# Asymmetric Syntheses. Part 11.[1] Reduction of Ketones and Related Ketone Oximes with Lithium Aluminium Hydride–3-*O*-Cyclohexylmethyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose Complex to give Optically Active Alcohols and Amines

**Stephen. R. Landor** *
*Department of Chemistry, University of the West Indies, Kingston, Jamaica*
**Yuet M. Chan and Olutunji O. Sonola**
*University of California, Berkeley, California*
**Austin R. Tatchell**
*Thames Polytechnic, London S.E.18*

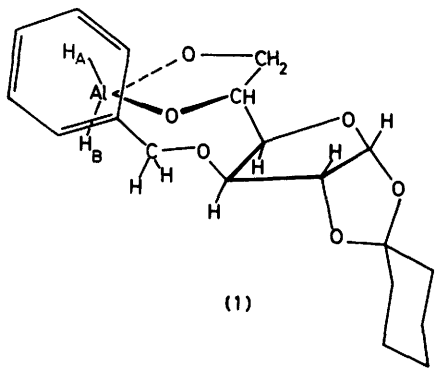
The asymmetric reduction of ketones and structurally related isoelectronic ketone oximes with lithium aluminium hydride–3-*O*-cyclohexylmethyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose complex yields optically active alcohols of up to 42% optical purity and optically active amines of up to 52% optical purity, respectively. The resulting alcohols as well as amines all have the *S*-configuration. When the asymmetric reduction is carried out with the ethanol-modified glucofuranose complex, the resulting alcohols and amines have the *R*-configuration.

In Parts 1—3,[2-3] 4,[4a] and 10,[1] we reported the asymmetric reduction of ketones, ketone oximes and their *O*-ether derivatives, and *N*-phenylazomethines by lithium aluminium hydride–3-*O*-benzyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose (1) to give optically active alcohols, primary amines, and secondary amines, respectively. We have now extended these investigations to the reduction of ketones and ketone oximes by the lithium aluminium hydride–monosaccharide complex derived from 3-*O*-cyclohexylmethyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose (2).

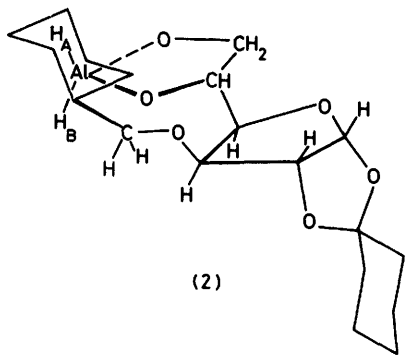
The 3-*O*-cyclohexylmethyl group in the monosaccharide moiety was used instead of the 3-*O*-benzyl group because of the observation that a higher percentage optical purity was obtained when cyclohexyl methyl ketone and cyclohexyl methyl ketone oxime were separately reduced with the aluminium hydride–glucofuranose complex (1) than that obtained from the reduction of acetophenone and acetophenone oxime.[2,4a]

In the asymmetric reduction of aromatic ketones and ketone oximes with the glucofuranose complex (1) it was postulated that the presence of aromatic residues led to π-π electronic interactions between the benzyl group of the monosaccharide derivative and phenyl groups of the ketones or ketone oximes. Consequently, the percentage optical purity of the resulting aromatic alcohols and amines was often lower than expected especially when compared with that resulting from the reduction of cyclohexyl methyl ketone and cyclohexyl methyl ketone oxime with the glucofuranose complex (1), which gave maximum optical yields of 68% for 1-cyclohexylethanol,[4b] and 56% for 1-cyclohexylethylamine.[4a]

It was reasoned, therefore, that the use of 3-*O*-cyclohexylmethyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose would eliminate the electronic effects arising from the benzyl group of the monosaccharide complex and the phenyl group of the ketone or ketone oxime to be reduced and should thus lead to higher selectivities in the reduction. It would appear that both mechanisms that we have mentioned in our earlier publications [1-4a] will apply in both cases, that is, a preferential hydride ion transfer, $H_B$ in (2), from the aluminium hydride complex effects reduction to give an alcohol having *S*-configuration whilst the asymmetric reduction of the ketone oxime proceeds by an intramolecular hydride ion transfer preferentially of $H_B$ from a second molecule of aluminium hydride–monosaccharide complex (2) to the carbon atom of the oxime group to give an optically active amine of the *S*-configuration (Scheme).




