Table I. Oxidation of Alcohols with Calcium Hypochlorite

entry	starting alcohol	catalyst/solvent/time (h)	ketone formed	% yield
1	cycloheptanol	none/CH_2Cl_2/12	cycloheptanone	24
		IRA 900, Cl^-/CCl_4/3		
		IRA 900, OH^-/CCl_4/3	cycloheptanone	trace
		IRA 900, AcO^-/CCl_4/3		
		IRA 900, OCl^-/CCl_4/3	cycloheptanone	85
		IRA 900, OCl^-/CH_2Cl_2/3	cycloheptanone	92
		IRA 900, OCl^-/ethyl acetate/3	cycloheptanone	85
		IRA 900, OCl^-/ethyl ether/3	cycloheptanone	85
2	cycloheptanol + *n*-heptanol	IRA 900, OCl^-/CCl_4/3	cycloheptanone	85
			n-heptanol	98
3	cycloheptanol	recovered IRA 900, OCl^-		
		2nd run/CCl_4/3	cycloheptanone	85
		3rd run/CCl_4/3		85
4	cyclohexanol	IRA 900, OCl^-/CCl_4/3	cyclohexanone	80
	cyclopentanol	IRA 900, OCl^-/CCl_4/3	cyclopentanone	90
	2-propanol	IRA 900, OCl^-/ethyl ether/3	acetone	95
5	2,6-dimethylcyclohexanol	IRA 900, OCl^-/CCl_4/3	2,6-dimethylcyclohexanone	60[a]
	menthol	IRA 900, OCl^-/CCl_4/3	menthone	28[a]
		IRA 900, OCl^-/CCl_4/12		92[a]

[a] Plus nonreacted alcohol.

polymer or with its hydroxy or acetate forms obtained by anion exchange. Competitive reaction between cycloheptanol and *n*-heptanol (entry 2) results in the oxidation of the secondary alcohol, demonstrating the good selectivity of the method and excluding the inhibition effect reported elsewhere.[3] In contrast with the results under homogeneous phase oxidation by sodium hypochlorite,[4] steric and geometric factors may affect rate constants (entry 5). It must be emphasized finally that the catalyst recovered, without any regeneration process, could be used again several times with no loss of activity (entry 3).

The theoretical aspect of this triphasic catalysis and the possibility of it being extended to other transformations is currently being investigated.

Experimental Section

Reaction mixtures were analyzed by VPC on a Perkin-Elmer Model Sigma 3B flame-ionization instrument, using a 3% Carbowax on a Chromosorb Q column ($^1/_8$ in. × 2 m). Appropriate response factors relative to the chlorobenzene as internal standard were determined for each constituent of the samples injected.

For spectroscopic determination we used a Perkin-Elmer R 12 A (NMR) and a Beckman Acculab (IR).

Starting alcohols were purified by distillation or recrystallization and purity was controlled by VPC. Pure grade solvents, commercial sodium hypochlorite solution[7] and calcium hypochlorite[6] were used without further purification.

Preparation of the Resin Catalysts. Thirty milliliters of commercial IRA 900 (Cl^- form)[8] was successively washed with deionized water (200 mL), 2 M aqueous sodium hydroxide (300 mL), deionized water until neutrality, sodium hypochlorite solution (300 mL), deionized water until neutrality, and anhydrous acetone (300 mL) and finally dried in vacuo at room temperature for several hours. The hypochlorite form thus obtained is noted IRA 900, OCl^- in Table I.

Oxidation of the Alcohols. General Procedure. The alcohol (0.01 mol) was slowly added to a well-stirred suspension of 4 g of calcium hypochlorite and 1 g of IRA 900, OCl^- in 25 mL of a suitable solvent, care being taken to keep the temperature below 40 °C. Stirring at room temperature was continued for 3 h. The solution was filtered (when conducted in CCl_4 the supernatent catalyst may be skimmed for further use) and subjected to VPC analysis and solvent distillation. Given yields, for a 3-h reaction time, have not been optimized.

Acknowledgment. We thank Rohm & Haas Co. for a gift of IRA 900 and are indebted to Miss C. Walton for technical assistance.

