorbed oxygen and formed polymer when exposed to air at room temperature. A purified sample had the following properties: NMR (CCl_4) δ 1.86 (d of d, 3 H, J = 7, 1 Hz), 5.55–6.80 (m, 6 H) 7.05–7.44 (m, 5 H); IR (CCl_4) 1690, 1652, 1622, 1500, 1450, 1378, 960 cm^{-1} UV max (cyclohexane) 304 nm (ϵ 35 000), 317 (40 500), 327 (28 800).

(*Z,Z,E*)-1-Phenyl-1,3,5-heptatriene (6). A sample of **5** was purified by thick-layer chromatography on silica gel with petroleum ether as the eluant. The purified **5** (104 mg) was hydrogenated over 50 mg of Lindlar catalyst in 15 mL of cyclohexane until 1 equiv of hydrogen had been absorbed. The light yellow oily product was chromatographed ($^1/_4$ in. × 4 ft column, 2.5% SE-30 at 155 °C), and the major product (54%) was isolated from the column: NMR (CCl_4) δ 1.84 (d, 3 H, J = 7 Hz), 5.48–6.68 (m, 6 H), 7.16 (s, 5 H); IR (neat) 1639, 1601, 1498, 1450, 945, 770, 695 cm^{-1}; UV max (cyclohexane) 297 nm (ϵ 40 000); mass spectrum, m/e (relative intensity) 170 (93), 155 (100), 141 (36), 138 (41), 115 (51), 91 (75); calcd for $C_{13}H_{14}$ m/e 170.110, found 170.110.

(*E,Z,Z*)-1-Phenyl-1,3,5-heptatriene (4). A freshly purified sample (2.11 g) of **3** was hydrogenated over 0.40 g of Lindlar catalyst in 25 mL of cyclohexane. The desired product was isolated by GLC ($^1/_4$ in. × 8 ft column, 9% SE-30, 165 °C) as the major fraction (85%): NMR (CCl_4) δ 1.90 (d of d, 3 H, J = 7, 1 Hz), 5.4–7.04 (m, 6 H), 7.1–7.4 (m, 5 H); IR (CCl_4) 1495, 1420, 1380, 1240, 965 cm^{-1}; UV max (cyclohexane 307 nm (sh), 318 (ϵ 43 000), 331 (sh).

***cis*-5-Phenyl-6-methyl-1,3-cyclohexadiene (7).** A sample of (*E,Z,E*)-1-phenyl-1,3,5-heptatriene was purified by preparative GLC (9% SE-30 on Chromosorb W at 115 °C or 3% SF-96 at 100 °C), and a 4% solution in spectral grade cyclohexane was degassed and sealed in a Pyrex tube which had been washed with ammonium hydroxide and then with distilled water before drying. The solution was heated in an oil bath for 3 h at 135 °C. An ultraviolet spectrum showed a maximum at 265 nm and residual absorption between 300 and 336 nm. The product was not isolated.

***cis* (and *trans*)-1-Phenyl-2-methylcyclohexane (8 and 9).** The solution from the thermolysis above was hydrogenated at atmospheric pressure over platinum oxide until hydrogen uptake ceased. The product was separated by GLC ($^1/_8$ in. × 14 ft column, 15% Carbowax 20M at 165 °C) into three products. In the order of elution these were 1-phenylheptane [20%; NMR (CCl_4) δ 0.90 (br t, 3 H), 1.3 (br s), 1.45–1.7 (m), 2.59 (t, 2 H, J = 7 Hz), 7.0–7.3 (m, 5 H)], *trans*-1-phenyl-2-methylcyclohexane (0.14%, identified by internal comparison with an authentic sample), and *cis*-1-phenyl-2-methylcyclohexane [80%; NMR (CCl_4) δ 0.66 (d, 3 H, J = 7.0 Hz), 1.2–2.2 (br m, 9 H)8 2.79 (d of t, 1 H, J = 11, 3.5 Hz), 7.0–7.3 (m, 5 H)], a spectrum which matches the literature[20] spectrum. Repeated integrations established the ratio of cis to trans isomers at 550:1.

1-Phenyl-6-methyl-1,3-cyclohexadiene (10). A sample of **6** was separated from overreduced products by thick-layer chromatography on silica gel with petroleum ether as the eluant. A 5% solution of this purified material in spectral grade cyclohexane was degassed and sealed as described above for **7**. The solution was heated in an oil bath for 50 h at 150 °C. Analysis by GLC (2.5% SE-30 on Chromosorb W, 155 °C) indicated the presence of two materials, unchanged starting material (46%) and a new compund (54%). The product was isolated by preparative GLC: UV max 304 nm; NMR (CCl_4) δ 1.04 (d, 3 H, J = 7 Hz), 1.68–2.00 (m), 5.5–6.1 (br m), 7.20 (br s, 5 H); IR (neat) 1600, 1490, 1450, 750, 690 cm^{-1}; mass spectrum, m/e (relative intensity) 170 (100), 155 (98), 129 (27), 128 (32), 115 (31), 91 (53).