(1)

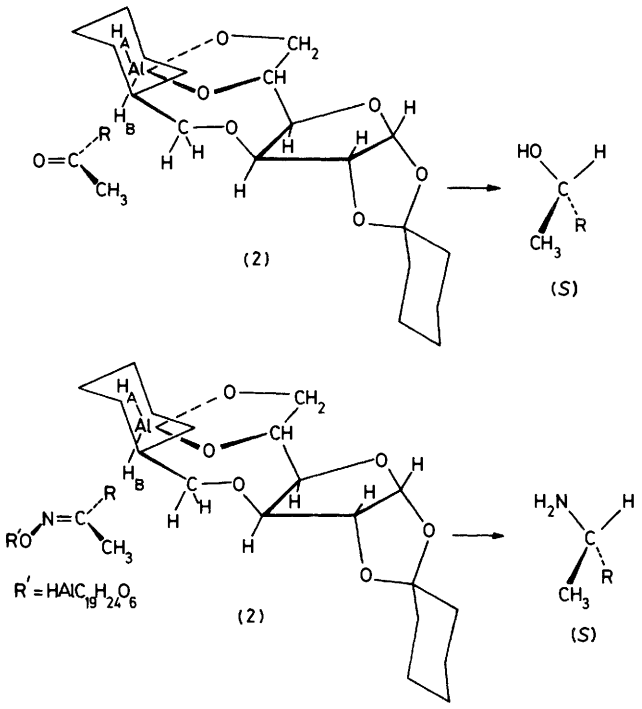



(2)

Tables 1 and 2 give details of the reduction of aromatic and aliphatic ketones, and Tables 3 and 4 similarly show the data obtained from the reduction of aromatic and aliphatic ketone oximes.

The results (Table 1) show that for aromatic ketones there is no substantial improvement in optical yield indicating unpredictable electronic interactions between the benzyl group and the aromatic substituents on the ketone which sometimes help and sometimes hinder the asymmetric process. Therefore, there appears to be no advantage in using complex (2) rather than complex (1) for aromatic ketones.

However the reduction of aromatic ketone oximes with complex (2) gave consistently two to three times the optical yields of those obtained with complex (1). Here the minimising




Scheme.

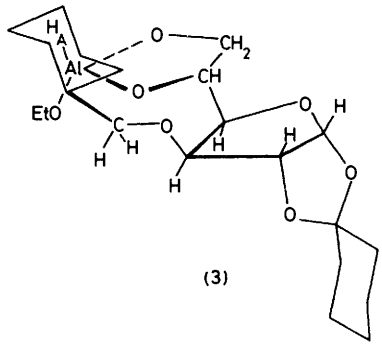
of electronic effects in the now doubly complexed transition state together with the greater bulk of the cyclohexylmethyl than the benzyl group lead to more effective shielding of $H_A$ and more efficient hydride transfer of $H_B$.

The asymmetric reduction of dialkyl ketones and dialkyl ketone oximes all (except for cyclohexyl methyl ketone and ketone oxime) show a marked improvement of optical yield with complex (2). In all probability this is caused by the greater steric bulk of the cyclohexylmethyl group which shields $H_A$, resulting once again in more efficient transfer of $H_B$. Here there is a substantial advantage in using complex (2).

Reduction of ketones with the ethanol-modified complex (3) gave alcohols of the *R*-configuration (Tables 5 and 6). This is a further confirmation of our proposed mechanistic scheme [2c] that the ethoxy group preferentially replaces $H_A$ and reduction could only be effected by $H_B$ leading to the *R*-alcohol.