Registry No. Cycloheptanol, 502-41-0; *n*-heptanol, 111-70-6; cyclohexanol, 108-93-0; cyclopentanol, 96-41-3; 2-propanol, 67-63-0; 2,6-dimethylcyclohexanol, 5337-72-4; menthol, 1490-04-6; cycloheptanone, 502-42-1; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; acetone, 67-64-1; 2,6-dimethylcyclohexanone, 2816-57-1; menthone, 89-80-5; calcium hypochlorite, 7778-54-3.

(7) From PROLABO (density 1.22; 3.5–4.4 M).
(8) From Rohm & Haas Co.

Palladium Catalysis as a Means for Promoting the Allylic C-Alkylation of Nitro Compounds

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Primary and secondary nitro compounds are valuable synthetic intermediates with one widely recognized limitation. The monoanions derived from them are more prone to alkylate on oxygen rather than on carbon in reactions with most alkyl halides.[1] It seems that virtually all nitro compounds suffer from this liability and that it is particularly pronounced for nitroalkanes. Ethyl α-nitroacetate does undergo some C-alkylation, but even here yields are rarely over 60%.[1,2] We have recently shown that (phenylsulfonyl)nitromethane undergoes C-alkylation, again in somewhat limited yield for simple primary alkyl iodides and benzylic bromides.[3]

Perhaps the most general way to circumvent O-alkylation of a primary nitro compound is to alkylate its α,α-dianion.[4] It is also possible to carry out $S_{RN}1$ reactions

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(2) See, for example: (a) Zen, S.; Kaji, E. *Org. Synth.* **1977**, *57*, 60. (b) Boyd, R. N.; Kelly, R. J. *J. Am. Chem. Soc.* **1952**, *74*, 4600. (c) Kaji, E.; Zen, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 337 (1973).
(3) Wade, P. A.; Hinney, H. R.; Amin, N. V.; Vail, P. D.; Morrow, S. D.; Hardinger, S. A.; Saft, M. S. *J. Org. Chem.* **1981**, *46*, 765.

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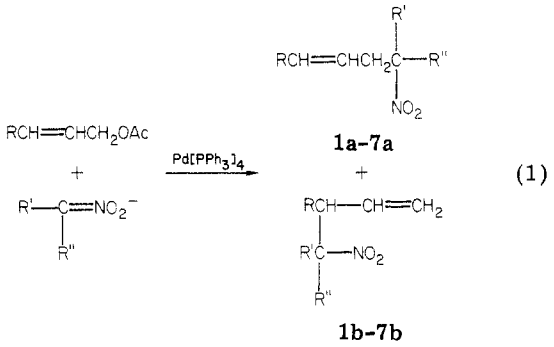
Table I. Palladium Catalyzed C-Alkylation Products

nucleophile	$RCH{=}CHCH_2OAc$	C-alkylate	% yield	a/b ratio
$Li^+CH_3CH{=}NO_2^-$	R = Ph	1; R′ = CH_3, R″ = H	54	87:13
Li^+n-BuCH$=NO_2^-$	R = Ph	2; R′ = n-Bu, R″ = H	57	86:14
$Li^+PhCH{=}NO_2^-$	R = Ph	3; R′ = Ph, R″ = H	84	79:21
$Li^+PhCH{=}NO_2^-$	R = CH_3	4; R′ = Ph, R″ = H	81	49:51
$Li^+EtO_2CCH{=}NO_2^-$	R = Ph	5; R′ = EtO_2C, R″ = H	73	>96:<4
$Li^+EtO_2CCEt{=}NO_2^-$	R = Ph	6; R′ = EtO_2C, R″ = Et	89	>97:<3
$Li^+(CH_3)_2C{=}NO_2^-$	R = Ph	7; R′ = CH_3, R″ = CH_3	29	>93:<7

in certain cases, and these invariably yield C-alkylates.[5] We present here an alternative procedure successful for allylic acetates. This procedure is an extension of work previously reported for (phenylsulfonyl)nitromethane where C-alkylation was found to occur in distinctly higher yield for allylic acetates via a palladium-catalyzed process than for more traditional alkylating agents.[3]

The monoanions of primary nitroalkanes, phenylnitromethane, and α-nitro esters are all preferentially C-alkylated by cinnamyl acetate and 2-butenyl acetate (eq 1).



