Table I. Summary of Results of Competitive Reduction Experiments

no.	aldehyde	ketone	zeolite	A^a	B^b
1	3-phenylpropionaldehyde	6-methoxy-1-indanone	3A, 5A, 13X	70	90
2	3-phenylpropionaldehyde	cyclohexanone	3A, 5A	75	
3	3-phenylpropionaldehyde	acetophenone	3A, 5A	78	
4	cyclohexanecarboxaldehyde	6-methoxy-1-indanone	3A, 5A, 13X	70	90
5	cyclohexanecarboxaldehyde	cyclohexanone	3A, 5A	75	
6	cyclohexanecarboxaldehyde	acetophenone	3A, 5A	70	

[a] A = percent of conversion to primary alcohol. [b] B = percent of ketone recovered.

reaction product consisted of polymeric compounds formed from the reactants by side reactions. The reactions carried out with 6-methoxy-1-indanone (numbers 1 and 4 in Table I) were carried out quantitatively, and the products of reaction were found to contain no unreacted aldehyde, whereas 90% of the ketone originally present was recovered.

Measurements of the adsorption of $LiBH_4$ on 5A sieve from dilute solution in THF (details are given below) show that at equilibrium the zeolite contains only about 0.5% wt of $LiBH_4$. This low equilibrium capacity suggests that the $LiBH_4$ does not penetrate the zeolite cage structure and is adsorbed only on the external surface of the zeolite crystals. This was confirmed by experiments with 3A sieve (smaller effective pore size through which $LiBH_4$ would certainly not penetrate), which showed about the same equilibrium capacity for $LiBH_4$. The aldehyde/ketone reduction experiments were therefore repeated, using similar reducing agents prepared from the 3A zeolite and from the 13X zeolite. The pore opening of the 13X sieve is large enough to freely admit both aldehyde and ketone molecules, as well as those of $LiBH_4$. As indicated in Table I, the reagents prepared from 3A and 13X zeolites showed almost the same selectivity in the reduction of aldehyde as did the original reagent prepared from the 5A zeolite. Clearly therefore the selectivity of the reducing agent does not arise, as originally postulated, from a simple molecular sieve effect since the evidence suggests that, at least with the 5A and 3A sieves, the reaction takes place on the external surface of the crystals, rather than in the interior, and the external surface is equally accessible to both aldehyde and ketone. Thus, although the potential usefulness of this type of reagent has been demonstrated, elucidation of the reaction mechanism will require a more detailed investigation.

Experimental Section

1. **Preparation of Reagent.** Molecular sieve crystals (70 g) (diameter ~ 1 μm) were dehydrated at 450 °C in a stream of He for 2 days and then suspended in 200 mL of dry THF. A solution of 1% $LiBH_4$ in THF (5 mL) was added, and the suspension was stirred in a dry atmosphere at 50 °C. Progress of the adsorption of $LiBH_4$ was followed by removing at intervals a drop of supernatant solution and testing it with wet pH paper. After about 8 h, a neutral reaction was obtained, indicating that all $LiBH_4$ had been adsorbed.

2. **Adsorption Experiments.** The adsorption experiments were carried out essentially as in (1) above, except that the quantities of reagents were modified. Experiments were carried out using various quantities of zeolite and $LiBH_4$ in order to establish the saturation concentration. The quantity of $LiBH_4$ remaining in the solution was estimated by titration. A small sample of the supernatant solution was removed and hydrolyzed by boiling it with water for 10 min in an Erlenmeyer flask. The solution was then titrated against standard HCl. The original $LiBH_4$ solution (1 mL) was also titrated, after hydrolysis, with the standard HCl solution, and the quantity of $LiBH_4$ adsorbed by the zeolite was then found by difference. The same procedure was repeated several times, using different quantities of the 1% $LiBH_4$ solution in THF, and it was found that on average 10 g of zeolite adsorbed about 0.05 g of $LiBH_4$.

