mL). The organic layers were combined and washed with saturated bicarbonate then brine and dried ($MgSO_4$). Addition of a weighed standard anisole was followed by GLC analysis of the benzaldehyde products (5% QF-1, 1.9 m × 0.63 cm, 80 °C, 60 cm^3/min He). Addition of a second weighed standard, methyl *p*-anisate, permitted GLC analysis of the benzophenone yield as above. We had shown earlier that substituted benzaldehydes are obtained nearly quantitatively by this isolation procedure[9b] so that the measured ratio of benzaldehydes is a true measure of the migratory aptitudes of substituted aromatic groups.

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Registry No. 2a, 5824-40-8; **2b**, 53060-13-2; **2c**, 53060-12-1; **2d**, 70428-89-6; **2e**, 53060-10-9; **2f**, 70428-90-9; **2g**, 70428-91-0; **3a**, 91-00-9; **3b**, 2538-34-3; **3c**, 55095-21-1; **3d**, 55095-20-0; **3e**, 28022-43-7; **3f**, 55095-14-2; **3g**, 70428-92-1; **3g** hydrochloride, 49703-61-9; **4b**, 2393-23-9; **4c**, 104-84-7; *p*-$OCH_3C_6H_4(C_6H_5)CO$, 611-94-9; *p*-$CH_3C_6H_4(C_6H_5)CO$, 134-84-9; *m*-$CH_3C_6H_4(C_6H_5)CO$, 643-65-2; *p*-$ClC_6H_4(C_6H_5)CO$, 134-85-0; *m*-$ClC_6H_4(C_6H_5)CO$, 1016-78-0; *m*-(trifluoromethyl)-benzophenone, 728-81-4; *p*-anisidine, 104-94-9; *p*-$OCH_3C_6H_4CHO$, 123-11-5; *p*-$CH_3C_6H_4CHO$, 104-87-0; *m*-$CH_3C_6H_4CHO$, 620-23-5; *p*-ClC_6H_4CHO, 104-88-1; *m*-ClC_6H_4CHO, 587-04-2; *m*-$CF_3C_6H_4CHO$, 454-89-7; benzophenone, 119-61-9; benzaldehyde, 100-52-7; *p*-toluidine, 106-49-0; *m*-(trifluoromethyl)phenyl bromide, 401-78-5; (*m*-(trifluoromethyl)phenyl)diphenylcarbinol, 742-91-6; (*m*-(trifluoromethyl)phenyl)diphenylmethyl chloride, 57381-92-7; (*m*-(trifluoromethyl)phenyl)phenylcarbinol, 728-80-3; *p*-NBSP, 6209-72-9; triphenylcarbinol, 76-84-6.

S_N2 Displacements and Reductive Coupling of Ketones with Olefins in *N,N*-Diethylacetamide and *N*-Ethylpyrrolidone

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N,N-Diethylacetamide (DEA) and *N*-ethylpyrrolidone (NEP) are complementary to hexamethylphosphoric triamide (HMPA), dimethylformamide, and dimethyl sulfoxide as solvents in which to carry out several reactions commonly conducted in polar, aprotic media. Reaction of neopentyl tosylates with lithium halides in DEA and NEP gives good yields of neopentyl halides. Ketones and terminal olefins are reductively coupled to tertiary alcohols in fair to good yields in mixtures containing NEP, sodium, and *tert*-butyl alcohol; 1-hepten-6-one and 1-octen-7-one are cleanly cyclized to five- and six-membered rings, respectively, in good yield by this same mixture. Terminal olefins are reduced to alkanes in fair yield by DEA–sodium–*tert*-butyl alcohol mixtures; di- and tetrasubstituted olefins are resistant to reduction by this mixture.

Hexamethylphosphoric triamide (HMPA) is a dipolar aprotic solvent[1,2] that is particularly valuable for such reactions as S_N2 displacement with anionic nucleophiles[3,4] and dissolving-metal reductions.[5] The routine use of HMPA has been discouraged by the announcement that it may be carcinogenic.[6] In the course of other studies, we required quantities of several neopentyl halides. Compounds of this type had proved in previous work to be most rapidly prepared by displacement of tosylate ion by halide ion using HMPA as solvent.[3,7] A recent paper by Young and Dewald reported that *N,N*-diethylacetamide (DEA) and other tertiary amide solvents dissolved sodium metal and gave blue solutions containing solvated electrons and metal anions.[8] Young and Dewald suggested in passing that the high sodium cation solvating ability and chemical stability indicated by this observation might find application in other types of reactions.[8] Here we describe experiments confirming that DEA and *N*-ethylpyrrolidone (NEP) are comparable to HMPA as solvents for displacement reactions and that they are of significant, but more limited value than HMPA for dissolving-metal reduction of olefins. In addition, we describe a useful new reaction which occurs in NEP (but not in HMPA) by which ketones and terminal olefins are reductively coupled to tertiary alcohols by sodium–*tert*-butyl alcohol mixtures.

Results and Discussion

Bimolecular Substitution in DEA and NEP. Table I lists the yields of alkyl halides detected following the treatment of neopentyl and cyclohexyl tosylates with ca. 2 equiv of lithium halide in various solvents. DEA, NEP, and *N*-acetylpyrrolidine (NAcP) afford marginally higher yields of neopentyl chloride than HMPA and significantly improved yields compared with yields obtained with the common dipolar aprotic solvents *N,N*-dimethylacetamide (DMA), DMF, and Me_2SO. Several analogues of DEA listed in this table proved to be less effective solvents for displacement than their parent structure. Although DEA is comparable to HMPA as a solvent for nucleophilic substitutions involving neopentyl tosylate and 2,2-dimethylpropanediyl 1,3-ditosylate, it is notably poorer than HMPA for nucleophilic displacement of tosylate from 2,2,3,3-tetramethylbutanediyl 1,4-ditosylate with lithium chloride: in addition to lower yields, NEP and DEA appear to give products contaminated by monohalogenated materials (ca. 10–15%); DMF and Me_2SO are again much less effective. The practical utility of DEA as a solvent for displacements at neopentyl centers is indicated by the isolation of good yields of neopentyl chloride, 1-chloro-2,2-diethylbutane, 1,4-dibromo-2,2-dimethylpropane, and pentaerythrityl tetrabromide from preparative-scale reactions. The experimental procedures followed in DEA

(1) For reviews of HMPA, see: Normant, H. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 1046–67; Normant, H. *Bull. Chim. Soc. Fr.* **1968**, 791–826.
(2) Gutmann, V. *CHEMTECH* **1977**, 255–63.
(3) Mosher, H. S.; Stephenson, B.; Solladié, G. *J. Am. Chem. Soc.* **1972**, *94*, 4184–8.
(4) Schlessinger, R. H.; Richman, J. E.; Lee C. S.; Herrmann, J. L.; Cregge, R. J. *Tetrahedron Lett.* **1973**, 2425–28.
(5) Ehmann, W. J.; Whitesides, G. M. *J. Org. Chem.* **1970**, *35*, 3565–7; and references contained therein.
(6) Lloyd, J. W. *J. Am. Ind. Hyg. Assoc.* **1975**, *36*, 917–9; Zapp, J. A., Jr. *Science* **1975**, *190*, 422–3.
(7) Gutowski, F. D.; Whitesides, G. M. *J. Org. Chem.* **1976**, *41*, 2882–5.
(8) Young, C. A.; Dewald, R. R. *J. Chem. Soc., Chem. Commun.* **1977**, 188–9.

