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ASYMMETRIC SYNTHESIS BY CHIRAL RUTHENIUM COMPLEXES

V *. HOMOGENEOUS REDUCTION OF KETONES: TRANSFER AND PRESSURE HYDROGENATION IN THE PRESENCE OF $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$

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Summary

The asymmetric transfer reduction of prochiral ketones in homogeneous phase in the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ as catalyst and secondary alcohols or indoline as hydrogen source is reported. Optical yields up to 9.8% were obtained at 120°C. The reduction of ketones with molecular hydrogen under pressure affords alcohols at a higher rate but in lower optical yields.

Introduction

In a previous paper we reported that $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ is an effective catalyst for the hydrogen transfer reduction of carbon—carbon double bonds present in α,β-unsaturated acids [2]. Saturated, optically active acids were obtained by this procedure from prochiral substrates. We have now extended our investigation on the catalytic activity of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ to the transfer hydrogenation of ketones, in order to examine the possibility of synthesizing optically active alcohols from prochiral compounds at atmospheric pressure.

A few examples of transfer hydrogenations of ketones in the presence of

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* Preliminary results presented at the IXth Conference on Organometallic Chemistry [1], for part IV of the series see ref. 2.

ruthenium complexes are known [3—11], but no asymmetric transfer reduction has previously been reported for any catalyst.

Results and discussion

The most appropriate hydrogen donor for our transfer reductions was selected through a series of experiments in which acetophenone was reduced using various hydrogen donors (Table 1). Acetophenone may be reduced to (—)(*S*)-1-phenylethanol at 120°C when propan-2-ol or indoline are used as hydrogen sources; no reaction takes place up to 180°C in the presence of dioxane, and at this temperature the catalyst decomposes.

The highest optical yield was obtained using propan-2-ol at 120°C. In the presence of sodium isopropylate the reaction is faster, but the optical purity of the alcohol formed is lower and of the opposite configuration. A similar influence of a base on the reaction rate was reported by Sharf et al. [4] for the transfer reduction of cyclohexanone in the presence of $RuCl_2(PPh_3)_3$.

Various secondary alcohols were tried as hydrogen sources (Table 2). In all the cases examined the only products obtained were the alcohol corresponding to the ketone used as substrate and the ketone formed as dehydrogenation product of the secondary alcohol used as hydrogen donor, with 100% selectivity (eq. 1).

$$R{-}CO{-}R' + CH_3{-}CH(OH){-}R'' \rightleftharpoons R{-}CH(OH){-}R' + CH_3{-}CO{-}R'' \qquad (1)$$

When only a small excess of the hydrogen donor is used the reaction does not go to completion but reaches an equilibrium composition. In the case of the acetophenone and propan-2-ol system (with a ketone/alcohol molar ratio of 0.5) the equilibrium composition lies at 60% conversion of the ketone. Reaction rates are generally low and similar for all the aliphatic secondary alcohols tested. The lowest rate observed was with benzyl alcohol as hydrogen donor. When the system has a boiling point of 120°C or higher, the reaction does not require a pressure vessel and may be performed in an ordinary glass flask.

The structure of the substrate employed has a significant influence on the

TABLE 1

REDUCTION OF ACETOPHENONE BY HYDROGEN TRANSFER FROM VARIOUS SOURCES

($H_4Ru_4(CO)_8[(—)\text{-DIOP}]_2$ 50 mg; acetophenone 0.111 mol; hydrogen donor 0.222 mol)

Hydrogen donor	T (°C)	Reaction time (h)	Yield (%)	Reaction product: 1-phenylethanol		
				$\alpha^{25}_{D(l=1)}$ (°) (neat)	O.Y. [a] (%)	Conf. [b]
Propan-2-ol	120	111	34.9	—1.906	4.3	(*S*)
	120 [c]	24	67.5	+0.105	0.2	(*R*)
Indoline	120	275	28.3	—0.308	0.7	(*S*)
Dioxane	120—180 [d]	no reaction				

[a] O.Y.: optical yield (see Table 7); [b] Conf.: configuration of the prevailing enantiomer (see Table 7); [c] Experiment carried out in the presence of $(CH_3)_2CHONa$ (0.652 mmol); [d] At 180°C the catalyst was partially decomposed.