## Experimental

Thin layer chromatography of carbohydrate derivatives was performed on silica gel with benzene–methanol (98 : 2) as the solvent system and a naphthoresorcinol–phosphoric acid spray for detection. The ether used in the reductions with lithium aluminium hydride complexes was repeatedly dried over sodium. Solutions in chloroform were dried over calcium chloride and ethereal solutions over magnesium sulphate. The purity of the secondary alcohols was established by g.l.c. on a 6-ft Silicone-Celite 545 column for aryl alcohols and a 6-ft dinonyl phthalate-Celite 545 for aliphatic alcohols. The purity of the amines was established by g.l.c. on a 5-ft glass column of Carbowax 20M on Chromosorb W. Optical rotations (±0.01°) were determined for neat samples unless otherwise stated with a Stanley photoelectric polarimeter and/or with a Perkin-Elmer 141 polarimeter at 20 °C. Maximum specific rotations and absolute configurations of the optically active alcohols have been reported in the literature, and these are listed in refs. 5—12. Those of the optically active amines have also been reported and are contained in Part 9 [4a] of this series, listed in the refs. therein (ref. nos. 6—17). Ether refers to diethyl ether.




3-O-*Cyclohexylmethyl*-1,2:5,6-*di*-O-*cyclohexylidene*-α-D-*glucofuranose*.—Potassium hydroxide (74 g, 1.35 mol) was added to a stirred suspension of recrystallised 1,2:5,6-*O*-cyclohexylidene-α-D-glucofuranose [2] (34 g, 0.10 mol) in cyclohexylmethyl bromide (60 g, 0.33 mol). The temperature was slowly raised to 120 °C during 1 h and maintained at this level for 4 h. The reaction mixture was cooled, diluted with water (250 ml) and the organic layer separated. The aqueous layer was extracted with chloroform (2 × 100 ml) and the combined organic layers and chloroform extracts washed with water (3 × 100 ml), dried ($CaCl_2$), and the chloroform evaporated. The light-yellow oily product which remained after removal of the last traces of chloroform was refrigerated for 2 days during which time a white crystalline material was deposited. The solid (4 g) was separated and after recrystallisation, shown to be unchanged starting material. The oily residue was dissolved in light petroleum (b.p. 40—60 °C) and successive refrigeration and concentration yielded a series of crops of white crystalline material which were combined and recrystallised from acetone–water (60 : 40) to give the pure *product* (36 g, 82%), m.p. 74 °C $[\alpha]_D^{20}$ −12.5° (*c* 4, $CHCl_3$) (Found: C, 68.75; H, 9.1. $C_{25}H_{40}O_6$ requires C, 68.80; H, 9.17%); $\nu_{max.}$ 1 160—1 070 (−C−O−C− str.) and 1 050—1 020 $cm^{-1}$ (1,3-dioxolane); τ 8.45 (31 H, m, cyclohex.), 6.60 (2 H, d, 6-H), 5.60—6.22 (5 H, m, 3-, 4-, 5-H and $CH_2O$), 5.52 (1 H, d, 2-H), and 4.15 (1 H, d, 1-H).

3-O-*Cyclohexylmethyl*-1,2-O-*cyclohexylidene*-α-D-*glucofuranose*.—3-*O*-Cyclohexylmethyl-1,2:5,6-di-*O*-cyclohexylidene-α-D-glucofuranose (50 g, 0.12 mol) was dissolved in aqueous acetic acid (210 ml; 75% v/v) and the solution maintained at a temperature of 70—80 °C with stirring for 3 h. The reaction mixture was cooled, diluted with water (200 ml) and the organic material removed by extraction with chloroform (4 × 100 ml). The combined chloroform extracts were washed sequentially with aqueous saturated sodium hydrogen carbonate (4 × 200 ml) to remove all traces of acetic acid, and water (5 × 100 ml), dried ($CaCl_2$) and the chloroform evaporated. The light-yellow residual oil was distilled under reduced pressure to give a product (30 g, 72%) [b.p. 185—190 °C/2 × $10^{-3}$ mmHg, $[\alpha]_D^{20}$ −35° (*c* 3, $CHCl_3$, optimised); $\nu_{max.}$ 3 400 (OH) and 1 160—1 020sh $cm^{-1}$ (C−O−C)] which exhibited one main component ($R_F$ 0.25) on t.l.c. analysis (benzene–methanol, 90 : 10) with a minor component at $R_F$ 0.85 corresponding to the dicyclohexylidene compound.