***cis*- and *trans*-1-Phenyl-2-methylcyclohexane.** The **10** from thermolysis of **6** was hydrogenated in cyclohexane over platinum oxide until no further hydrogen was absorbed. The product had a UV maximum at 268 nm. Analysis by GLC as above showed the presence of 1-phenylheptane (16%), **9** (6%), and **8** (78%). Under these conditions reduction of the diene gives 93% **8** and 7% **9**.

From 1-Phenyl-2-(and 6-)methylcyclohexenes. A mixture of 1-phenyl-2-(and 6-)methylcyclohexenes was prepared from 2-methylcyclohexanone by the procedure of Pines, Sih, and Lewicki.[20] This mixture (987 mg) was purified by treatment over Raney nickel at atmospheric pressure. The Raney nickel was removed, and 30 mg of platinum oxide was added, and hydrogenation continued until 1.03 equiv of hydrogen had been added. Analysis by GLC as above gave 90% **8** and 10% **9**. The cis isomer was isolated by preparative GLC and had an NMR spectrum identical with the literature[20] spectrum.

Kinetic Studies. All kinetics studies were made in sealed ampules which were washed in concentrated hydroxide, rinsed in distilled water, and dried at 120 °C under nitrogen.

(*E,Z,E*)-1-Phenyl-1,3,5-heptatriene. A sample purified from overhydrogenated products by GLC was made up to a 0.002 M solution in spectral grade cyclohexane. Sealed ampules were heated in an oil bath thermostated to ±0.01 °C. Samples were removed at intervals and analyzed by UV spectrometry at 320 nm. Infinity measures indicated the presence of an unreactive impurity having a strong absorption in that region. This was assumed from its UV spectrum to be (*E,E,E*-1-phenyl-1,3,5-heptatriene [lit.[9] UV max 310 nm (ϵ 38 000), 324 (40 000), 340 (28 100)]. The results were as follows: 113.6 °C, k = 2.24 ± 0.13 × 10^{-5} s^{-1}, 123.5 °C, k = 8.14 ± 0.11 × 10^{-5} s^{-1}; 134.4 °C, k = 2.10 ± 0.05 × 10^{-4} s^{-1}; 143.6 °C, k = 4.26 × 0.04 × 10^{-4} s^{-1}.

(*E,Z,Z*)-1-Phenyl-1,3,5-heptatriene. A GLC-purified sample was made up to 0.01 M in spectral grade cyclohexane containing acenaphthalene (0.005 M) as an internal standard. Sealed ampules were heated in the thermostated oil bath as above, and the products were analyzed by GLC (3% XF-1150 on Chromosorb W at 130 °C). Results were as follows: 177.5 °C, k = 2.34 ± 0.20 × 10^{-5} s^{-1}; 191.4 °C, k = 5.49 ± 0.71 × 10^{-5} s^{-1}.

(*Z,Z,E*)-1-Phenyl-1,3,5-heptatriene. A sample purified by thick-layer chromatography was made up to 0.004 M in spectral grade cyclohexane. Sealed ampules were heated in the thermostated oil bath, and samples were analyzed by GLC (2.5% SE-30 on Chromosorb W at 155 °C). At 150 °C samples were removed at 6, 12, 21, 28, and 36 h and gave k = 4.2 × 10^{-6} s^{-1}.

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Registry No. **1**, 87764-03-2; **2**, 3893-05-8; **3**, 87764-04-3; **4**, 87764-06-5; **5**, 87764-05-4; **6**, 87764-07-6; **7**, 87764-08-7; **10**, 59581-49-6; (*E*)-PhCH=CHBr, 588-72-7; (*Z*)-PhCH=CHBr, 588-73-8; (*E*)-MeCH=CHC≡CH, 2004-69-5; (*Z*)-MeCH=CHC≡CH, 1574-40-9; 2-methylcyclohexanone, 583-60-8.

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A Simple Preparation of a β-Iodo Acetal and a β-Iodo Ketal

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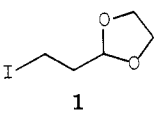
In recent years the ethylene acetal of 3-iodopropanal (**1**)[1] and ketals of 4-iodo-2-butanone[2] have seen frequent use



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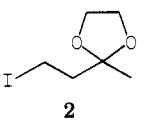

2

(1) (a) Overman, L. E.; Malone, T. C. *J. Org. Chem.* **1982**, *47*, 5297. (b) Iwamoto, M.; Kubota, N.; Takagi, Y.; Kogami, K.; Hayashi, K. *Agric. Biol. Chem.* **1982**, *46*, 2383.

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