TABLE 2

REDUCTION OF KETONES BY HYDROGEN TRANSFER FROM VARIOUS ALCOHOLS

($H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ 50 mg; mol substrate/mol H donor = 0.5; T 120°C; reaction mixture 30 ml)

Substrate RCOR′	Hydrogen donor	Reaction time (h)	Yield (%)	Reaction product: RCH(OH)R′		
				$\alpha^{25}_{D(l=1)}$ (°) (neat)	O.Y. [a] (%)	Conf. [b]
$C_6H_5COCH_3$	$CH_3CH(OH)CH_3$	111	34.9	−1.906	4.3	(*S*)
	$CH_3CH(OH)C_2H_5$	116	27.6	−0.652	1.5	(*S*)
	$CH_3CH(OH)(CH_2)_2CH_3$	142	31.8	−1.219	2.8	(*S*)
	$CH_3CH(OH)(CH_2)_5CH_3$	94	48.8	−1.352	3.1	(*S*)
	$C_6H_5CH_2OH$	190	19.1	−0.580	1.3	(*S*)
$C_6H_5COCH_2CH(CH_3)_2$	$CH_3CH(OH)CH_3$	86	37.1	−0.551 [c]	9.8	(*S*)
	$CH_3CH(OH)(CH_2)_2CH_3$	159	28.9	−0.438 [d]	8.4	(*S*)
$CH_3COCH(CH_3)_2$	$CH_3CH(OH)CH_3$	261	31.0	−0.054	1.2	(*R*)
	$CH_3CH(OH)(CH_2)_2CH_3$	288	28.4	−0.030	0.7	(*R*)
$CH_3CO(CH_2)_3CH_3$	$CH_3CH(OH)CH_3$	185	26.0	−0.041 [e]	0.4	(*R*)
	$CH_3CH(OH)(CH_2)_2CH_3$	88	26.6	−0.117 [e]	1.2	(*R*)

[a] O.Y.: optical yield (see Table 7); [b] Conf.: configuration of the prevailing enantiomer (see Table 7); [c] Measured at 26°C (c 17.46, *n*-heptane); [d] Measured at 26°C (c 16.05, *n*-heptane); [e] Measured at 20°C.

rate and on the optical purity of the alcohol obtained in the reduction of ketones by hydrogen transfer from propan-2-ol in the presence of $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ (Table 3). Alkyl phenyl ketones having a primary alkyl group attached to the carbonyl group react at a higher rate than those having a sec-

TABLE 3

REDUCTION OF SOME ALKYL PHENYL AND ALKYL METHYL KETONES BY HYDROGEN TRANSFER FROM PROPAN-2-OL

($H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ 50 mg; mol substrate/mol H donor = 0.5; T 120°C; reaction mixture 30 ml)

Substrate RCOR′	Reaction time (h)	Yield (%)	Reaction product: RCH(OH)R′		
			$\alpha_{D(l=1)}$ [a] (°) (neat)	O.Y. [b] (%)	Conf. [c]
$C_6H_5COCH_3$	111	34.9	−1.906	4.3	(*S*)
$C_6H_5COCH_2CH_3$	139	44.1	−1.365	4.8	(*S*)
$C_6H_5CO(CH_2)_2CH_3$	143	25.9	−0.092 [d]	3.1	(*S*)
$C_6H_5COCH(CH_3)_2$	255	39.0	−0.137 [e]	3.9	(*S*)
$C_6H_5CO(CH_2)_3CH_3$	160	34.4	−0.504	2.5	(*S*)
$C_6H_5COCH_2CH(CH_3)_2$	86	37.1	−0.551 [f]	9.8	(*S*)
$C_6H_5COC(CH_3)_3$	283	36.3	−0.219 [g]	6.7	(*S*)
$CH_3COCH_2CH_3$	326	26.9	−0.035	0.3	(*R*)
$CH_3CO(CH_2)_2CH_3$	408	26.9	−0.030	0.3	(*R*)
$CH_3COCH(CH_3)_2$	261	31.0	−0.054	1.2	(*R*)
$CH_3CO(CH_2)_3CH_3$	185	26.0	−0.041	0.4	(*R*)
$CH_3COCH_2CH(CH_3)_2$	422	29.3	−0.049	0.3	(*R*)
$CH_3COC(CH_3)_3$	476	21.8	+0.120	1.9	(*S*)

[a] Measured at the temperature for which the maximum value of specific rotation is known (see Table 7); [b] O.Y.: optical yield (see Table 7); [c] Conf.: configuration of the prevailing enantiomer (see Table 7); [d] Measured in solution (c 6.50, benzene); [e] Measured in solution (c 7.30, diethylether); [f] Measured in solution (c 17.46, *n*-heptane); [g] Measured in solution (c 9.04, diethylether).

ondary or tertiary alkyl group, and than dialkyl ketones.