*Reduction of Ketones*.—*(i) With the lithium aluminium hydride–*3-O-*cyclohexylmethyl*-1,2-O-*cyclohexylidene*-α-D-*glucofuranose complex*. A solution of the glucofuranose (8.8 g,

**Table 1.** Reduction of aromatic ketones with the glucofuranose complex (2)[a]

| $LiAlH_4$ (mol) | Cyclohexyl phenyl ketone to cyclohexylphenylmethanol [b] | | Acetophenone to 1-phenylethanol [c] | | 2-Naphthyl methyl ketone to 1-(2-naphthyl)ethanol [d] | | 1-Naphthyl methyl ketone to 1-(1-naphthyl)ethanol [e] | |
|---|---|---|---|---|---|---|---|---|
| | $[\alpha]_D^{20}$ | E.e. (%) [f] | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) |
| 0.01 | −1.43 | 6.4 | −5.3 | 12.7 | −5.3 | 12.7 | −1.4 | 1.8 |
| 0.02 | −1.60 | 7.1 | −9.6 | 22.9 | −10.6 | 25.4 | −4.2 | 5.3 |
| 0.03 | −1.89 | 8.4 | −12.0 | 28.6 | −15.1 | 36.0 | −9.5 | 12.1 |
| 0.04 | −1.07 | 4.8 | −8.8 | 20.8 | −9.9 | 23.7 | −3.6 | 4.6 |
| 0.05 | −0.62 | 2.7 | −5.84 | 13.9 | −7.9 | 19.0 | −0.2 | 0.25 |
| 0.06 | −0.73 | 3.3 | −4.5 | 10.7 | | | | |

[a] Yields of the alcohols 60—70%. [b] B.p. 101 °C/3.5 mmHg, max. rotn. reported [9] $[\alpha]_D^{20}$ +22.5° (*c* 5 in EtOH). [c] B.p. 80 °C/1.7 mmHg, max. rotn. reported[10] $[\alpha]_D^{20}$ +41.94° (*c* 5 in EtOH). [d] B.p. 103 °C/0.3 mmHg, max. rotn. reported [11] $[\alpha]_D^{20}$ −41.9° (*c* 5 in EtOH). [e] B.p. 106 °C/0.4 mmHg, max. rotn. reported [12] $[\alpha]_D^{20}$ −78.9° (*c* 5 in EtOH). [f] E.e. = enantiomeric excess = (observed rotation × 100)/maximum rotation.

**Table 2.** Reduction of aliphatic ketones with the glucofuranose complex (2)[a]

| $LiAlH_4$ (mol) | Cyclohexyl methyl ketone to 1-cyclohexylethanol [b] | | $LiAlH_4$ (mol) | t-Butyl methyl ketone to 1-t-butylethanol [c] | | $LiAlH_4$ (mol) | Methyl isopropyl ketone to 1-isopropylethanol [d] | | Ethyl methyl ketone to butan-2-ol [e] | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $[\alpha]_D^{20}$ | E.e. (%) | | $[\alpha]_D^{20}$ | E.e. (%) | | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) |
| 0.012 | +1.28 | 15.0 | 0.01 | +0.26 | 5.5 | 0.020 | +0.60 | 11.3 | +0.69 | 6.3 |
| 0.018 | +2.06 | 24.2 | 0.02 | +0.48 | 9.85 | 0.025 | +1.04 | 19.5 | +1.27 | 11.6 |
| 0.025 | +3.65 | 42.8 | 0.03 | +0.67 | 13.80 | 0.030 | +1.35 | 25.4 | +1.68 | 15.3 |
| 0.032 | +1.91 | 22.4 | 0.04 | +0.53 | 10.90 | 0.035 | +1.04 | 19.5 | +0.83 | 7.6 |
| 0.039 | +1.20 | 14.1 | 0.05 | +0.32 | 6.55 | 0.040 | +0.50 | 9.4 | +0.32 | 2.9 |
| 0.045 | +0.55 | 6.5 | | | | | | | | |