(1)

The products 1–6 were obtained in 54–89% isolated yields (Table I). As synthetic procedures, these reactions have several attractive features. The monoanions are readily prepared by using lithium methoxide whereas the corresponding dianions would require a much stronger base, on the order of n-butyllithium.[4] It is not necessary for the rigorous exclusion of water; in fact, water is necessary for successful reaction with the anions of nitroalkanes. Secondary nitro compounds can also be alkylated as shown for ethyl 2-nitrobutanoate and 2-nitropropane. The α-nitro ester gave C-alkylate in 89% yield. With 2-nitropropane the C-alkylate was also obtained, but the yield was only 29%. Here the main product was cinnamaldehyde, derived from O-alkylation.

One disadvantage in these reactions is the formation of allylic rearrangement products. This problem appears to result from competitive attack at two sites of a π-allylpalladium intermediate.[6,7] Alternatively, equilibrating σ intermediates might be involved.[8] Particular lack of selectivity was encountered with 2-butenyl acetate, where a 51:49 internal–terminal attack ratio was observed. Factors favoring attack at one of several sites in other palladium-catalyzed reactions have been delineated.[6,7] For cinnamyl acetate, it would seem that steric control and product stability combine to favor terminal attack. The selectivity for terminal attack is high for ethyl 2-nitrobutanoate and 2-nitropropane, two of the bulkier nucleophiles. On the other hand, phenylnitromethane gives considerable internal alkylation despite its size, and ethyl nitroacetate strongly favors the terminal position even though it is not particularly bulky. Clearly the relative isomer ratio depends on several factors and is not simply due to nucleophile size.

Experimental Section

General Methods. Cinnamyl and 2-butenyl acetate were prepared from the corresponding alcohols by using excess acetic anhydride. Phenylnitromethane,[9] 1-nitropentane,[10] ethyl 2-nitrobutanoate,[11] and $Pd[PPh_3]_4$[12] were prepared by standard procedures. Lithium alkoxides were prepared by reaction of Li° with absolute methanol and ethanol. All reactions were run under nitrogen with no special precautions to avoid traces of oxygen. Column chromatographies were performed on "Baker Analyzed" reagent silica gel (60–200 mesh); elution was with 50:50 methylene chloride–carbon tetrachloride. Reactions were routinely worked up by extraction with methylene chloride, washing the organic phase with water, drying over anhydrous sodium sulfate, and concentration at reduced pressure. Other general experimental details have been recently published.[3]

Alkylation of Nitroethane. An ice-cold solution containing lithium methoxide (526 mg, 13.9 mmol) in methanol (10 mL) was treated with nitroethane (1.18 g, 15.7 mmmol), and after 10 min, the volatiles were stripped off under vacuum. The resulting white solid was dissolved in water (5 mL), and THF (65 mL), $Pd[PPh_3]_4$ (0.39 g, 0.34 mmol), triphenylphosphine (0.89 g, 3.39 mmol), and cinnamyl acetate (593 mg, 3.37 mmol) were added. The mixture was refluxed for 2 h, cooled, and added to water–methylene chloride. Acetic acid (20 mL) was added, and the organic layer was separated, washed, dried, and concentrated. The residue was chromatographed to afford the C-alkylate (347 mg, 54% yield) as an oil. VPC analysis indicated this to be an 88:12 mixture of 4-nitro-1-phenyl-1-pentene (**1a**) and 4-nitro-3-phenyl-1-pentene (**1b**), respectively. Kugelrohr distillation gave the analytical sample as a mixture of isomers: bp 70–85 °C (0.1 torr); IR (film) 1570 and 1390 cm^{-1} (NO_2); NMR δ 7.28 (s, 5 H), 6.50 (d, 1 H of **1a**, J = 16 Hz), 6.01 (dt, 1 H of **1a**, J = 7, 16 Hz), 4.8–5.3 (m, 2 H of **1b**), 3.82 (m, 1 H of **1b**), 2.72 (m, 1 H of **1a**), 1.52 (d, 3 H of **1a**, J = 7 Hz), 1.30 (d, 3 H of **1b**, J = 7 Hz).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.82; H, 7.18; N, 7.30.