For the series of alkyl methyl ketones an increase in the branching of the alkyl moiety (by substitution of the hydrogen atoms on carbon atom in position 3 by methyl groups) increases the optical purity of the alcohol formed: (—)(*R*)-butan-2-ol, (—)(*R*)-3-methylbutan-2-ol and (+)(*S*)-3,3-dimethylbutan-2-ol are obtained with optical purities of 0.3, 1.2, and 1.9%, respectively.

The increase in chain length and in the number of branches on the carbon atom in β-position to the carbonyl group does not affect the optical yield, which is low (about 0.3%) in all cases. The dominant configuration of the alcohol formed was (*R*) in all cases, except for 3,3-dimethylbutan-2-ol, which had the (*S*) configuration.

Alkyl phenyl ketones yield alcohols having an optical purity much higher (by about ten times) than that of the alcohols obtained from alkyl methyl ketones. For the series of alkyl phenyl ketones the influence of the alkyl moiety is different from that in the aliphatic series: the highest optical yield (9.8%) was achieved in the reduction of 3-methyl-1-phenylbutan-1-one. In the aromatic series the alcohols formed always had the (*S*) configurations.

We have also examined the influence of the temperature on the reduction of acetophenone by hydrogen transfer from (*R*)(*S*)-octan-2-ol in the 120—180°C range. The data obtained (Table 4) show that the rate increases with temperature as expected, while the optical yield decreases from 3.1% at 120°C to 1.9% at 180°C: at this latter temperature considerable decomposition of the catalyst was observed, with formation of solid material.

The addition of an excess of phosphine to the reactants in order to stabilize the catalytic intermediate when phosphine-substituted catalysts were used has sometimes been suggested [12]. Such addition, however, not only stabilizes the catalyst but often affects the rate [12]. In our case too, as shown in Table 5, an excess of phosphine causes a remarkable decrease in rate, while the optical purity of the reaction products is lowered. Furthermore, in the case of 1-phenylethanol the configuration is inverted, suggesting the intervention of catalytic species different from those operating in the absence of added phosphine. A similar effect of an excess of (—)-DIOP was found in the reduction of ketones under pressure with the same catalytic system [13].

TABLE 4

INFLUENCE OF REACTION TEMPERATURE ON THE REDUCTION OF ACETOPHENONE BY HYDROGEN TRANSFER FROM (R)(S)-OCTAN-2-OL

($H_4Ru_4(CO)_8$[(—)-DIOP]$_2$ 50 mg; mol substrate/mol H donor = 0.5; reaction mixture 30 ml)

Reaction temperature (°C)	Reaction time (h)	Yield (%)	Reaction product: 1-phenylethanol		
			$\alpha^{25}_{D(l=1)}$ (°) (neat)	O.Y. [a] (%)	Conf. [b]
120	94	48.8	—1.352	3.1	(S)
150	32	42.0	—1.154	2.6	(S)
180 [c]	22	49.4	—0.822	1.9	(S)

[a] O.Y.: optical yield (see Table 7); [b] Conf.: configuration of the prevailing enantiomer (see Table 7);
[c] At this temperature the catalyst was partially decomposed.

TABLE 5

INFLUENCE OF (—)-DIOP EXCESS IN THE REDUCTION OF KETONES BY HYDROGEN TRANSFER FROM VARIOUS ALCOHOLS

($H_4Ru_4(CO)_8$[(—)-DIOP]$_2$ 50 mg; mol substrate/mol H donor = 0.5; *T* 120°C; reaction mixture 30 ml)

Substrate RCOR	Hydrogen donor	mol (—)-DIOP / mol catalyst	Reaction time (h)	Yield (%)	Reaction product: RCH(OH)R′		
					$\alpha_{D(l=1)}^{25}$ (°) (neat)	O.Y. [a] (%)	Conf. [b]
$C_6H_5COCH_3$	$CH_3CH(OH)CH_3$	0.0	111	34.9	−1.906	4.3	(*S*)
	$CH_3CH(OH)CH_3$	4.5	360	36.4	+0.736	1.7	(*R*)
	$CH_3CH(OH)(CH_2)_2CH_3$	0.0	142	31.8	−1.219	2.8	(*S*)
	$CH_3CH(OH)(CH_2)_2CH_3$	4.5	776	40.5	+0.048	0.1	(*R*)
$C_6H_5COCH_2CH(CH_3)_2$	$CH_3CH(OH)CH_3$	0.0	86	37.1	−0.551 [c]	9.8	(*S*)
	$CH_3CH(OH)CH_3$	4.5	351	29.4	−0.128 [d]	2.5	(*S*)