One experiment was carried out with a large excess of zeolite (30 g Davison 3A sieve with 150 mL of THF and 3 mL of the 1% solution of $LiBH_4$ in THF). After 10 h, a sample of the zeolite was removed, filtered, and washed with THF and dried in vacuo. Both this sample of sieve and a sample of the supernatant solution were analyzed for Li by atomic absorption spectrophotometry. No detectable amount (<0.1 ppm) of Li was found in the THF solution, whereas the sieve sample contained 199 ppm of Li. This experiment confirms that in the presence of an excess of zeolite virtually all the $LiBH_4$ is adsorbed.

3. **Reduction of 3-Phenylpropionaldehydes in the Presence of 6-Methoxy-1-indanone.** Reagent (70 g) was prepared as in (1) above. To the suspension of the reagent in THF were added 0.15 g of 6-methoxy-1-indanone and 0.125 g of 3-phenylpropionaldehyde. The mixture was stirred for 6 h in a dry atmosphere at room temperature. Distilled water (100 mL) was added and the mixture stirred for a further period of 1 h. The suspension was then filtered and washed with THF (2 × 100 mL) and then diethyl ether (100 mL). The solvents were removed under reduced pressure, and the residual liquid was extracted with ether. The extract was dried over $MgSO_4$ (anhydrous) and then evaporated to dryness under reduced pressure. The residual products were separated by chromatography on silica gel to afford 0.135 g (90%) of unreacted 6-methoxy-1-indanone and 0.09 of g 3-phenylpropanol in 70% yield: IR (CCl_4) 3440 cm^{-1} (OH); NMR (CCl_4) δ 7.1 (s, 3), 3.5 (t, 2), 2.63 (m, 2), 1.8 (m, 2); mass spectrum parent (70 eV) *m/e* 136. IR, NMR, and MS were identical with those of 3-phenylpropanol obtained directly from reduction of 3-phenylpropionaldehyde by direct reduction with $LiBH_4$ in THF solution.

The procedure for the reactions with cyclohexanone and acetophenone was essentially the same except that in the workup the solvents were carefully distilled, using a 4 in. fractionating column. Here also 3-phenylpropanol was obtained in 70–80% yield with no trace of the corresponding secondary alcohol.

Acknowledgment. The atomic absorption analyses were performed by Dr. K. T. Kan of the Department of Civil Engineering, and this assistance is gratefully acknowledged.

Registry No. 3-Phenylpropionaldehyde, 104-53-0; cyclohexanecarboxaldehyde, 2043-61-0; 3-phenylpropanol, 122-97-4; cyclohexanemethanol, 100-49-2.

Methylene Dioxime Formation Using Phase-Transfer Catalysis

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Received April 6, 1979

The use of phase-transfer catalysis has been an important tool in the construction of compounds in organic preparations.[1] Dichloromethane has been commonly employed as the solvent in these reactions; however, dichloromethane has also been used as the electrophile in phase-transfer catalysis to form bis(aryloxy)methanes,[2]

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[1] E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, 16, 493 (1977).

Table I. Preparation of Dioximes (Eq 1)[d]

R_1	R_2	Q^+X^- [a]	isolated yield of 1, %	mp, °C [b]	NMR (CH_2), ppm
Me	Me	A	53	43-44	5.52
Et	Et	A	50	[55 (0.065 mm)]	5.55
cyclo-C_6H_{11}		A	79	48-50	5.50
Ph	Me	A	85	99-101	5.83
Ph	Me	B	1	99-101	5.83
Ph	Me	C	100	99-101	5.83
Ph	Me	D	100	99-101	5.83
Ph	Ph	A	81	85-87	5.83
p-tolyl	C(Me)$_3$	A	90	151-152	5.42
2,4-$Cl_2C_6H_3$	Me	A	81	140-141	5.80
3,4-$Cl_2C_6H_3$	Me	A	91	120-121	5.83
2,5-$Cl_2C_6H_3$	Me	A	81	107-108	5.80
2-thienyl	Me	A	89	114-116	5.80
cyclo-C_3H_5	cyclo-C_3H_5	A	57	69-71	5.52
4-$NO_2C_6H_4$	Me	D	95	162-164	5.95
3-$NO_2C_6H_4$	Me	D	97	147-150	5.95
4-$MeOC_6H_4$	Me	D	90	79-82	5.85
2,4-$(MeO)_2C_6H_3$	Me	D	70	174-175	5.70
4-ClC_6H_4	Me	D	50	176-180	5.71
$Et_2NCH_2CH_2$	Me	A	55	[130 (0.11 mm)][c]	5.60