Alkylation of 1-nitropentane was performed analagously to the alkylation of nitroethane. Column chromatography of the crude product afforded a 59% yield of the C-alkylate as an 86:14 mixture (VPC) of 3-nitro-1-phenyl-1-octene (**2a**) and 3-nitro-3-phenyl-1-octene (**2a**), respectively. These were separated by preparative VPC. Compound **2a** was isolated as an oil: IR (film) 1540, 1370 (NO_2), 960 cm^{-1} ((*E*)-CHR=CHR); NMR[13] δ 7.27 (m, 5 H), 6.45 (d, 1 H, J = 16 Hz), 6.02 (dt, 1 H, J = 7, 16 Hz), 4.53 (m, 1 H), 2.5–2.9 (m, 2 H), 0.8–2.1 (m, 9 H).

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(6) For reviews, see: (a) Trost, B. M. *Acc. Chem. Res.* **1980**, *13*, 385. (b) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615.
(7) (a) Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* **1976**, *41*, 3215. (b) Trost, B. M.; Weber, L.; Strege, P.; Fullerton, T. J.; *J. Am. Chem. Soc.* **1978**, *100*, 3426.
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(10) Prepared similar to 1-nitrooctane: Kornblum, N.; Powers, J. W. *J. Org. Chem.* **1957**, *22*, 455.
(11) Kornblum, N.; Blackwood, R. K. "Organic Syntheses"; Wiley: New York, 1963; Colect. Vol. IV, p 454.
(12) Coulson, D. R. *Inorg. Synth.* **1972**, *13*, 121.
(13) At 250 MHz. We thank Mr. Robert Zipkin and Dr. George Furst (Department of Chemistry, University of Pennsylvania) for obtaining these spectra.

Anal. Calcd for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.80; H, 8.40; N, 6.01.

Compound **1b** was isolated as an oil: IR (film) 1550, 1360 (NO_2), 980, 920 cm^{-1} ($RCH{=}CH_2$); NMR[13] δ 7.15–7.4 (m, 5 H), 5.8–6.1 (m, 1 H), 5.75 (m, 1 H), 3.74 (m, 1 H), 0.8–2.0 (m, 11 H).

Alkylation of 2-Nitropropane. Performed analagously to alkylation of nitroethane except that acetic acid was not added during work-up. Column chromatography of the crude product afforded cinnamaldehyde in 50% yield, identified by its spectra and comparison to an authentic sample. Further elution of the column afforded 4,4-dimethyl-4-nitro-1-phenyl-1-butene (**7a**) in 29% yield. VPC analysis indicated this to be >93% pure with a small amount of the internal isomer. Kugelrohr distillation gave the analytical sample: bp 95–105 C (0.02 torr); IR (film) 1540, 1360 (NO_2), 960 cm^{-1} ((*E*)-RCH=CHR); NMR δ 7.38 (s, 5 H), 6.55 (d, 1 H, J = 16 Hz), 6.02 (dt, 1 H, J = 7, 16 Hz), 2.78 (d, 2 H, J = 7 Hz), 1.62 (s, 6 H).

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.97; H, 7.09; N, 6.96.

Alkylation of Phenylnitromethane. Procedure A: Cinnamyl Acetate. An ice-cold solution containing lithium methoxide (536 mg, 14.1 mmol) in methanol (10 mL) was treated with phenylnitromethane (2.00 g, 14.6 mmmol) and after 10 min, the volatiles were stripped off under vacuum. To the resulting white solid THF (50 mL), $Pd[PPh_3]_4$ (0.40 g, 0.35 mmol), triphenylphosphine (0.89 g, 3.39 mmol), and cinnamyl acetate (618 mg, 3.51 mmol) were added. The mixture was refluxed for 2 h, cooled, and added to water–methylene chloride. Acetic acid (20 mL) was added, and the organic layer was separated, washed, dried, and concentrated. The residue was chromatographed to afford the C-alkylate (746 mg, 84% yield) as a 79:21 mixture (VPC) of 4-nitro-1,4-diphenyl-1-butene (**3a**) and 4-nitro-3,4-diphenyl-1-butene (**3b**), respectively. The major isomer was purified by repeated recrystallization from aqueous ethanol; three recrystallizations were necessary: mp 69–71 °C; IR (KBr) 1534 and 1359 cm^{-1} (NO_2); NMR δ 7.1–7.5 (m, 10 H), 6.53 (d, 1 H, J = 16 Hz), 6.03 (dt, 1 H, J = 7, 16 Hz), 5.55 (dd, 1 H, J = 6, 8 Hz), 2.7–3.7 (m, 2 H).