[a] O.Y.: optical yield (see Table 7); [b] Conf.: configuration of the prevailing enantiomer (see Table 7); [c] Measured at 26°C (c 17.46, *n*-heptane); [d] Measured at 26°C (c 15.90, *n*-heptane).

TABLE 6

HYDROGENATION UNDER PRESSURE OF PROCHIRAL KETONES

($H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ 100 mg; substrate 5 g; toluene 15 ml; T 120°C; $p(H_2)$ 130 atm at 20°C)

Substrate RCOR'	Reaction time (h)	Yield (%)	Reaction product: RCH(OH)R'		
			$\alpha_{D(l=1)}$ [a] (°) (neat)	O.Y. [b] (%)	Conf. [c]
$C_6H_5COCH_3$ [d]	14	96.0	+0.555	1.3	(*R*)
$C_6H_5COCH_2CH_3$	33	42.9	+0.379	1.3	(*R*)
$C_6H_5CO(CH_2)_2CH_3$	134	67.7	−0.010 [e]	0.3	(*S*)
$C_6H_5COCH(CH_3)_2$	180	82.7	−0.003 [f]	0.1	(*S*)
$C_6H_5CO(CH_2)_3CH_3$	183	63.8	−0.053	0.3	(*S*)
$C_6H_5COCH_2CH(CH_3)_2$	38	87.5	−0.320 [g]	5.4	(*S*)
$C_6H_5COC(CH_3)_3$	183	100	−0.231 [h]	0.6	(*S*)
$CH_3COCH_2CH_3$	112	99.5	−0.014	0.1	(*R*)
$CH_3CO(CH_2)_2CH_3$	233	100	−0.049	0.4	(*R*)
$CH_3COCH(CH_3)_2$	21	42.2	−0.076	1.8	(*R*)
$CH_3CO(CH_2)_3CH_3$	232	77.4	−0.004	<0.1	(*R*)
$CH_3COCH_2CH(CH_3)_2$	408	41.1	−0.002	<0.1	(*R*)
$CH_3COC(CH_3)_3$	258	61.8	−0.041	0.6	(*R*)

[a] Measured at the temperature for which the maximum value of specific rotation is known (see Table 7); [b] O.Y.: optical yield (see Table 7); [c] Conf.: configuration of the prevailing enantiomer (see Table 7); [d] From ref. 13; [e] Measured in solution (c 6.38, benzene); [f] Measured in solution (c 7.01, diethyl ether); [g] Measured in solution (c 18.24, *n*-heptane); [h] Measured in solution (c 9.07, diethyl ether).

The results of the reduction of the same ketones by molecular hydrogen under pressure (130 atm) with the same catalytic system ($H_4Ru_4(CO)_8$-$[(-)\text{-DIOP}]_2$) at the same temperature (120°C) are reported in Table 6. On comparing these data with those reported in Table 3 we see that hydrogenation under pressure is faster than the hydrogen transfer process. However the optical yields obtained in the latter reaction are much higher. 3-Methyl-1-phenylbutan-1-one gives the highest optical yield and the highest reaction rate in both reactions.