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Table I. Conversion of Alkyl Tosylates to the Corresponding Alkyl Halides by Reaction with Lithium Halides in Various Solvents[a]

solvent[b]		GC yield, %					
structure	abbrev	$(CH_3)_3CCH_2Cl$	$(C_2H_5)_3CCH_2Cl$	$[(CH_3)_2CCH_2Cl]_2$	$(CH_3)_2C(CH_2Br)_2$	$C(CH_2Br)_4$	c-$C_6H_{11}Cl$
$CH_2CH_2CH_2CONCH_2CH_3$	NEP	89		52			33[c]
$CH_3CON(CH_2CH_3)_2$	DEA	87 (69)[d,e]	(71)[d,f]	68[g]	101 (70)[d,g]	(65)[d,h]	26
$CH_2(CH_2)_3NCOCH_3$	NAcP	83					
$CH_3CH_2CON(CH_2CH_3)_2$	DEP	79					
$((CH_3)_2N)_3P{=}O$	HMPA	78 (62)[d,i]		102 (85)[d]	102		25
$CH_3CON(CH_3)_2$	DMA	74					24
$CH_2CH_2CH_2CONCH_3$	NMP	70					
$CH_3CON(CH_2CH_2)_2NCH_3$	NMPA	69					
$HCON(CH_3)_2$	DMF	61		24			22
$(CH_3)_2CHCON(CH_2CH_3)_2$	DEB	57					
$CH_3CON(CH_2CH_2)_2O$	NAcM	46					
CH_3SOCH_3	Me_2SO	45	<1	7			14
$CH_3CON(CH(CH_3)_2)_2$	DPA	37					

[a] Unless specified otherwise, displacement reactions on neopentyl tosylates were carried out at 103–110 °C over 12–14-h periods by employing approximately 2 equiv of lithium halide and tosylate concentrations of ca. 0.26 M; the substitution of cyclohexyl tosylate was conducted at 68–72 °C over 20-h periods by employing approximately 2 equiv of lithium chloride and a tosylate concentration of ca. 0.26 M. [b] Abbreviations: NEP, *N*-ethylpyrrolidone; DEA, *N,N*-diethylacetamide; NAcP, *N*-acetylpyrrolidine; DEP, *N,N*-diethylpropionamide; HMPA, hexamethylphosphoric triamide; DMA, *N,N*-dimethylacetamide; NMP, *N*-methylpyrrolidone; NMPA, *N*-methyl-*N'*-acetylpiperazine; DMF, *N,N*-dimethylformamide; DEB, *N,N*-diethylisobutyramide; NAcM, *N*-acetylmorpholine; Me_2SO, dimethyl sulfoxide; DPA, *N,N*-diisopropylacetamide. [c] Cyclohexene (66–70%) was the major product from the treatment of cyclohexyl tosylate with lithium chloride in various solvents. Material balances were 90–99%. [d] The yield was determined by isolation. [e] The concentration of neopentyl tosylate was 0.3 M. [f] The substitution of 2,2-diethylbutyl 1-tosylate was carried out at 150–160 °C over a 36-h period by employing 1.4 equiv of lithium chloride. [g] The concentration of ditosylate was 0.14 M. [h] The substitution of pentaerythrityl tetramesylate was carried out at 135–140 °C over a 48-h period by employing 1.5 equiv of lithium bromide and a mesylate concentration of 0.5 M. [i] Reference 3.

preparations are analogous to those employed with HMPA.[9] Products are easily isolated by dilution of the reaction mixture with 1–2 volumes of water and extraction with an immiscible solvent such as hexane.

Displacement reactions on cyclohexyl rings generally do not proceed well.[10] Table I includes the yields of cyclohexyl chloride obtained from the reaction of cyclohexyl tosylate with lithium chloride in various solvents. Cyclohexyl tosylate primarily undergoes elimination in all of the solvents tested, giving cyclohexene (65–67%) and modest yields of cyclohexyl chloride (14–33%). DEA and NEP appear to offer no special advantage to HMPA or DMF as solvents for this reaction.

Dissolving-Metal Reduction in DEA. Dilute blue solutions are formed when DEA, NEP, and *N,N*-diethylpropionamide (DEP) are stirred vigorously with sodium shot. In comparison, DMA is rapidly decomposed under these conditions and HMPA gives concentrated, almost opaque, blue-black solutions. The blue solutions formed by these *N*-ethylamides are considerably less stable than that formed by HMPA,[11] and persist at room temperature only 2–3 min after removal from the metal. Whereas HMPA–metal solutions are stable even to 1 equiv of *tert*-butyl alcohol, *N*-ethylamide–metal solutions are decolorized instantly by it. HMPA–sodium–*tert*-butyl alcohol mixtures are effective for reducing nonconjugated alkenes and polyalkylated aromatic compounds.[5] We attempted analogous reactions with some simple olefins, and these results are summarized in Table II. Terminal olefins are reduced slowly in fair yield in DEA, DEP, and *N,N*-diethylisobutyramide (DEB), but multiply alkyl-substituted double bonds resist reduction. Various attempts to improve the reducing medium were unsuccessful. For example, sodium–potassium alloy (78 wt % K) and lithium, sodium, and sodium–alumina dispersions appear to reduce DEA[12] and afford only low conversions of 1-hexene to *n*-hexane. HMPA–sodium–*tert*-butyl alcohol mixtures are noticeably stabilized by the addition of THF as a cosolvent, although their reactivity toward reducible substances seems undiminished.[11] The addition of THF or TMEDA to DEA as cosolvents did not enhance the solubility of sodium or stabilize the resultant blue solution

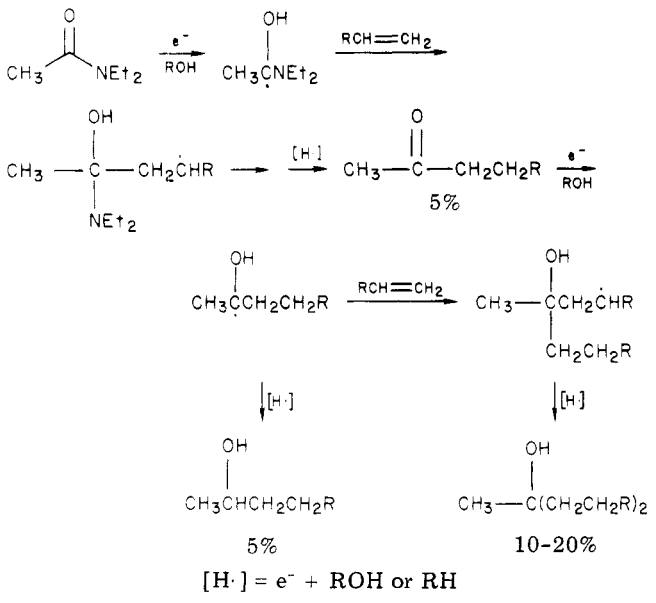
Table II. Reduction of Olefins to Hydrocarbons with Sodium and *tert*-Butyl Alcohol[a]

reactant	solvent[b]	product	yield, % (starting material, %)
1-hexene	HMPA	*n*-hexane	98[c]
	DEP		69 (4)
	DEB		62 (19)
	DEA		55 (3)
	DPA		37 (46)
	NEP		16 (17)
	NMPA		1 (75)
	NAcP		1 (64)
cyclohexene	HMPA	cyclohexane	99[c]
	DEA		15 (80)
	DEP		10 (90)
tetramethylethylene	DEA	2,3-dimethylbutane	<1 (100)

[a] Reactions were carried out by vigorously stirring a mixture of sodium shot (ca. 0.3 g, 13 mmol), olefin (1.2 mmol), and *tert*-butyl alcohol (0.3-mL aliquots (ca. 3 mmol) added at 6–8-h intervals) in the specified solvent (6.0 mL) at ambient temperature over 17–24-h periods. [b] Abbreviations are the same as those used in Table I. [c] Reference 5.