Anal. Calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.96; H, 5.89; N, 5.58.

Procedure B: 2-Butenyl Acetate. Procedure A was repeated except that 2-butenyl acetate (367 mg, 3.21 mmol) was substituted for cinnamyl acetate. The crude product was chromatographed to afford the C-alkylate (499 mg, 51% yield) as a 49:51 mixture (VPC) of 5-nitro-5-phenyl-2-pentene (**4a**) and 3-methyl-4-nitro-4-phenyl-1-butene (**4b**), respectively. Kugelrohr distillation gave the same mixture of isomers: bp 45–50 °C (0.2 torr). Analytical samples were prepared by preparative VPC. Compound **4a** was obtained as an oil: IR (film) 1547, 1361, (NO_2), 959 cm^{-1} ((*E*)-RCH=CHR); NMR[13] δ 7.37–7.5 (m, 5 H), 5.5–5.7 (m, 1 H) 5.46 (dd, 1 H, J = 6, 8 Hz), 5.2–5.4 (m, 1 H), 2.6–3.2 (m, 2 H), 1.62 (d, 3 H, J = 6.5 Hz).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.88; H, 6.88; N, 7.24.

Compound **4b** was obtained as an oil: IR (film) 1550, 1360 (NO_2), 985, 920 cm^{-1} ($RCH{=}CH_2$); NMR[13] δ 7.3–7.6 (m, 5 H), 4.9–5.9 (m, 4 H), 3.2–3.4 (m, 1 H), 1.17 (d, 3 H of one diastereomer, J = 7 Hz), 0.80 (d, 3 H of one diastereomer, J = 7 Hz).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.15; H, 6.93; N, 7.33.

Alkylation of Ethyl Nitroacetate. Performed in the same manner as the alkylation of phenylnitromethane. Ethyl nitroacetate was removed from the crude product by heating at 37–40 °C (0.02 torr) for 8 h. The residue was chromatographed to afford the C-alkylate in 73% yield as an oil. VPC analysis indicated predominantly (>96:4) ethyl 2-nitro-5-phenyl-4-pentenoate (**5a**). The analytical sample was crystallized from aqueous ethanol: mp 57.5–58.5 °C; IR (KBr) 1750 (C=O), 1560, 1370 cm^{-1} (NO_2); NMR δ 7.33 (s, 5 H), 6.65 (d, 1 H, J = 16 Hz), 6.12 (dt, 1 H, J = 7, 16 Hz), 5.23 (t, 1 H, J = 7 Hz), 4.32 (q, 2 H, J = 7 Hz), 3.12 (t, 2 H, J = 7 Hz), 1.28 (t, 3 H, J = 7 Hz).

Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.41; H, 5.95; N, 5.53.

Also isolated in early fractions from the column was the dialkylate ethyl 2-nitro-5-phenyl-2-(3-phenyl-2-propenyl)-4-pentenoate (72 mg, 11% yield) as an oil: IR (film) 1740 (C=O), 1550, 1370 cm^{-1} (NO_2); NMR δ 7.33 (m, 10 H), 6.57 (d, 2 H, J = 16 Hz), 6.05 (dt, 2 H, J = 7, 16 Hz), 4.28 (q, 2 H, J = 7 Hz), 3.15 (d, 4 H, J = 7 Hz), 1.25 (t, 3 H, J = 7 Hz).