TABLE 7

MAXIMUM ROTATORY POWER AND SIGN-CONFIGURATION RELATION REPORTED IN THE LITERATURE FOR THE ALCOHOLS OBTAINED

Alcohol	$[\alpha]^{T}_{D\,max}$	T (°C)	Medium	Ref.	Relation sign-conf.	Ref.
$C_6H_5CH(OH)CH_3$	43.6	25	neat	19	(+)(*R*)	20
$C_6H_5CH(OH)CH_2CH_3$	28.9	25	neat	21	(+)(*R*)	20
$C_6H_5CH(OH)(CH_2)_2CH_3$	45.93	27	c 6.1, benzene	22	(+)(*R*)	20
$C_6H_5CH(OH)CH(CH_3)_2$	47.7	20	c 7.0, diethyl ether	20	(+)(*R*)	20
$C_6H_5CH(OH)(CH_2)_3CH_3$	20.72	20	neat	23	(+)(*R*)	20
$C_6H_5CH(OH)CH_2CH(CH_3)_2$	32.3	26	c 16.6, *n*-heptane	20	(+)(*R*)	20
$C_6H_5CH(OH)C(CH_3)_3$	36.2	20	c 9.0, diethyl ether	20	(+)(*R*)	20
$CH_3CH(OH)CH_2CH_3$	13.83	20	neat	24	(−)(*R*)	25
$CH_3CH(OH)(CH_2)_2CH_3$	13.70	20	neat	26	(−)(*R*)	27
$CH_3CH(OH)CH(CH_3)_2$	5.34	25	neat	28	(−)(*R*)	29
$CH_3CH(OH)(CH_2)_3CH_3$	11.57	20	neat	26	(−)(*R*)	27
$CH_3CH(OH)CH_2CH(CH_3)_2$	21.19	19.5	neat	30	(−)(*R*)	31
$CH_3CH(OH)C(CH_3)_3$	7.84	20	neat	32	(−)(*R*)	33

We conclude that for some substrates the hydrogen transfer reaction appears a convenient synthetic method for preparing optically active alcohols.

We are at present trying to collect evidence on the course of the transfer and on the reactions under pressure, and to find out the structures of the catalytically active intermediates, which are probably different in the two cases. In fact, alcohols having opposite configeration were obtained by subjecting the same substrate to the two different reduction procedures.

Experimental

GLC analyses were performed on a Perkin Elmer F 30 instrument; NMR spectra were recorded on a Perkin Elmer R 32 spectrometer; rotatory powers were measured with a Perkin Elmer 241 polarimeter; IR spectra were recorded with a Perkin Elmer 580 spectrophotometer.

Materials

All ketones, with the exception of 3-methyl-1-phenylbutan-1-one and 1-phenylpentan-1-one, were commercial products. 1-Phenylpentan-1-one was prepared according to Ford et al. [14]. 3-Methyl-1-phenylbutan-1-one (b.p. 239—240°C, n_D^{20} 1.5123 [15]) was prepared from 3-methylbutanoyl chloride (b.p. 117—118°C, n_D^{20} 1.4156) (63 g), $AlCl_3$ (74.5 g) and dry benzene (123 ml) according to the procedure described by Vogel [16] for the synthesis of 1-phenylbutan-1-one. Dioxane was purified according to Hess and Frahm [17]. $H_4Ru_4(CO)_8[(-)\text{-DIOP}]_2$ was prepared as previously described [18].

Hydrogenation procedures

Hydrogen transfer experiments were carried out in a 125 ml stainless steel rocking autoclave. The air was evacuated from the autoclave containing the catalyst and eventually the (—)-DIOP, alcohol and ketone were introduced by suction, and finally the vessel was charged with nitrogen to atmospheric pressure. The autoclave was then rocked and heated at the appropriate temperature in an oil bath.

Hydrogenations were performed by the same technique, but with introduction of hydrogen up to the pressure of 130 atm into the autoclave after all the other species.

Conversions were determined by submitting the crude product mixtures to GLC analyses using 2 m columns packed with Carbowax 20M (15%) on Chromosorb W (85%).

In order to recover the reaction product, the volatile materials were separated from the catalyst by distillation at reduced pressure and the products were then separated by preparative GLC from the enriched fractions (3 m Butandiolsuccinate (10%) on Chromosorb A (90%) at appropriate temperatures).

Pure reaction products were identified by comparing their IR and NMR spectra with those of authentic samples prepared from the corresponding ketones by $LiAlH_4$ reduction. The optical rotations of the alcohols were measured on pure liquids or on solutions (see Tables) and the optical purities derived by comparing the values of the specific rotations with the maxima values reported in literature (Table 7). The values of densities of the various pure compounds were taken from the literature.

The configurations were assigned by comparison with literature data (see Table 7).

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References

1 M. Bianchi, P. Frediani, U. Matteoli, G. Menchi, F. Piacenti, C. Botteghi and S. Gladiali, IXth International Conference on Organometallic Chemistry, Dijon (France), September 3—7, 1979, Abstract no. P46T.