[a] A, tetra-*n*-butylammonium hydrogen sulfate; B, *n*-propyltriphenylphosphonium bromide; C, cetyltrimethylammonium bromide; D, methyltrialkylammonium chloride (alkyl = C_8-C_{10}; available as Adogen 464 from Ashland Chemical Co.). [b] The boiling point value is listed within brackets. [c] Kugelrohr boiling point. [d] Satisfactory elemental analysis and diagnostic spectra were obtained for each new compound.

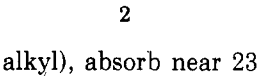
methylene diesters,[3] and dithioethers.[4]

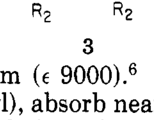
We wish to report the formation of methylene dioximes 1, a previously unknown class of molecules, from keto oximes using a quaternary ammonium salt (Q^+X^-) with 50% aqueous solutions of sodium hydroxide, with dichloromethane used as both solvent and electrophile (eq 1). The probable route of formation of 1 is by successive

$$2R_1R_2C{=}NOH + CH_2Cl_2 \xrightarrow[0\text{-}5\ °C]{NaOH,\ H_2O,\ Q^+X^-} \underset{1}{(R_1R_2C{=}NO)_2CH_2} \quad (1)$$

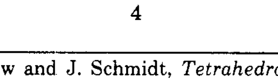
alkylations of dichloromethane by the conjugate base of the oxime. We prepared the methylene dioximes listed in Table I in isolated yields of 50–100%. The yield of the methylene dioxime derivative for acetophenone oxime varied dramatically with Q^+X^-. This variation is in agreement with the reaction[5] of thiophenoxide with 1-bromooctane in benzene–water, in which the quaternary phosphonium salts are less effective than the quaternary ammonium salts as phase-transfer catalysts.

Hypothetical alternate products 2 and 3 are eliminated on the basis of ultraviolet spectra. Nitrones, similar to


2


3

2 (R = alkyl), absorb near 230 nm (ε 9000).[6] Nitroso compounds, similar to 3 (R = alkyl), absorb near 300 nm (ε 100) and 665 nm (ε 20).[7] Methylene dioxime 4 has absorptions at 263 nm (ε 102) and 270 nm (ε 87).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Experimental Section

Melting points are uncorrected. UV spectra were taken with a Cary 14 recording spectrophotometer. Infrared spectra were recorded with Perkin-Elmer Model 237, 257, and 457 spectrophotometers. NMR spectra were obtained with Varian EM-360, T-60, and XL-100 spectrometers. Mass spectra were taken with LKB-9000 and AEI-MS-30 mass spectrometer systems.

Starting Materials. The oximes were prepared from the corresponding carbonyl compounds by standard procedures. The catalysts were obtained from Aldrich Chemical Co. Dichloromethane was used without purification from Fisher Scientific Co.

General Procedure for Methylene Dioxime Formation. The preparation of bis(*m*-nitroacetophenone) *O,O′*-methylenedioxime serves as a typical example. To a solution of *m*-nitroacetophenone oxime (5.60 g, 30.0 mmol) and tetra-*n*-butylammonium hydrogen sulfate (0.60 g, 2.0 mmol) in 110 mL of dichloromethane at 0 °C was added dropwise 4 mL of a 50% aqueous sodium hydroxide solution. The reaction mixture was stirred at 25 °C for 16 h and diluted with 100 mL of water. The aqueous portion was separated and extracted with methylene chloride. The organic layers were combined and washed with water until the aqueous portion was neutral. After a final brine wash, the organic portion was dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The product was recrystallized from ethanol, affording 5.4 g (97%) of the desired dioxime: mp 147–150 °C; UV max ($CHCl_3$) 253 nm (ε 33 550), 235 (25 890); IR ($CHCl_3$) 1620 (C=NO, w), 1525, 1355 (aromatic NO_2), 1015 cm^{-1} (OCH_2O); NMR ($CDCl_3$) δ 8.6–7.4 (8, complex m, aromatic H), 5.95 (2, s, OCH_2O), 2.35 (6, s, CH_3); mass spectrum (70 eV), *m/e* 372 (m^+). Anal. Calcd for $C_{17}H_{16}N_4O_6$: C, 54.8; H, 4.3; N, 15.0. Found: C, 55.0; H, 4.3; N, 15.0.

