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A Facile, Stereospecific Preparation of Olefins from Pinacols

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Considerable attention has been drawn to stereospecific or stereoselective olefin syntheses.[1] Among them, the deoxygenation of pinacols constitutes a convenient route to olefins, especially symmetric ones.[2] The desulfurization of thioncarbonates of pinacols with phosphite[3] is well known, but the method requires not-easily-available thiocarbonyldiimidazole as well as a high reaction temperature. The reaction of benzaldehyde acetal of pinacols with *n*-butyllithium[4] proceeds at a low temperature and has been successfully applied to the preparation of *trans*-cyclooctene, but the attempt to prepare stilbene from dihydrobenzoin has been reported to be unfruitful. In contrast, a third method, discovered by Eastwood *et al.*[5], has proven to be quite useful in the preparation of alkylsubstituted stilbenes and cyclic olefins. The present note will describe the experimental details of these new applications.

A mixture of the pinacol **1b**, for example, an excess of ethyl orthoformate, and a catalytic amount of benzoic acid was heated at 100 °C for 2 hr and subsequently at 170—190 °C for 2 hr to afford, stereospecifically, the **2b** olefin in a good yield. The results are summarized in Table 1, which shows that the sequence provides a beneficial route to stilbestrol.[6] Since the pure *threo* diols, **1d** and **1f**, were unaccessible, a mixture of diastereomers was subjected to the reaction in the case of **1d**. The yields of the *trans*-olefins, **2d** and **2f**, were improved by the isomerization of the corresponding *cis*-olefins (**2c** and **2e**).

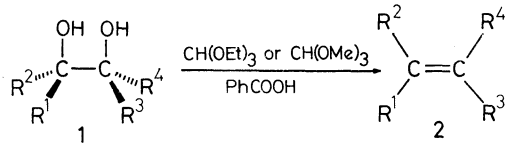

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Table 1. Yields of olefins from pinacols

	Pinacol	Olefin	Y(%)
a: $R^1=R^3=$Ph, $R^2=R_4=$Me	**1a**	**2a**	100
b: $R^1=R^4=$Ph, $R^2=R^3=$Me	**1b**	**2b**	83
c: $R^1=R^3=p$-$MeOC_6H_4$, $R^2=R^4=$Et	**1c**	**2c**	86
d: $R^1=R^4=p$-$MeOC_6H_4$, $R^2=R^3=$Et	**1d** (+**1c**)[a]	**2d**	37[b]
e: $R^1=R^3=p$-$MeOC_6H_4$, $R^2=R^4=$H	**1e**	**2e**	[c]
f: $R^1=R^4=p$-$MeOC_6H_4$, $R^2=R^3=$H	**1e**	**2f**	36
g: R^1, $R^4=-(CH_2)_6-$, $R^2=R^3=$H	**1f**	**2g**	53
h: R^1, $R^3=-(CH_2)_8-$, $R^2=R^4=$H	**1h**	**2h**	67

a) A mixture of stereoisomers obtained by pinacolic reduction.
b) The yield based on *p*-methoxypropiophenone.
c) Not isolated. See experimental.

The method was further found to be applicable to the preparation of *trans*-cyclooctene. *trans*-Cyclooctane-1,2-diol (**1g**) was subjected to the reaction sequence, and the product was immediately distilled off to afford the *trans*-olefin, **2g**, almost quantitatively. Redistillation gave a gas-chromatographically pure sample in a 53% yield. *cis*-Cyclodecene (**2h**) was also obtained stereospecifically in a 67% yield from **1h**.[7]

Experimental

Preparation of trans-*2,3-Diphenyl-2-butene (**2b**).* A mixture of *dl*-2,3-diphenylbutane-2,3-diol (**1b**, 642 mg, 2.65 mmol), ethyl orthoformate (600 mg, 5.6 mmol), and benzoic acid (20 mg, 0.16 mmol) was stirred at 100 °C for 2 hr. The subsequent evaporation of the produced ethanol and the excess orthoformate *in vacuo* gave the crude 1,3-dioxolane (IR 1120—1050 cm^{-1}). Benzoic acid (300 mg) was then added, and the mixture was heated at 170—190 °C for 2 hr, during which time the evolution of carbon dioxide and the refluxing of ethanol were observed. After cooling, dichloromethane (20 ml) was added, and the solution was washed with saturated sodium bicarbonate (four 5 ml portions) and dried with anhydrous potassium carbonate. Concentration gave crystalline **2b** (593 mg). Recrystallization from methanol afforded an analytically-pure sample (460 mg); mp 103—104 °C (lit,[9] 106 °C). NMR (δ, CCl_4): 1.85 (s, 6H) and 7.15 (s, 10H). Mass spectrum: *m/e* 208 (M^+, 100%).

cis-*2,3-Diphenyl-2-butene (**2a**)* (402 mg) was obtained from **1a** (484 mg). NMR (δ, CCl_4): 2.10 (s, 6H) and 6.85 (s, 10H).

cis-*3,4-Di*-p-*methoxyphenyl-3-hexene (**2c**).* The heating of **1c** (660 mg, 2 mmol), ethyl orthoformate (300 mg), and benzoic acid (50 mg) at 170 °C for 1 hr and a subsequent work-up gave **2c** (510 mg); bp 190 °C (bath temperature)/4 mmHg. NMR (δ, CCl_4): 0.90 (t, 6H), 2.44 (q, 4H), 3.52 (s, 6H), 6.40 (d, J=8.4 Hz, 4H), and 6.68 (d, J=8.4 Hz, 4H). Mass spectrum: *m/e* 296 (M^+, 100%).

trans-*3,4-Di*-p-*methoxyphenyl-3-hexene (**2d**).* An isomer mixture of the **1c** and **1d** pinacols obtained by the redcution[6] of *p*-methoxypropiophenone (2.80 g, 17 mmol) was heated at

1) D. J. Faulkner, *Synthesis*, 175 (1971); J Reucroft and P. E. Sammes, *Quart. Rev.* (London), **25**, 135 (1971).