2 M. Bianchi, U. Matteoli, G. Menchi, P. Frediani, F. Piacenti and C. Botteghi, J. Organometal. Chem., 195 (1980) 337.

3 L.Kh. Freidlin, V.Z. Sharf, V.N. Krutii and S.I. Shcherbakova, J. Org. Chem. USSR, 8 (1972) 986.

4 V.Z. Sharf, L.Kh. Freidlin, V.N. Krutii and T.V. Lysyak, Izv. Akad. Nauk SSSR, Ser. Khim., (1972) 2195; Chem. Abstr., 78 (1973) 71087.

5 V.Z. Sharf, L.Kh. Freidlin and V.N. Krutii, Izv. Akad. Nauk SSSR, Ser. Khim., (1973) 2264; Chem. Abstr., 80 (1974) 59533.

6 V.Z. Sharf, L.Kh. Freidlin, V.N. Krutii and I.S. Shekoyan, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 1330; Chem. Abstr., 81 (1974) 177132.

7 H. Imai, T. Nishiguchi and K. Fukuzumi, J. Org. Chem., 41 (1976) 665.

8 H. Imai, T. Nishiguchi and K. Fukuzumi, J. Org. Chem., 41 (1976) 2688.

9 V.Z. Sharf, L.Kh. Freidlin and V.N. Krutii, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 735; Chem. Abstr., 87 (1977) 38552.

10 V.Z. Sharf, L.Kh. Freidlin, I.S. Shekoyan and V.N. Krutii, Izv. Akad. Nauk SSSR, Ser. Khim., (1977) 834; Chem. Abstr., 87 (1977) 133953.

11 V.Z. Sharf, L.Kh. Freidlin, I.S. Shekoyan and V.N. Krutii, Izv. Akad. Nauk SSSR, Ser. Khim., (1978) 1064; Chem. Abstr., 89 (1978) 42539.

12 F. Piacenti, M. Bianchi, E. Benedetti and P. Frediani, J. Organometal. Chem., 23 (1970) 257.

13 C. Botteghi, M. Bianchi, E. Benedetti and U. Matteoli, Chimia, 29 (1975) 256.

14 J.H. Ford, C.D. Thompson and C.S. Marvel, J. Amer. Chem. Soc., 57 (1935) 2619.

15 D.P. Evans and J.J. Gordon, J. Chem. Soc., (1938) 1434.

16 A.J. Vogel, Practical Organic Chemistry, IIIrd Ed. Longmans, London, 1964, p. 732.

17 K. Hess and H. Frahm, Chem. Ber., 71 (1938) 2627.

18 C. Botteghi, S. Gladiali, M. Bianchi, U. Matteoli, P. Frediani, P.G. Vergamini and E. Benedetti, J. Organometal. Chem., 140 (1977) 221.

19 E.L. Eliel, J. Amer. Chem. Soc., 71 (1949) 3970.

20 R. MacLeod, F.J. Welch and H.S. Mosher, J. Amer. Chem. Soc., 82 (1960) 876.

21 a) G.P. Giacomelli, R. Menicagli and L. Lardicci, Tetrahedron Lett., (1971) 4135; b) J.S. Birtwistle, K. Lee, J.D. Morrison, W.A. Sanderson and H.S. Mosher, J. Org. Chem., 29 (1964) 37.

22 K. Mislow and C.L. Hamermesh, J. Amer. Chem. Soc., 77 (1955) 1590.

23 A. Horeau, J.P. Guetté and R. Weidmann, Bull. Soc. Chim. France, (1966) 3513.

24 J. Kenyon, H. Phillips and V.P. Pittman, J. Chem. Soc., (1935) 1072.

25 K.B. Wiberg, J. Amer. Chem. Soc., 74 (1952) 3891.

26 R.H. Pickard and J. Kenyon, J. Chem. Soc., 99 (1911) 45.

27 W. Klyne, Progress in Stereochemistry, Vol. 1, Butterworths, London, 1954.

28 D. Nasipuri and G. Sarkar, J. Indian Chem. Soc., 44 (1967) 165.

29 P.G. Stevens, J. Amer. Chem. Soc., 54 (1932) 3732.

30 J. Kenyon and H.E. Strauss, J. Chem. Soc., (1949) 2153.

31 P.A. Levene and R.E. Marker, J. Biol. Chem., 90 (1931) 669; Chem. Zentr., 102 I (1931) 3224.

32 V. Prelog, E. Philbin, E. Watanabe and M. Wilhelm, Helv. Chim. Acta, 39 (1956) 1086.

33 J. Jacobus, Z. Majerski, K. Mislow and P. von Ragué Schleyer, J. Amer. Chem. Soc., 91 (1969) 1998.