Acknowledgment. The authors are grateful to Dr. K. M. Hurst for helpful discussions and for the services provided by the members of the Analytical Chemistry Department of Sandoz, Inc.

Registry No. 1 (R_1 = R_2 = Me), 71516-50-2; 1 (R_1 = R^2 = Et), 71516-51-3; 1 (R_1 = R_2 = c-C_6H_{11}), 71516-52-4; 1 (R_1 = Ph; R^2 = Me), 71516-53-5; 1 (R_1 = R^2 = Ph), 71516-54-6; 1 (R_1 = *p*-tolyl; R_2 = CMe_3), 71516-55-7; 1 (R_1 = 2,4-$Cl_2C_6H_3$; R_2 = Me), 71516-56-8; 1 (R_1 = 3,4-$Cl_2C_6H_3$; R_2 = Me), 71516-57-9; 1 (R_1 = 2,5-$Cl_2C_6H_3$; R_2 = Me), 71516-58-0; 1 (R_1 = 2-thienyl; R_2 = Me), 71516-59-1; 1 (R_1 = R_2 = c-C_3H_5), 71516-60-4; 1 (R_1 = 4-$NO_2C_6H_4$; R_2 = Me), 71516-61-5; 1 (R_1 = 3-$NO_2C_6H_4$; R_2 = Me), 71516-62-6; 1 (R_1 = 4-$MeOC_6H_4$; R_2 = Me), 71516-63-7; 1 (R_1 = 2,4-$(MeO)_2C_6H_3$; R_2 = Me), 71516-64-8; 1 (R_1 = 4-ClC_6H_4; R_2 = Me), 71516-65-9; 1 (R_1 = $Et_2NCH_2CH_2$; R_2 = Me), 71516-66-0; acetone oxime, 127-06-0; 3-pentanone oxime, 1188-11-0;

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cyclohexyl ketone oxime, 6316-03-6; acetophenone oxime, 613-91-2; benzophenone oxime, 574-66-3; *p*-tolyl *tert*-butyl ketone oxime, 31007-19-9; 2′,4′-dichloroacetophenone oxime, 71516-67-1; 3′,4′-dichloroacetophenone oxime, 71516-68-2; 2′,5′-dichloroacetophenone oxime, 71516-69-3; 2-thienyl methyl ketone oxime, 1956-45-2; cyclopropyl ketone oxime, 1453-52-7; 4′-nitroacetophenone oxime, 10342-64-0; 3′-nitroacetophenone oxime, 7471-32-1; 4′-methoxyacetophenone oxime, 2475-92-5; 2′,4′-dimethoxyacetophenone oxime, 23997-80-0; 4′-chloroacetophenone oxime, 1956-39-4; 2-(diethylamino)ethyl ketone oxime, 71516-70-6; acetone, 67-64-1; 3-pentanone, 96-22-0; cyclohexyl ketone, 1121-37-5; acetophenone, 98-86-2; benzophenone, 119-61-9; *p*-tolyl *tert*-butyl ketone, 30314-44-4; 2′,4′-dichloroacetophenone, 2234-16-4; 3′,4′-dichloroacetophenone, 2642-63-9; 2′,5′-dichloroacetophenone, 2476-37-1; 2-thienyl methyl ketone, 88-15-3; cyclopropyl ketone, 1121-37-5; 4′-nitroacetophenone, 100-19-6; 3′-nitroacetophenone, 121-89-1; 4′-methoxyacetophenone, 100-06-1; 2′,4′-dimethoxyacetophenone, 829-20-9; 4′-chloroacetophenone, 99-91-2; 2-(diethylamino)ethyl ketone, 71516-71-7; dichloromethane, 75-09-2.