(9) Morris, F. H.; Le Nobel, W. J. *J. Org. Chem.* **1969**, *34*, 1969–73.
(10) Hsia, D. Y.; Parries, G. S.; Shaw, J. E.; Sawyer, T. K. *J. Org. Chem.* **1978**, *43*, 1017–8.
(11) Bowers, K. W.; Giese, R. W.; Grimshaw, J.; House, H. O.; Kolodny, N. H.; Kronberger, K.; Roe, D. K. *J. Am. Chem. Soc.* **1970**, *92*, 2783–99.
(12) Larcheveque, M.; Cuvigny, T.; Normant, H. *C. R. Hebd. Seances Acad. Sci., Ser.* **1973**, *276*, 209–12.

Scheme I



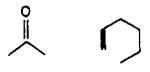
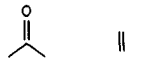
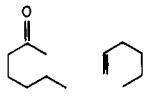
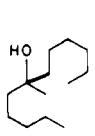
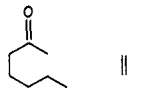
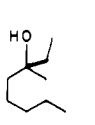
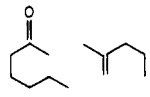
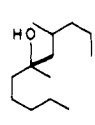
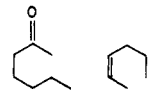
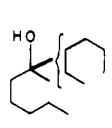
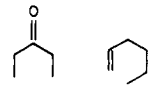
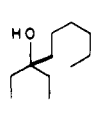
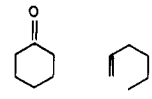
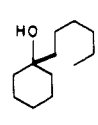
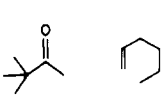
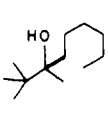
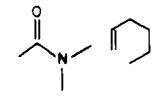
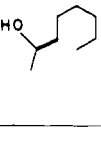
toward *tert*-butyl alcohol; poor conversions of terminal olefin to reduced hydrocarbon resulted from use of these mixed solvents. Attempts to employ proton donors less acidic than *tert*-butyl alcohol (e.g., *n*-propylamine, ethylenediamine, morpholine) gave low yields of *n*-hexane from 1-hexene. The incremental addition of alcohol to blue DEA–sodium–1-hexene mixtures also produced low yields of *n*-hexane.

Our qualitative observations indicate that the dissolution of sodium in HMPA, liquid ammonia, and ethylenediamine is considerably more facile than in *N*-ethylamide solvents and that HMPA is superior for the dissolving-metal reductions of olefins to saturated hydrocarbons.

Reductive Coupling of Ketones with Olefins in NEP. Examination of the side products formed during reduction of 1-hexene to *n*-hexane in DEA–sodium–*tert*-butyl alcohol mixtures revealed small amounts of chain-extended products such as 2-octanone (ca. 5%), 2-octanol (≤5%), and 7-methyl-7-tridecanol (10–20%) (Scheme I). These and related products incorporating solvent moieties from DEA or other solvents make up the major part of the mass balance not reported as *n*-hexane or 1-hexene in Table I. The C8 and C14 products observed in DEA are probably produced by the addition of α-aminol and α-hydroxy radicals (or DEA and 2-octanone radical anions) to the terminal carbon of 1-hexene. The reduction of these intermediate radicals to saturated products can then occur either by single-electron reduction and protonation or by hydrogen atom abstraction from the solvent. The addition of α-hydroxy radicals generated from primary or secondary alcohols under free-radical conditions to terminal olefins is well-known,[13] but α-aminol additions have not been reported. Development of this reaction established that moderate to good yields of tertiary alcohols could be prepared by reductive coupling of ketones and terminal alkenes on a small scale (1–5 mmol) in NEP, but other types of carbonyl compounds (e.g., amides, esters, aldehydes) did not result in significant yields of coupled products. Representative reactions are summarized in Table III. In a typical example, 1 equiv of 2-heptanone and excess *tert*-butyl alcohol were added in portions to a vigorously stirred 1-hexene–sodium–NEP mixture at 25

(13) Sosnovsky, G. "Free Radical Reactions in Preparative Organic Chemistry"; Macmillan: New York, N.Y., 1964; pp 121–5; and references included therein.

Table III. Intermolecular Reductive Coupling of Carbonyl Groups with Olefins in NEP[a]

Carbonyl Cmpd.	Olefin	Product	Carbonyl: Olefin Ratio	GLC Yield %[b]
			1:1	52
			2:1	75 [19-35][c]
			1:2	51
				55[d]
			1:1	65
			2:1	81
			1:2	63
				51[d]
			1:1	21
			2:1	41
			1:1	≤5
			1:1	51
			2:1	62
			1:2	59
			1:1	42
			2:1	54
			1:2	40
			1:1	11
			1:1	9[e]
			3:1	18

[a] Olefin and ketone (1–5 mmol) were allowed to react in the specified stoichiometry with vigorously stirred sodium shot (ca. 0.69, 26 mg-atom) and tert-butyl alcohol (0.8 mL, 9 mmol) in NEP (6.0 mL) at ambient temperature. In each product structure, the newly-formed carbon–carbon bond is indicated with a heavy line to simplify interpretation. [b] Yields are based on the limiting reagent. [c] The yield of 2-methyl-2-octanol was determined by isolation following chromatography of the crude residue over silica gel and distillation. The yield of product decreases in the process of scaling up the reaction: acetone (51 mmol) and 1-hexene (27 mmol) reacted with sodium shot (0.22 g-atom) and tert-butyl alcohol (0.1 mol) in NEP (50 mL) at ca. 20°C and gave 2-methyl-2-octanol in only 48% yield as determined by internal standard technique and GLC. [d] Ketone was allowed to react with sodium–tert-butyl alcohol in NEP under a static head of ethylene (40 psi). The yield is based on ketone.

°C over a 1-h period. The mixture was worked up by cautiously quenching the supernatant solution with an equal volume of water and extracting with pentane; the extract was found to contain *n*-hexane (5%), 1-hexene (17%), 2-heptanol (16%), and 6-methyl-6-dodecanol (66%). Employing a two- or threefold excess of 2-heptanone increased the yield of coupled product to 75–81%, based on the limiting reactant 1-hexene; using an excess of 1-hexene with various ketones generally did not improve the yield over that of the 1:1 stoichiometry. The proportion of ketone reduction to alcohol and reductive coupling with 1-hexene depends on the solvent used: the reduction of 2-heptanone and 1-hexene in liquid ammonia–ether affords no 6-methyl-6-dodecanol (<1%), but modest yields are obtained in ethylenediamine–ether (6%), HMPA (ca. 10%), and the *N*-ethylamides DEB (9%), DEP (21%), and DEA (40%). The coupling procedure fails if the ketone is converted to enolate by the accumulating strong bases arising from amide or lactam decompositions,[12] and a relatively acidic proton source, like *tert*-butyl alcohol, is required in moderate excess. Warming a 2-heptanone–1-hexene–NEP mixture to 48 °C resulted in lowered yields of coupled products (56%), and cooling a mixture to −20 °C slowed the reaction to an impractical rate. The presence of cosolvents such as HMPA or EDA had no influence on the yield.

The reductive coupling reaction proceeded in lower yield in larger scale trials (0.03–0.12 mol (ca. 0.6 M) 1-hexene) and isolated yields of product following chromatography over silica gel and distillation were only 20–30%. Control experiments established that reduction of ketone to alcohol becomes more important relative to coupling of ketone and olefin when the reaction is scaled up. It is possible that changes in the surface to volume ratio of the sodium metal are responsible for the decreased yields of coupled product. Vigorous stirring of these larger preparations beats the sodium shot into a large, smooth lump, once the particle surfaces have become chemically clean in the presence of the solvent. A Hershberg type of stirrer (braided wire strands) was no more effective than a Teflon paddle for dispersing the soft metal lump. The inclusion of diluent particles such as fine sand (ca. 15 wt %), glass powder, or polyacrylamide polymer particles (ca. 25 wt %) did not alleviate the problem noticeably or improve the yield of coupled product. The presence of the dispersing agent oleic acid (4 wt %) had no effect on the reaction course. We attempted to reduce the malleability of the sodium by preparing a high-melting 25% bismuth alloy in situ from sodium–NEP and bismuth tribromide.[14] The reduction of bismuth tribromide produced a fine, gray suspension, but this mixture had low reactivity: 2-heptanone in the presence of 1-hexene and *tert*-butyl alcohol was incompletely reduced and a mixture of 2-heptanone (19%), 2-heptanol (21%), and couple (6-methyl-6-dodecanol, 4%) was obtained. We are continuing to investigate the effects of other amide solvents and the composition and form of dissolving metals such as sodium on carbonyl–olefin reductive coupling.