2) Sharpless and Flood have reported recently direct deoxygenation of vicinal diols using tungsten (IV): I. B. Sharpless and T. C. Flood, *Chem. Commun.*, **1972**, 370. The reaction proceeds with poor stereospecificity.

3) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem Soc.*, **87**, 934 (1965); E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, **1968**, 3655.

4) J. N. Hines, M. J. Peagram, G. H. Whitham, and M. Wright, *Chem. Commun.*, **1968**, 1593.

5) J. S. Josan and F. W. Eastwood, *Aust. J. Chem.*, **21**, 2013 (1968); G. Crank and F. W. Eastwood, *ibid.*, **17**, 1392 (1964). See also, F. W. Eastwood, K. J. Harrington, J. S. Josan, and J. L. Pura, *Tetrahedron Lett.*, **1970**, 5223.

6) K. Sisido and H. Nozaki, *J. Amer. Chem. Soc.*, **70**, 776 (1948).

7) The glycol **1h** (mp 130—131 °C) was obtained by sodium borohydride reduction of sebacoin. Cf. ref 11).

8) All temperatures are uncorrected. Infrared spectra were taken on a Shimadzu IR-27G, NMR spectra on a JEOL C-60H, mass spectra on a Hitachi RMU-6L. Benzoic acid used was recrystallized from benzene. Commercial orthoformates were distilled before use.

9) J. K. Cline, E. Campaingne, and J. W. Spies, *J. Amer. Chem. Soc.*, **66**, 1136 (1944).

170—180 °C for 2 hr with ethyl orthoformate (4 ml) and benzoic acid (0.5 g). The addition of *n*-hexane precipitated unchanged **1c** (230 mg). The concentration of the filtrate and the recrystallization of the residue (1.8 g) gave **2d** (640 mg); mp 118—120 °C (lit,[6] 124 °C). The mother liquor was concentrated (*ca.* 1.0 g), and dissolved in chloroform (10 ml) and iodine (0.5 g). The solution was then heated under reflux for 3.5 hr, washed thoroughly with aqueous sodium bisulfite and then with water and dried (sodium sulfate). The subsequent concentration of the solution, followed by the recrystallization of the residue, gave additional **2d** (420 mg). A total of 1.06 g of **2d** was obtained. NMR (δ, CCl_4): 0.75 (t, 6H), 2.09 (q, 4H), 3.74 (s, 6H), 6.72 (d, J=8.4 Hz, 4H), and 6.98 (d, J=8.4 Hz, 4H). Mass spectrum: *m/e* 296 (M^+, 100%).

trans-p,p'-*Dimethoxystilbene (**2f**)*. The heating of hydroanisoin (**1e**) (822 mg, 3 mmol) with ethyl orthoformate (900 mg) for 1 hr at 170—180 °C, followed by the evaporation of the excess orthoformate and ethanol *in vacuo*, gave an oil (**2e**) (1.2 g). This oil was heated with iodine (0.50 g) in chloroform (10 ml) under reflux for 3 hr. Work-up and recrystallization (*n*-hexane–acetone) afforded colorless needles (260 mg); mp 216—218 °C (lit,[10] 214—215 °C).

trans-*Cyclooctene (**2g**)*. *trans*-Cyclooctane-1,2-diol (**1g**) (385 mg, 2.7 mmol), methyl orthoformate (0.5 ml), and benzoic acid (20 mg) were heated at 90—100 °C for 2 hr. The methanol and excess orthoformate were then evaporated under reduced pressure. Benzoic acid (50 mg) was added, and the mixture was heated at 160—170 °C. The olefin thus produced was distilled as were carbon dioxide and methanol. The distillate was placed in dichloromethane, washed with aqueous sodium bicarbonate, and dried (sodium sulfate). Concentration gave crude **2g** quantitatively. Distillation at 90—100 °C (bath temperature)/95 mmHg gave **2g** (155 mg). IR (neat): 3020, 1650, and 982 cm^{-1}. Gas-chromatographic analysis (High Vacuum Silicone Grease, 10%, on Celite 545, 2 m, 60 °C) showed a single peak.

cis-*Cyclodecene (**2h**)*. *cis*-Cyclodecane-1,2-diol (**1h**) (860 mg, 5 mmol), methyl orthoformate (1.0 ml), and benzoic acid (50 mg) were heated at 90—100 °C for 2 hr. After concentration *in vacuo*, benzoic acid (100 mg) was added and the mixture was heated at 160—170 °C for 1 hr. Work-up gave **2h** (465 mg); bp 120—130 °C (bath temperature)/106 mmHg. IR (neat)[11]: 706 cm^{-1}.

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10) P. Hoerings and K. P. Gralert, *Ber.*, **42**, 1204 (1909).

11) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, *J. Amer. Chem. Soc.*, **74**, 3636 (1952).