[a] Yields of alcohols 50—70%. [b] B.p. 38—40 °C at 1 mmHg, max. rotn. [5] $[\alpha]_D^{20}$ +5.68° (neat); +8.52 (*c* 5 in EtOH). [c] B.p. 121 °C, max. rotn. reported [6] $[\alpha]_D^{20}$ +4.87° (*c* 5 in EtOH). [d] B.p. 110 °C, max. rotn. reported [7] $[\alpha]_D^{20}$ +5.34° (*c* 5 in EtOH). [e] B.p. 99 °C, max. rotn. reported $[\alpha]_D^{20}$ +11.0° (*c* 5 in EtOH).

**Table 3.** Reduction of aromatic ketone oximes with the glucofuranose complex (2)

| $LiAlH_4$ (mol) | Acetophenone oxime to α-phenylethylamine | | Propiophenone oxime to 1-phenylpropylamine | | 1-Phenylpropan-2-one oxime to 1-phenyl-2-propylamine | |
|---|---|---|---|---|---|---|
| | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) |
| 0.012 | −3.4 | 8.9 | −2.8 | 14.2 | +6.2 | 17.4 |
| 0.018 | −6.4 | 17.2 | −4.3 | 21.7 | +13.9 | 38.9 |
| 0.025 | −9.7 | 25.5 | −7.6 | 38.4 | +14.28 | 40.1 |
| 0.032 | −14.2 | 39.3 | −9.1 | 45.7 | +15.5 | 43.6 |
| 0.039 | −8.7 | 22.8 | −6.6 | 33.1 | +10.4 | 29.25 |
| 0.045 | −6.6 | 17.4 | −4.9 | 24.8 | +5.1 | 14.4 |

0.025 mol)[2,13,14] in dry ether (50 ml) was added to a measured volume of a standardised ethereal solution of lithium aluminium hydride (18—20 g $l^{-1}$). The mixture was heated with stirring under reflux for 90 min, after which a solution of the ketone (0.025 mol) in dry ether (20 mol) was added. Heating under reflux with stirring was continued for 2.5 h, after which the mixture was cooled, the excess of reducing complex was decomposed with water (15 ml) and the precipitated hydroxide was filtered off and washed with ether (2 × 40 ml). The combined filtrate and washings were dried ($MgSO_4$) and the solvent evaporated to give a pale-yellow oily residue. The secondary alcohols were isolated by fractional distillation leaving the very high boiling sugar complex behind. The purity of the products was established by g.l.c. and their identity established by i.r. and n.m.r. spectroscopy. Optical rotations were then determined (Tables 1 and 2).

(*ii*) *With the ethanol-modified complex.* A solution of the glucofuranose (8.8 g, 0.025 mol)[2,13,14] in dry ether (50 ml) was added to the standardised ethereal solution of lithium aluminium hydride (1 g, 0.025 mol). The mixture was heated under reflux for 90 min, after which various amounts of ethanol in ether solution were added and heating under reflux with stirring continued for 2.5 h. The mixture was then cooled, and the excess of reducing complex decomposed with water (75 ml). The products were separated as in (i) (Tables 5 and 6).