The proportion of ketone–olefin coupling and ketone reduction in NEP decreases as the steric bulk of the alkyl substituents around either functional group increases. Acetone, 2-heptanone, and 3-pentanone gave 50–65% yields of coupled product with 1-hexene, but pinacolone gave a very low yield (10%). The terminal olefin 1-hexene and ethylene reacted with 2-heptanone (50–65% yield of coupled product), but the geminally disubstituted olefin 2-methyl-1-pentene underwent addition poorly (20%), and vicinal di- and trisubstituted olefins gave only traces (<5%) of coupled products.

Extension of the reductive addition reaction to other carbonyl compounds was not successful. Heptanal and other aldehydes containing α protons appeared to suffer base-catalyzed condensation before reduction took place; pivaldehyde, which does not bear α protons, did undergo reduction to neopentanol but afforded only traces of coupled product with 1-hexene (<5%). The addition of anhydrous formaldehyde to 1-hexene in an NEP–sodium–*tert*-butyl alcohol mixture did not produce 1-heptanol (<1%). Acyl derivatives may react with 1-hexene to give products incorporating one or two olefin units: a threefold excess of DMA relative to 1-hexene affored both 2-octanol (18%) and traces of 7-methyl-7-tridecanol (5%), but ethyl acetate, acetyl chloride, and acetic anhydride did not give coupled products. A ketimine (acetone *N*-propylimine) and an aldimine (acetaldehyde *N*-propylimine) did not undergo addition to 1-hexene to give secondary amines under the conditions we examined. Reductive coupling of acetone with either 1,3-butadiene or isoprene in these mixtures did not take place (traces of materials were isolated that had spectroscopic properties consistent with *N*-pentenyl- and *N*-hexenylpyrrolidone from 1,3-butadiene and isoprene, respectively, suggesting the trapping of solvent-derived radicals by the diene reactant). Terminal acetylenes appeared to undergo predominantly reduction to terminal alkenes, which then underwent reductive coupling with acetone to give fully saturated tertiary alcohols. Internal alkynes were unreactive: 4-octyne was recovered in 80% yield from reaction with acetone under these reductive coupling conditions.

Intramolecular ketone–olefin[15] and ketone–alkyne[16] reductive coupling by dissolving-metal mixtures has been observed previously only in stereochemically rigid systems, but five- and six-membered tertiary alcohols have been prepared by *electrochemical* cyclization of nonconjugated enones in either diethyl ether or DMF.[17] We found that nonconjugated enones can also be reductively cyclized to five- and six-membered rings in good yield by NEP–sodium–*tert*-butyl alcohol mixtures, and representative examples are summarized in Table IV. For example, 1-hepten-6-one afforded a diasteromeric mixture of 1,2-dimethylcyclopentanols accompanied by only traces of 1-methylcyclohexanol and noncyclized alcohol (≤3%). Similarly, 1-octen-7-one cyclized to a mixture of 1,2-dimethylcyclohexanols (80%), attended by traces of 1-octen-7-ol (≤3%). The regioselective exo closure of these precursors to five- or six-membered 1,2-dimethylcycloalkanols is in accord with numerous observations in the literature.[18,19] Intramolecular cyclization of 1-hexen-5-one apparently did not compete with intermolecular coupling, and only low yields of 1-methylcyclopentanol and 1,2-dimethylcyclobutanols (≤5%) and 1-hexen-5-ol (5%) were detected. Modest yields of intermediate rings were obtained from 1-nonen-8-one by this method: both endo product 1-methylcyclooctanol (12%) and exo product 1,2-dimethylcycloheptanol (6%) were formed; 1-nonen-8-ol

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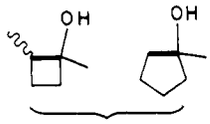
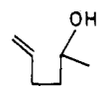
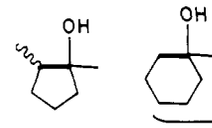
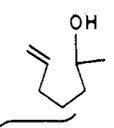
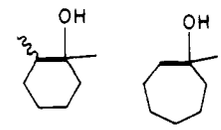
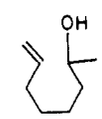
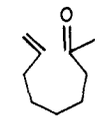
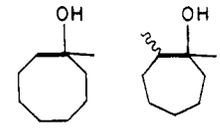
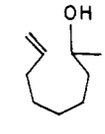
Table IV. Intramolecular Reductive Coupling of Ketoolefins in NEP[a]

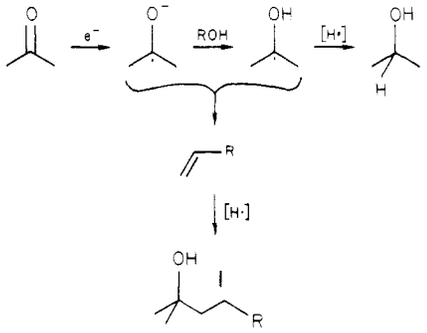
Enone	Products (GLC Yields, %)		
			
	<5		<5
			
	65		<3
			
	80	<1	<3
			
	12	6	<20

[a] The ketoolefin (2.0 mmol) was allowed to react with vigorously stirred sodim shot (ca. 0.6 g, 26 Mg-atom) and tert-butyl alcohol (0.8 mL, 9 mmol) in NEP (6.0 mL) at ambient temperature.

and 2-nonanol (≤20%) and intermolecular coupling products presumably completed the material balance.

Some suggestions about the essential mechanistic features of the reductive coupling of ketones with terminal olefins can be drawn from these observations. The C–C bond-forming step probably involves the addition of the intermediate ketyl radical anion or α-hydroxy radical derived from one-electron reduction of the ketone to the exo carbon of the terminal olefin[13,18] (Scheme II). This intermediate alkyl radical could undergo subsequent reduction by single-electron transfer and protonation or by hydrogen atom abstraction from any one of several good hydrogen donors that are present. The ketyl anion or α-hydroxy radical that does not add appears to suffer reduction to the secondary alcohol by these same sequences. Examples of C–C bond formation by the addition of either reactive intermediate to a terminal olefin have appeared. Generating α-hydroxy radicals from primary or secondary alcohols and initiators in the presence of terminal olefins gives preparatively useful yields of the coupled product.[13] The electrochemical reductive cyclization of 1-octen-7-one gives comparable yields of 1,2-dimethylcyclohexanol under protic (1:9 (v/v) methanol/dioxane–tetraethylammonium *p*-toluenesulfonate) or

Scheme II



[H·] = e⁻ + ROH or RH

aprotic conditions (anhydrous DMF–tetraethylammonium *p*-toluenesulfonate).[17] Thus either reactive species is capable of facile olefin addition, and it is not possible to distinguish which is involved in reductive coupling in sodium–*tert*-butyl alcohol–NEP mixtures on this basis. A mechanism involving the addition of olefin radical anions or sodium alkyls to the ketone carbonyl in reductive coupling by NEP–sodium–*tert*-butyl alcohol does not appear probable. The reduction of terminal olefins by *N*-ethylamide–sodium–*tert*-butyl alcohol mixtures proceeds to 50% completion after 5–10 h, and olefins do not visibly react with blue *N*-ethylamide–sodium solutions. In contrast, ketones instantly decolorize these blue solutions, and the reductive coupling reaction is complete within 1 h. Thus, the rate of reaction of olefins in NEP–sodium–*tert*-butyl alcohol is not fast enough to account for the observed rate of formation of coupled product.