Reduction of Diphenylethylenes and Related Compounds with Magnesium in Methanol

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Received April 17, 1979

Diphenylethylenes and diphenylethanes appear rather frequently in the chemical literature, particularly within realms of medicinal interest, either in the open-chained forms or as closed-ring analogues.[1] In many cases, the syntheses of particular diphenylethylene derivatives and their dihydro analogues were carried out independently by parallel reaction schemes with different starting materials;[2] thus it would appear that, at least in some cases, the synthesis of diphenylethane derivatives could have been facilitated if an efficient method were available for the reduction of the corresponding diphenylethylenes.

The most commonly used reduction procedures for simple diphenylethylenes include catalytic hydrogenation over palladium or platinum,[3] which allows rapid reduction of the 1,1-diphenylethylenes but reduces the stilbenes less readily;[4] furthermore, the course of reduction could be inhibited by the presence of a bivalent sulfur[5] or nitrogen atom,[6] as in the case of iminostilbenes. Sodium borohydride in trifluoroacetic acid has been reported to reduce 1,1-diphenylethylene in good yield, yet it fails to saturate the olefinic double bonds in a dibenzo[*a*,*d*]cyclohepten-5-ylidene derivative.[7] Lithium–ammonia has been used successfully in reducing the central double bond of phenanthrene;[8] metal–ammonia reductions of simple 1,1-diphenylethylenes, however, tend to give large amounts of dimeric products.[9] Numerous other methods of reduction have also shown merit in specific examples, but their general applicability has not been demonstrated.[10]

In connection with our work directed toward the synthesis of some dihydrodibenz[*b*,*f*]oxepins and dihydrodibenzo[*b*,*f*]thiepins, we have discovered that the use of magnesium in methanol can effectively reduce a variety of 1,1- and 1,2-diphenylethylenes as well as related compounds. Previously, magnesium in methanol (or other alcohols) has only been used in the reduction of carbon–heteroatom double bonds[11,12] and nitrogen oxides,[13] and, more recently, its success in selective reduction of various α,β-unsaturated nitriles has been demonstrated.[14] Under somewhat modified conditions,[15] we have found that the reduction of diphenylethylenes can proceed in virtually quantitative yields, except in cases where the double bond is part of an aromatic ring. Results of this study are summarized in Table I.

In addition to its efficiency, economy, and convenience, the magnesium in methanol reduction also offers the advantage of being applicable to systems incorporating nuclear halogen substituents and heteroatoms, such as a bivalent sulfur, oxygen, and basic nitrogen, as demonstrated by the reduction of **8a** in Table I.[15,16]

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting-point apparatus and are uncorrected. The vapor-phase chromatographic (VPC) analyses were performed using either a 2 mm i.d. × 6 ft 3% OV-17 on 60/80 Gas Chromosorb Q silanized glass column or a 4 mm i.d. × 6 ft 3% OV-1 on 100/120 Chromosorb W-H.P. stainless steel column in a Perkin-Elmer Model 3920B gas chromatograph with a flame ionization detector. All percent-composition values are reported as relative peak areas without correction for relative detector response. Infrared spectra were recorded on a Perkin-Elmer Model 727 grating spectrometer. ^{1}H NMR spectra were obtained on a JEOL C60-HL spectrometer; chemical shifts (δ) are reported relative to Me_4Si. Mass spectra were obtained using a Finnigan Model 4000 quadrupole mass spectrometer at 70 eV, equipped with the INCOS data system; when chemical ionization was used, methane was the reagent gas.

In all workup procedures, "brine" refers to saturated sodium chloride solution. The drying process involved standing the solution over $MgSO_4$ and filtering it prior to evaporation. Magnesium shavings were obtained from Matheson Coleman and

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(16) Unpublished results by J. A. Profitt and H. H. Ong.

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