*Reduction of Ketone Oximes with the Lithium Aluminium Hydride–*3-O-*Cyclohexylmethyl*-1,2-O-*cyclohexylidene*-α-D-*glucofuranose Complex.*—A solution of the glucofuranose (8.8 g, 0.025 mol)[2,13,14] in dry ether (50 ml) was added to a measured volume of a standardised ethereal solution of lithium aluminium hydride (*ca.* 18—20 g $l^{-1}$). The mixture was heated under reflux with stirring for 90 min, then the solution of the oxime (0.0125 mol) in dry ether was added. Heating under reflux with stirring was continued for 2.6 h, after which the mixture was cooled, the complex decomposed with water (15 ml) and the precipitated hydroxide filtered off and washed with ether (2 × 30 ml). The combined filtrate and washings were extracted

**Table 4.** Reduction of aliphatic ketone oximes with the glucofuranose complex (2)[a]

| $LiAlH_4$ (mol) | Ethyl methyl ketone oxime to 2-aminobutane | | n-Butyl methyl ketone oxime to 2-aminohexane | | Isobutyl methyl ketone oxime to 4-amino-2-methylpentane | | n-Hexyl methyl ketone oxime to 2-amino-octane | | Cyclohexyl methyl ketone oxime to 1-cyclohexyl-ethylamine | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) |
| 0.012 | +1.1 | 14.9 | +0.57 | 13.2 | +0.76 | 18.2 | +0.69 | 10.4 | | |
| 0.018 | +1.9 | 25.8 | +0.92 | 21.3 | +0.89 | 21.4 | +1.66 | 17.5 | +0.92 | 28.6 |
| 0.025 | +3.1 | 41.7 | +1.53 | 35.6 | +1.28 | 30.5 | +1.88 | 28.4 | +1.28 | 40.2 |
| 0.032 | +2.4 | 32.5 | +1.93 | 44.8 | +1.83 | 43.6 | +3.27 | 49.3 | +1.68 | 52.4 |
| 0.039 | +1.5 | 21.3 | +1.30 | 30.3 | +1.27 | 29.2 | +2.10 | 31.7 | +1.22 | 38.2 |
| 0.045 | +0.94 | 12.7 | +0.89 | 20.75 | +0.82 | 19.5 | +1.28 | 19.3 | +0.69 | 21 |

[a] Physical constants of amines are as reported by us in Part 9 [4a] of this series.

**Table 5.** Reduction of aliphatic ketones with the ethanol-modified aluminium hydride complexes of 3-*O*-cyclohexylmethyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose[a]

| EtOH (mol) | Cyclohexyl methyl ketone to 1-cyclohexylethanol | | t-Butyl methyl ketone to 1-t-butylethanol | | EtOH (mol) | Methyl isopropyl ketone to 1-isopropylethanol | | Ethyl methyl ketone to butan-2-ol | |
|---|---|---|---|---|---|---|---|---|---|
| | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) | | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) |
| 0.012 | −1.64 | 19.2 | −0.53 | 10.8 | 0.036 | −0.46 | 8.4 | −1.13 | 10.3 |
| 0.014 | −2.84 | 33.4 | −1.07 | 21.9 | 0.038 | −0.99 | 18.5 | −1.76 | 16.0 |
| 0.016 | −3.08 | 36.2 | −1.65 | 33.9 | 0.040 | −1.32 | 24.6 | −2.32 | 20.2 |
| 0.018 | −2.16 | 25.4 | −2.47 | 50.70 | 0.042 | −0.83 | 15.5 | −1.62 | 14.8 |
| 0.020 | −1.51 | 17.7 | −1.41 | 23.9 | 0.044 | −0.42 | 7.8 | −0.90 | 8.2 |
| 0.022 | −1.17 | 13.8 | −0.95 | 19.5 | | | | | |

[a] Yields of alcohols 60—75%; b.p. and maximum rotations are as reported in Table 2.