Conclusions

DEA and NEP are comparable to HMPA, and superior to other polar aprotic solvents, as media in which to carry out nucleophilic displacement reactions at neopentyl centers. Both are sufficiently stable toward reduction that they allow the reductive coupling of ketones with olefins in the presence of sodium and *tert*-butyl alcohol (Scheme II). Reductions of olefins to hydrocarbons can also be accomplished by these solvents in the absence of ketones, but this reaction is unlikely to prove useful in synthesis in other than unusual circumstances.

Several characteristics of the interesting reductive coupling reaction deserve brief comment. First, DEA and NEP are considerably more stable toward dissolved sodium than dimethylformamide, dimethylacetamide, and *N*-methylpyrrolidone. The relatively low stability of DMF in the presence of strong bases is well-known and seems to be a result of rapid base-catalyzed decarbonylation. The mechanistic origin of the difference in stability between (di)methylamides and (di)ethylamides (and higher (di)-alkylamides) is not presently clear but is important in choosing amide-containing solvents for these strongly reducing reactions. Second, it is unclear whether the reductive coupling reaction occurs at the sodium surface or in solution. DEA and NEP do dissolve sodium and give blue solutions, but reaction mixtures are colorless during the reductive coupling reaction. Further, HMPA forms much more concentrated solutions of sodium than do DEA and NEP, but only the latter solvents yield the tertiary alcohols derived from reductive coupling: in HMPA, reduction of ketone to alcohol is the only important reaction. Although this difference might simply reflect the partitioning of an intermediate ketyl or protonated ketyl between addition to olefin and reduction to alcohol(ate), it may also indicate some more major difference in

mechanism. Third, in a practical sense, this reaction is presently only useful for the preparation of small quantities (<5 mmol) of products: yields decrease significantly when the reaction is scaled up. Our qualitative observations suggest that the aggregation of sodium during the reaction, and the consequent decrease in sodium surface, is an important contributor to this decrease in yield. It may be possible to circumvent this problem by high-speed stirring or by other mechanical or chemical means of maintaining a high sodium surface area. Alternatively, electrochemical reductions in DEA or NEP might prove valuable. Until these possibilities have been tested experimentally, however, the reaction should be considered only for small-scale preparations.

Although toxicity data regarding DEA and other amides are scarce,[20] these solvents have the combination of high solvent power and miscibility with both organic solvents and water which would be expected to make them effective in facilitating passive transport of both organic and inorganic materials through the skin and cell walls. Solutions of toxic substances in these solvents should be handled with care.

Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Boiling points are uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer Model 567 grating infrared spectrometer and are reported in wavenumbers. Proton NMR spectra were determined on a Varian Associates Model T-60 spectrometer and are reported in parts per million downfield from Me_4Si. Mass spectra were obtained on a Varian Model MAT 44 instrument at an ionizing voltage of 70 eV. Elemental analyses were performed by Robertson Laboratory, Florham Park, N.J. GLC analyses were carried out on a Perkin-Elmer Model 990 or 3920B gas chromatograph equipped with a flame ionization detector. Neopentyl and cyclohexyl halides were analyzed by using a 9-ft column of 20% SE-30 on 80–100 Chrom P; hydrocarbons were analyzed with a 30-ft column of 10% TCEP on 80–100 Chrom P; secondary alcohols and ketones were separated on a 9-ft column of 5% Carbowax 20M on 80–100 Chrom W; tertiary alcohols were detected following chromatography on a 12-ft HiPak column of UC-W98 on 80–100 WHP. Products were identified by peak-height enhancement resulting from coinjection of an authentic sample and by mass spectroscopy on a Hewlett-Packard 5992A GC/MS. Reagent grade HMPA, DMA, NMP, DEA, NEP, DEP, Me_2SO, and DMF were obtained from commercial sources and were purified by distillation from calcium hydride through a 26-cm column at reduced pressure. HMPA (bp 88.9–89.0 °C (8 torr)), DEA (bp 105.0–107.0 °C (61 torr)), NEP (bp 78.0–78.5 °C (90 torr)), and DEP (bp 81.3–82.0 °C (10 torr)) were redistilled through the same column from molten sodium.[21] Reagent grade *tert*-butyl alcohol was distilled from sodium metal under nitrogen. Reactants such as olefins and ketones were purified immediately before use by passage through a 2-in. column of grade I alumina. Dissolving-metal reductions and couplings were performed in 15-mL polymerization tubes (Lab Glass) that were sealed with 0.25-in. butyl rubber septa and crown caps. All reactions were carried out in flame-dried glassware under an inert atmosphere of prepurified nitrogen or argon by using routine techniques for handling oxygen- and moisture-sensitive materials.[22]

General Preparation of Ethylamides. Additional amides were prepared by routine methods.[23] *N*-Acetylmorpholine (79%): bp 139.0–139.8 °C (26 torr) (lit.[24] 117–118 (13 torr)); ^1H NMR ($CDCl_3$) δ 3.60 (8 H, broadened, split s), 2.1 (3 H, s). *N*-methyl-*N'*-acetylpiperazine (39%): bp 129.0–129.8 °C (19.5 torr) (lit.[25] 168 °C (760 torr)); ^1H NMR ($CDCl_3$) δ 3.50 (4 H, m), ca. 2.3 (7 H, superimposed s and m), 2.10 (3 H, s). *N*-Acetylpyrrolidine (51%): bp 111.0–113.0 °C (15 torr); ^1H NMR ($CDCl_3$) δ 3.21 (4 H, t), 2.0 (7 H, superimposed s and m). *N,N*-Diisopropylacetamide (85%): bp 97.5–99.0 °C (24 torr) (lit.[24] 80 °C (13 torr)); ^1H NMR ($CDCl_3$) δ 3.6 (2 H, broad m), 2.05 (3 H, s), 1.25 (12 H, "t"). *N,N*-Diethylisobutyramide was prepared from isobutyric acid by conversion to its acid chloride (63%) with thionyl chloride and treatment with 2 equiv of diethylamine in diethyl ether:[23] bp 90.0–92.0 °C (19 torr) (lit.[26] 75.0–76.0 °C (8 torr)); ^1H NMR ($CDCl_3$) δ 3.38 (4 H, q), 3.70 (1 H, sep), 1.1 (12 H, superimposed d and t).