Alkylation of ethyl 2-nitrobutanoate was performed in the same manner as the alkylation of phenylnitromethane except that acetic acid was not added. Column chromatography of the crude product afforded the C-alkylate in 89% yield as an oil. VPC analysis indicated this to be predominantly (>97:3) ethyl 2-ethyl-2-nitro-5-phenyl-4-pentenoate (**6a**): NMR δ 7.27 (s, 5 H), 6.50 (d, 1 H, J = 16 Hz), 5.97 (dt, 1 H, J = 7, 16 Hz), 4.25 (q, 2 H, J = 7 Hz), 3.07 (d, 2 H, J = 7 Hz), 2.27 (q, 2 H, J = 7 Hz), 1.23 (t, 3 H, J = 7 Hz), 0.93 (t, 3 H, J = 7 Hz).

Anal. Calcd for $C_{15}H_{19}NO_4$: C, 64.97; H, 6.91. Found: C, 64.71; H, 6.85.

Registry No. 1a, 79918-44-8; **1b**, 79918-45-9; **2a**, 79918-46-0; **2b**, 79918-47-1; **3a**, 79918-48-2; **3b**, 79918-49-3; **4a**, 79918-50-6; **4b**, 79918-51-7; **5a**, 79918-52-8; **6a**, 79918-53-9; **7a**, 79918-54-0; $Pd(PPh_3)_4$, 14221-02-4; nitroethane, 79-24-3; cinnamyl acetate, 103-54-8; 1-nitropentane, 628-05-7; 2-nitropropane, 79-46-9; phenylnitromethane, 622-42-4; 2-butenyl acetate, 628-08-0; ethyl nitroacetate, 626-35-7; ethyl 2-nitro-4-phenyl-2-(3-phenyl-2-propenyl)-3-butenoate, 79918-55-1; ethyl 2-nitrobutanoate, 2531-81-9; cinnamaldehyde, 104-55-2.

Disproportionation of Aryl Alcohols and Cis to Trans Isomerization of Styryl Derivatives on Palladium/Carbon Catalyst

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Hydrogenolysis of a carbon–oxygen bond α to the aromatic ring in derivatives of benzyl alcohol occurs under a variety of conditions.[1] We found recently that benzyl ethers of carbohydrates (*O*-benzyl derivatives) undergo facile catalytic transer hydrogenolysis at room temperature to toluene and the corresponding sugar in the presence of palladium/carbon, with formic acid as the hydrogen donor and methanol as the solvent.[2] In extending the study to some related classes of compounds, a variety of other reactions have been found to occur on palladium/carbon; these are described here.

In addition to an *O*-benzyl substituent, *O*-triphenylmethyl was readily removed by catalytic transfer hydrogenation in the presence of formic acid. As triphenylmethane was the product, this reaction was analogous to the formation of toluene from the benzyl ether. The corresponding alcohol, triphenylmethanol (**1**), also gave triphenylmethane under the same reaction conditions (Table I), whereas benzyl alcohol (**2**) was unaffected. However, diphenylmethanol (**3**) yielded diphenylmethane, showing that the presence of two adjacent phenyl groups is sufficient to induce hydrogenolysis of the carbon–oxygen bond.

In the *absence* of formic acid, diphenylmethanol (**3**) produced a mixture of benzophenone and diphenylmethane. That is, without an added hydrogen donor, the palladium/carbon functioned as a disproportionation (oxidation–reduction) catalyst.[3] Analogous behavior was

(1) H. O. House, "Modern Synthetic Reactions", 2nd ed., W. A. Benjamin, New York, 1972, p 23.

(2) V. S. Rao and A. S. Perlin, *Carbohydr. Res.*, **83**, 175 (1980).

(3) (a) Disproportionation during heterogeneous catalysis is well-known and may occur as well during homogeneous catalysis; for example, see P. M. Maitlis, "The Organic Chemistry of Palladium", Academic Press, New York, 1971, p 143; (b) M. J. Andrews and C. N. Pillai, *Indian J. Chem., Sect. B*, **16B**, 465 (1978); these authors reported the disproportionation of diphenylcarbinol (**3**) on Raney nickel in xylene at 90 °C.

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