**Table 6.** Reduction of aromatic ketones with the ethanol-modified lithium aluminium hydride complexes of 3-*O*-cyclohexylmethyl-1,2-*O*-cyclohexylidene-α-D-glucofuranose[a]

| EtOH (mol) | Cyclohexyl phenyl ketone to cyclohexylphenyl-methanol | | Acetophenone to 1-phenylethanol | | EtOH | 2-Naphthyl methyl ketone to 1-(2-anphthyl)ethanol | | 1-Naphthyl methyl ketone to 1-(1-naphthyl)ethanol | |
|---|---|---|---|---|---|---|---|---|---|
| | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) | | $[\alpha]_D^{20}$ | E.e. (%) | $[\alpha]_D^{20}$ | E.e. (%) |
| 0.010 | −0.78 | 3.5 (*S*) | +3.73 | 8.9 (*R*) | | | | | |
| 0.012 | −0.47 | 2.8 (*S*) | +6.82 | 16.4 (*R*) | 0.012 | +1.88 | 4.5 | +4.1 | 5.2 (*R*) |
| 0.016 | −0.43 | 1.9 (*S*) | +11.80 | 28.2 (*R*) | 0.014 | +3.31 | 7.9 | +11.8 | 15.0 (*R*) |
| 0.020 | −0.34 | 1.5 (*S*) | +15.6 | 37.2 (*R*) | 0.016 | +4.52 | 10.8 | +13.5 | 17.1 (*R*) |
| 0.024 | +0.87 | 3.9 (*R*) | +18.22 | 43.5 (*R*) | 0.018 | +8.10 | 19.3 | +9.9 | 12.6 (*R*) |
| 0.028 | +0.39 | 1.7 (*R*) | +7.35 | 17.6 (*R*) | 0.020 | +15.90 | 38.0 | +3.7 | 4.7 (*R*) |
| | | | | | 0.022 | +10.22 | 24.5 | +1.2 | 1.5 (*R*) |

[a] Yields of alcohols 65—80%; b.p. and maximum rotations are as reported in Table 1.

with dilute hydrochloric acid (3 × 20 ml) to separate all basic components. The aqueous acid layer was strongly basified (6M-NaOH) and extracted with ether (3 × 50 ml) and the extract washed with water (2 × 30 ml), dried ($MgSO_4$) and evaporated to give an oily product. The optically active primary amine was isolated by fractional distillation under reduced pressure and characterised by i.r. and n.m.r. spectra; its purity was checked by g.l.c. Optical rotations were then determined (Tables 3 and 4).

## References


1 Part 10, S. R. Landor, O. O. Sonola, and A. R. Tatchell, *J. Chem. Soc. Perkin Trans. 1*, 1978, 605.
2 S. R. Landor, B. J. Miller, and A. R. Tatchell, *J. Chem. Soc. C*, (*a*) 1966, 1822; (*b*) 1966, 2280; (*c*) 1967, 197.
3 S. R. Landor, A. R. Tatchell, and R. H. Williams, unpublished work.
4 (*a*) S. R. Landor, O. O. Sonola, and A. R. Tatchell, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1902; (*b*) S. R. Landor, A. R. Tatchell, and Y. M. Chan, unpublished work.
5 A. Dolmeo and J. Kenyon, *J. Chem. Soc.*, 1926, 1842.
6 (*a*) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 1914, 1128; (*b*) K. Mislow, R. O. O'Brien, and H. Schaifer, *J. Am. Chem. Soc.*, 1960, **82**, 5512.
7 J. Kenyon, *J. Chem. Soc.*, 1913, 1957.
8 J. Kenyon, H. Phillips, and V. Pittman, *J. Chem. Soc.*, 1935, 1077.
9 J. Kenyon, *J. Chem. Soc.*, 1951, 377.
10 See ref. 6*a*.
11 T. A. Collyer and J. Kenyon, *J. Chem. Soc.*, 1940, 676.
12 J. Kenyon, *J. Chem. Soc.*, 1946, 797.
13 R. S. Brimacombe, *Carbohydr. Res.*, 1966, **2**, 167.
14 R. C. Hockett, R. E. Miller, and A. Scattergood, *J. Am. Chem. Soc.*, 1949, **71**, 3072.


*Received* 30*th June* 1983; *Paper* 3/1129