Preparation of Authentic Samples of Alcohol Products. Samples of various tertiary alcohols were prepared in routine fashion from ketones and Grignard or lithium reagents[27] and were characterized by standard spectroscopic techniques and comparison of physical properties with literature values, when available. The boiling points and mass spectral data of a series of alcohols that were prepared from *n*-hexylmagnesium chloride and the appropriate ketone are listed as follows. 7-Methyl-7-tridecanol: bp 156–158 °C (19 torr); mass spectrum *m/e* (relative intensity) 199 (7), 130 (11), 119 (100), 111 (6), 71 (7), 69 (42), 58 (5), 57(6), 55 (11), 45 (5), 43 (15), 41 (8). 6-Methyl-6-dodecanol: bp 118–122 °C (5 torr); mass spectrum *m/e* (relative intensity) 185 (6), 130 (7), 129 (70), 116 (8), 115 (100), 114 (5), 111 (6), 99 (7), 97 (20), 85 (6), 83 (6), 71 (21), 70 (6), 69 (57), 59 (10), 58 (19), 57 (15), 56 (14), 55 (54), 45 (32), 44 (9), 43 (83), 42 (13), 41 (43). 3-Ethyl-3-nonanol: bp 123.5–125.0 °C (30 torr); mass spectrum *m/e* (relative intensity) 144 (8), 143 (80), 88 (6), 87 (100), 85 (10), 83 (27), 73 (6), 70 (5), 69 (63), 59 (18), 57 (33), 55 (22), 45 (28), 43 (24), 41 (24), 39 (6). 2-Methyl-2-octanol: bp 127.0–128.5 °C (87 torr) (lit.[28] 80 °C (12.5 torr)); mass spectrum *m/e* (relative intensity) 129 (13), 69 (17), 59 (100), 58 (5), 55 (6), 43 (14), 41 (10). 1-*n*-Hexylcyclohexanol: bp 125.0–127.0 °C (7 torr) (lit.[29] 172 °C (100 torr)): mass spectrum *m/e* (relative intensity) 141 (8), 114 (4), 113 (12), 100 (7), 99 (100), 81 (34), 72 (6), 71 (9), 67 (8), 58 (8), 57 (16), 55 (17), 43 (13), 41 (13), 29 (7). A sample of 2,2,3-trimethyl-3-nonanol was prepared from 1-lithiohexane and pinacolone: bp 122.0–123.0 °C (24 torr); mass spectrum *m/e* (relative intensity) 130 (6), 129 (75), 102 (6), 101 (79), 85 (13), 83 (36), 71 (19), 70 (7), 69 (100), 59 (27), 58 (12), 57 (33), 55 (38), 45 (20), 43 (57), 41 (43), 39 (9), 29 (30). 2,2-Dimethyl-3-nonanol was prepared from pivaldehyde and *n*-hexylmagnesium chloride: bp 145.0–146.0 °C (92 torr) (lit.[30] 90 °C (13 torr)); mass spectrum *m/e* (relative intensity) 115 (11), 97 (45), 96 (8), 87 (16), 71 (10), 70 (7), 69 (25), 58 (6), 57 (68), 55 (100), 54 (7), 45 (13), 44 (15), 43 (52), 42 (17), 41 (75), 40 (10), 39 (21). A sample of 4,6-dimethyl-6-undecanol was prepared from 2-heptanone and 2-methylpentyl-1-magnesium bromide: bp 174.0–175.0 °C (98 torr); mass spectrum *m/e* (relative intensity) 129 (54), 116 (7), 115 (100), 111 (9), 97 (16), 85 (18), 83 (8), 71 (29), 70 (10), 69 (33), 59 (27), 58 (11), 57 (18), 56 (11), 55 (44), 45 (16), 43 (59), 41 (30), 39 (7), 29 (22). The addition of ethylmagnesium bromide to heptanone afforded 3-methyl-3-octanol: bp 113.0–114.5 °C (58 torr) (lit.[31] 80–81 °C (15 torr)); mass spectrum *m/e* (relative intensity) 129 (13), 115 (40), 97 (9), 74 (11), 73 (100), 71 (8), 70 (8), 69 (10), 59 (13), 57 (8), 55 (33), 45 (9), 43 (17), 41 (11). 2-Methyl-2-butanol was obtained commercially.

Authentic samples of cyclic tertiary alcohols were prepared from the appropriate cycloalkanone and methyllithium. A sample of 2-methylcyclooctanone was synthesized according to a literature procedure;[32] all other ketones were obtained commercially.

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Spectral and physical properties of this series of compounds are as follows. 1-Methylcyclopentanol: bp 74.0–75.5 °C (64 torr) (lit.[33] 134 °C (760 torr)); mass spectrum *m/e* (relative intensity) 85 (14), 84 (6), 72 (8), 71 (100), 70 (7), 67 (14), 59 (6), 58 (71), 57 (27), 56 (8), 55 (27), 53 (5), 45 (8), 44 (5), 43 (96), 42 (12), 41 (29), 40 (7), 39 (19). Racemic 1,2-dimethylcyclopentanol: bp 83.0–86.0 °C (65 torr) (lit.[34] 70 °C (25 torr)); mass spectrum *m/e* (relative intensity) 99 (5), 86 (12), 85 (21), 84 (19), 83 (5), 81 (9), 72 (18), 71 (84), 70 (10), 69 (7), 59 (53), 58 (50), 57 (26), 56 (9), 55 (26), 53 (6), 51 (15), 49 (44), 48 (6), 47 (8), 45 (11), 44 (6), 43 (100), 42 (26), 41 (36), 40 (11), 39 (20). 1-Methylcyclohexanol: bp 87.0–89.0 °C (61 torr) (lit.[35] 69–70 °C (30 torr)); mass spectrum *m/e* (relative intensity) 99 (12), 98 (9), 86 (14), 85 (10), 84 (23), 83 (6), 81 (15), 72 (13), 71 (100), 70 (14), 69 (11), 59 (17), 58 (41), 57 (12), 56 (7), 55 (51), 54 (8), 53 (7), 51 (22), 50 (6), 49 (65), 48 (10), 47 (12), 45 (7), 43 (73), 42 (41), 40 (18), 39 (23). Racemic 1,2-dimethylcyclohexanol: bp 94.5–95.0 °C (60 torr) (lit.[34] 83 °C (25 torr)); mass spectrum *m/e* (relative intensity) 128 (7, M^+), 113 (8), 86 (17), 85 (26), 84 (23), 83 (6), 81 (7), 72 (15), 71 (100), 70 (11), 69 (10), 68 (15), 67 (8), 59 (12), 58 (39), 57 (21), 56 (7), 55 (21), 53 (7), 41 (21), 50 (5), 49 (65), 48 (10), 47 (12), 45 (12), 44 (16), 43 (83), 42 (19), 41 (38), 40 (17), 39 (21). 1-Methylcycloheptanol: bp 60.5–62.0 °C (3 torr) (lit.[36] 75 °C (12 torr)); mass spectrum *m/e* (relative intensity) 113 (19), 95 (10), 86 (5), 85 (12), 72 (10), 71 (100), 69 (6), 68 (10), 67 (6), 59 (6), 58 (25), 57 (6), 55 (7), 43 (29), 41 (13). 1-Methylcyclooctanol: bp 72.0–74.0 °C (3 torr); mass spectrum *m/e* (relative intensity) 127 (12), 99 (7), 82 (10), 72 (7), 71 (100), 67 (9), 59 (10), 58 (42), 57 (8), 55 (11), 43 (31), 41 (15), 39 (8). 1,2-Dimethylcycloheptanol: bp 103.0–103.5 °C (34 torr) (lit.[37] 83–86 °C (8 torr)); mass spectrum *m/e* (relative intensity) 142 (6), 127 (12), 109 (9), 99 (10), 86 (10), 85 (49), 83 (18), 82 (10), 72 (20), 71 (100), 69 (16), 68 (6), 67 (12), 59 (9), 58 (25), 57 (19), 55 (15), 45 (7), 43 (43), 42 (6), 41 (20), 39 (10).

The nonconjugated enones 1-hexen-5-one, 1-hepten-6-one, 1-octen-7-one, and 1-nonen-8-one were prepared satisfactorily by ethyl acetoacetate alkylation with α,ω-haloolefins,[38] base-catalyzed hydrolysis,[39] and acid-catalyzed decarboxylation.[39]

A Sample of *N*-propylpropionaldimine was prepared by the usual reaction:[40] bp 98.0–100.0 °C (760 torr); ^{1}H NMR ($CDCl_3$) δ 7.63 (1 H, t), 3.25 (2 H, t), 2.2 (2 H, m), 1.4 (2 H, m), ca. 1.0 (6 H, two superimposed t); IR (neat) 1675 (s). A sample of *N*-propyl-2-propanone imine was prepared as reported elsewhere:[41] bp 107.0–107.5 °C (760 torr) (lit.[41] 107.0 °C (760 torr)); ^{1}H NMR ($CDCl_3$) δ 3.20 (2 H, t), 2.02 (3 H, s), 1.87 (3 H, s), ca. 1.6 (2 H, m), 0.97 (3 H, t); IR (neat) 1667 (vs).

Reductive Coupling of 2-Heptanone with 1-Hexene. Representative Procedure. A 15-mL polymerization tube containing ca. 0.1 g of washed, ignited sand and a Teflon-coated stirring bar was capped with a No-Air septum and flame dried under a nitrogen stream. A suspension of sodium sand (0.22 g, 9 mmol) in xylene was transferred to the tube by using a disposable pipet. Solvent was decanted by cannula, and the sodium was washed with three 6-mL portions of degassed pentane. Gently warming the tube while purging with nitrogen removed the pentane. The tube was then capped with a butyl rubber septum and crown cap. NEP (5 mL) was added and vigorous stirring for several minutes gave a deep blue color and conglomerated the sodium sand. The 1-hexene (0.22 mL, 0.15 g, 1.8 mmol) was added directly by syringe and stirred for several minutes. The 2-heptanone (0.24 mL, 0.19 g, 1.7 mmol) and *tert*-butyl alcohol (0.65 mL) were added in three aliquots to the vigorously stirred mixture over a 1-h period, and the mixture was stirred an additional 0.5 h. Cyclohexane (0.16 mL, 0.12 g) and *n*-tridecane (0.25 mL, 0.19 g) were added as internal standards. The supernatant was decanted from the unreacted sodium and cautiously treated with water (10 mL). The mixture was extracted with three 15-mL volumes of pentane (98%), and the combined extracts were washed with three 15-mL volumes of water. The solution was dried over magnesium sulfate. GLC analysis revealed 6-methyl-6-dodecanol (65%), 2-heptanol (37%), 2-heptanone (<1%), *n*-hexane (5%), and 1-hexene (17%), based on 2-heptanone.

Preparative Reductive Coupling of Acetone and 1-Hexene. A three-necked, 100-mL flask was equipped with a mechanical stirrer and a 10-mL addition funnel. A xylene slurry of sodium shot (4.22 g, 0.184 g atom) and washed, ignited sand (1.26 g) were added. The solvent was decanted by cannula and the solids were washed with four 20-mL volumes of pentane; solvent traces were removed by gently warming while flushing with nitrogen. NEP (50 mL) was added, and the mixture was cooled to ca. 15 °C in a dry ice–2-propanol bath. A deep blue solution formed after 25 min of vigorous stirring, and the sodium shot agglomerated into a faceted lump. Neat 1-hexene (2.26 g, 27 mmol) was added, discoloring the solution slightly. Neat *tert*-butyl alcohol (2.41 g, 21 mmol) was added, instantly dispelling the color. A solution of acetone (3.14 g, 54 mmol) and *tert*-butyl alcohol (3.87 g, 52 mmol) was added over a 50-min period to the vigorously stirred mixture. Additional *tert*-butyl alcohol (1.57 g, 21 mmol) was introduced, and the mixture was allowed to stir for 2 h. The liquid was cautiously decanted onto water (100 mL) at 0 °C. The mixture was extracted with four 30-mL volumes of pentane. The combined extracts were washed with water (50 mL) and two 50-mL volumes of saturated sodium chloride solution and were dried over powdered sodium sulfate. The solution was concentrated to ca. 10 mL by distillation of solvent through a 12-in. Holtzman column. The yellow residue was subjected to chromatography over silica gel (60 g, 0.2–0.5 mm), with diethyl ether–pentane (40:60 (v/v), 600 mL) as elutant. The solution was reduced to a 50-mL volume by distillation of solvent through a 24-in. column packed with glass helices and then to 3 mL by distillation with a 12-in. Holtzman column. The product was distilled through a short-path apparatus, giving 2-methyl-2-octanol (0.72 g, 19%); bp 115.5–117.0 °C (79 torr). Elemental analysis for this compound was acceptable.

Preparation of Neopentyl Chloride in DEA. Neopentyl tosylate (26.2 g, 0.11 mol), anhydrous lithium chloride (6.5 g, 0.15 mol), and DEA (50 mL) were combined in a 200-mL flask containing a Teflon-coated stirring bar. The No-Air stopper was replaced with a condenser, and the mixture was warmed to 110 °C. The solids dissolved readily at this temperature. The solution was stirred at 110 ± 4 °C for 14 h. A trace of white precipitate appeared by the end of this period. The mixture was poured into 100 mL of water in a 250-mL separatory funnel and extracted with four 50-mL volumes of diethyl ether. The combined ether fractions were washed with four 50-mL volumes of water and were dried over anhydrous $MgSO_4$. Solvent was effectively removed by a rapid distillation through a 22-in. Teflon spinning band column. The residue was distilled through an 8-in. stainless steel spinning band column, giving 7.5 g (69%) of neopentyl chloride: bp 84.0–85.5 °C (lit.[42] 84.3 °C); ^{1}H NMR ($CDCl_3$) δ 3.30 (2 H, s), 1.00 (9 H, s). Elemental analysis was acceptable.

Diethyl 2,2,3,3-Tetramethylsuccinate was prepared from ethyl isobutyrate by oxidation of the lithium enolate with iodine as reported by Brocksom and co-workers:[43] bp 127.0–129.0 °C (20 torr) (lit.[44] 125–127 °C (20 torr)); ^{1}H NMR ($CDCl_3$) δ 4.1 (2 H, q), ca. 1.15 (9 H, superimposed t and s).

Preparation of 2,2,3,3-Tetramethylbutane-1,4-diol. A flame-dried, nitrogen-flushed, 3-L flask containing 150 mL of diethyl ether and a Teflon-coated stirring bar was chilled to 0 °C, and 25.0 g (0.66 mol) of lithium aluminum hydride was slowly added. A solution of 152 g (0.659 mol) of diethyl tetramethylsuccinate in ca. 500 mL of ether was added over a 60-min period to the vigorously stirred slurry at 0 °C. The viscous mixture was allowed to warm to ambient temperature and was stirred for 12 h. The mixture was treated with 25 mL of water, 25 mL of 15%

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sodium hydroxide, and 75 mL of water at 0 °C over a 60-min period. The flocculant white precipitate was collected on a 18.5-cm diameter Buechner funnel and was triturated with three 300-mL portions of ether; the solids were extracted for 12 h in a Soxhlet apparatus and the ether fractions were combined. Solvent was removed on a rotary evaporator giving ca. 100 mL of a slurry of white crystals. The diol was conveniently recrystallized from 4 L of hot hexane, giving 59.2 g (62%) of white, feathery crystals: mp 209.5–211.5 °C; IR (KBr) ca. 3300 (br, s), 2940 (s), 2880 (s), 1480 (s), 1378 (m), 1370 (m), 1152 (m), 1150 (s); ^{1}H NMR ($CDCl_3$) δ 5.55 (2 H, s), 3.39 (4 H, s), 0.89 (12 H, s); mass spectrum m/e (relative intensity) 98 (12), 83 (22), 73 (11), 72 (12), 71 (12), 69 (13), 58 (8), 57 (100), 56 (50), 55 (53), 54 (6), 53 (7), 45 (12), 44 (6), 43 (46), 42 (11), 41 (60), 40 (10), 39 (21). Elemental analysis was acceptable.

Preparation of 2,2,3,3-Tetramethylbutanediyl 1,4-Ditosylate. In a 3-L flask containing a Teflon-coated stirring bar were combined 50.2 g (0.34 mol) of 2,2,3,3-tetramethylbutane-1,4-diol and 1.0 L of pyridine that had been freshly distilled from barium oxide under nitrogen. Tosyl chloride (mp 66.5–68.5 °C) was ground into a fine powder and 189 g (0.99 mol) was added over a 40-min period to the stirred solution at 0 °C. The resulting yellow solution was stored for 7 days in a freezer, during which time a large quantity of pyridine–hydrochloride precipitated. The yellow mixture was poured onto 1.0 L of ice in a 4-L beaker and 2 L of chloroform was added. The mixture was separated in a 6-L funnel, and the aqueous layer was extracted with two 700-mL portions of chloroform. The combined organic extracts were washed with four 500-mL portions of a 3:1 solution of water and concentrated hydrochloric acid and with two 1.5-L portions of water. The chloroform solution was dried over powdered sodium sulfate, and solvent was removed on a rotary evaporator. The resultant yellow oil (100 mL) crystallized upon standing for 12 h and the product was recrystallized from ca. 1.0 L of hot 1:1 chloroform–hexane. Filtration gave 110 g (71%) of irridescent white flakes: mp 109.5–111.0 °C; IR (KBr) 2950 (m), 2870 (m), 1600 (m), 1493 (m), 1475 (m), 1455 (m), 1380 (w), 1350 (s), 1190 (s), 1165 (s), 1100 (m), 963 (s), 855 (s), 820 (m), 668 (s), 660 (m), 558 (s), 483 (m); ^{1}H NMR ($CDCl_3$) δ 7.80 (2 H, d, J_{ortho} = 9 Hz), 7.35 (2 H, d, J_{ortho} = 9 Hz), 3.80 (2 H, s), 2.30 (3 H, s), 0.84 (6 H, s). Elemental analysis was acceptable.

Preparation of 1,4-Dichloro-2,2,3,3-tetramethylbutane in HMPA. In a 1-L flask containing a Teflon-coated stirring bar were combined 2,2,3,3-tetramethylbutanediyl 1,4-ditosylate (130 g, 0.066 mol), anhydrous lithium chloride (7.3 g, 0.174 mol), and HMPA (500 mL). The mixture was warmed to 105 ± 4 °C for 12 h. The yellow solution was poured into 600 mL of water in a 3-L separatory funnel and the resulting mixture was extracted with three 300-mL volumes of hexane. The hexane fractions were washed with five 200-mL volumes of water and dried over $MgSO_4$. Solvent was removed at reduced pressure on a rotary evaporator. Distillation afforded 10.6 g (85%) of dihalide: bp 88.0–91.0 °C (6 torr); mp 44.0–46.0 °C; IR (CCl_4) 2980 (br, s), 2890 (s), 1470 (s), 1438 (m), 1400 (m), 1385 (s), 1373 (m), 1300 (s), 1292 (s), 1138 (s), 1130 (s), 940 (w), 897 (w); ^{1}H NMR (CCl_4) δ 3.53 (4 H, s), 1.03 (12 H, s); mass spectrum m/e (relative intensity) 133 (5), 97 (6), 91 (9), 90 (5), 69 (7), 63 (7), 57 (61), 56 (100), 55 (89), 54 (8), 53 (12), 49 (16), 43 (32), 41 (70), 39 (42). Elemental analysis was satisfactory.

Reduction of 1-Hexene. Representative Procedure. A 15-mL polymerization tube containing ca. 0.1 g of washed, ignited sand and a Teflon-coated stirring bar was capped with a No-Air septum and flame dried under a nitrogen stream. A suspension of sodium sand (0.216 g, 9.4 mg atom) in xylene was transferred to the tube by disposable pipet. Solvent was decanted by cannula, and the metal was washed with three 5-mL aliquots of degassed pentane. The pentane was removed by gently warming under a nitrogen stream. The tube was capped with a butyl rubber septum. DEA (2.0 mL) was added to the mixture, and vigorous stirring produced a deep blue color after several minutes. A solution of 1-hexene (0.147 g, 1.80 mmol) in DEA (5 mL) was added in drops over 2 min, maintaining the color. An aliquot of *tert*-butyl alcohol (0.3 mL, ca. 0.2 g, 3 mmol) was introduced, instantly dispelling the color. The mixture was vigorously stirred for 11 h under 5 psi of nitrogen. A second aliquot of *tert*-butyl alcohol (0.3 mL) was added to the resulting colorless solution, and the mixture was stirred at ambient temperature for an additional 13 h. Cyclohexane (0.20 mL, 0.165 g) was added as an internal standard, and GLC analysis showed the presence of 0.077 g (51%) of *n*-hexane and 0.0015 g (1%) of 1-hexene.

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Registry No. DEA, 685-91-6; NEP, 2687-91-4; *N*-acetylmorpholine, 1696-20-4; *N*-methyl-*N'*-acetylpiperazine, 60787-05-5; *N*-acetylpyrrolidine, 4030-18-6; *N,N*-diisopropylacetamide, 759-22-8; *N,N*-diethylisobutyramide, 33931-44-1; 7-methyl-7-tridecanol, 19016-75-2; 3-ethyl-3-nonanol, 51246-24-3; 2-methyl-2-octanol, 628-44-4; 1-*n*-hexylcyclohexanol, 3964-63-4; 2,2,3-trimethyl-3-nonanol, 70178-78-8; 2,2-dimethyl-3-nonanol, 25966-64-7; 4,6-dimethyl-6-undecanol, 70178-79-9; 3-methyl-3-octanol, 5340-36-3; 1-methylcyclopentanol, 1462-03-9; *cis*-1,2-dimethylcyclopentanol, 16467-13-3; 1-methylcyclohexanol, 590-67-0; *cis*-1,2-dimethylcyclohexanol, 19879-11-9; 1-methylcycloheptanol, 3761-94-2; 1-methylcyclooctanol, 59123-41-0; *cis*-1,2-dimethylcycloheptanol, 70178-80-2; *N*-propylpropionaldimine, 7707-70-2; *N*-propyl-2-propanone imine, 28916-23-6; 1-hexene, 592-41-6; 2-heptanone, 110-43-0; 6-methyl-6-dodecanol, 62958-40-1; 2-heptanol, 543-49-7; *n*-hexane, 110-54-3; acetone, 67-64-1; neopentyl tosylate, 2346-07-8; neopentyl chloride, 753-89-9; diethyl 2,2,3,3-tetramethylsuccinate, 33367-54-3; 2,2,3,3-tetramethylbutane-1,4-diol, 10519-69-4; 2,2,3,3-tetramethylbutanediyl 1,4-ditosylate, 70178-81-3; 1,4-dichloro-2,2,3,3-tetramethylbutane, 70178-83-5; 2,2-diethylbutaneyl 1-tosylate, 70178-84-6; 2,2-dimethylpropanediyl 1,3-ditosylate, 22308-12-9; cyclohexane tosylate, 953-91-3; 2,2-diethyl-1-chlorobutane, 70178-82-4; 2,2-dimethyl-1,3-dibromopropane, 5434-27-5; 1,3-dibromo-2,2-dibromomethylpropane, 3229-00-3; bromocyclohexane, 108-85-0; cyclohexene, 110-83-8; cyclohexane, 110-82-7; tetramethylethylene, 563-79-1; 2,3-dimethylbutane, 79-29-8; ethene, 74-85-1; 2-methyl-2-butanol, 75-85-4; 2-methyl-1-pentene, 763-29-1; 2-hexene, 592-43-8; 3-pentanone, 96-22-0; cyclohexanone, 108-94-1; 3,3-dimethyl-2-butanone, 75-97-8; *N,N*-dimethylacetamide, 127-19-5; 2-octanol, 123-96-6; 1-hexen-5-one, 109-49-9; *cis*-1,2-dimethylcyclobutanol, 1594-23-6; 1-hexen-5-ol, 626-94-8; 1-hepten-6-one, 21889-88-3; 1-hepten-6-ol, 13311-76-7; 1-octen-7-one, 3664-60-6; 1-octen-7-ol, 39546-75-3; 1-nonen-8-one, 5009-32-5; 1-nonen-8-ol, 65727-63-1; *trans*-1,2-dimethylcyclopentanol, 16467-04-2; *trans*-1,2-dimethylcyclohexanol, 19879-12-0; *trans*-1,2-dimethylcyclobutanol, 1551-58-2; *trans*-1,2-dimethylcycloheptanol, 35099-39-9; 2,2-dihydroxymethyl-1,3-propanediol tetratosylate, 1522-89-0; $C_{13}H_{28}O$, 70178-77-7.