Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 109, No. 1, February 1997, pp. 15–20.

Stereochemistry of *cis*- and *trans*-4,6-diaryltetrahydropyran-2-ones

H SURYA PRAKASH RAO* and B BHARATHI
Department of Chemistry, Pondicherry University, Pondicherry 605 014, India

MS received 7 May 1996; revised 30 September 1996

Abstract. *cis*- and *trans*-4,6-Diaryltetrahydropyran-2-ones were synthesised from the corresponding ketoesters. High resolution NMR spectral data reveal that they are stabilised in half-chair conformations.

Keywords. Stereochemistry of diaryltetrahydropyran-2-ones; NMR spectral analysis; half-chair conformation.

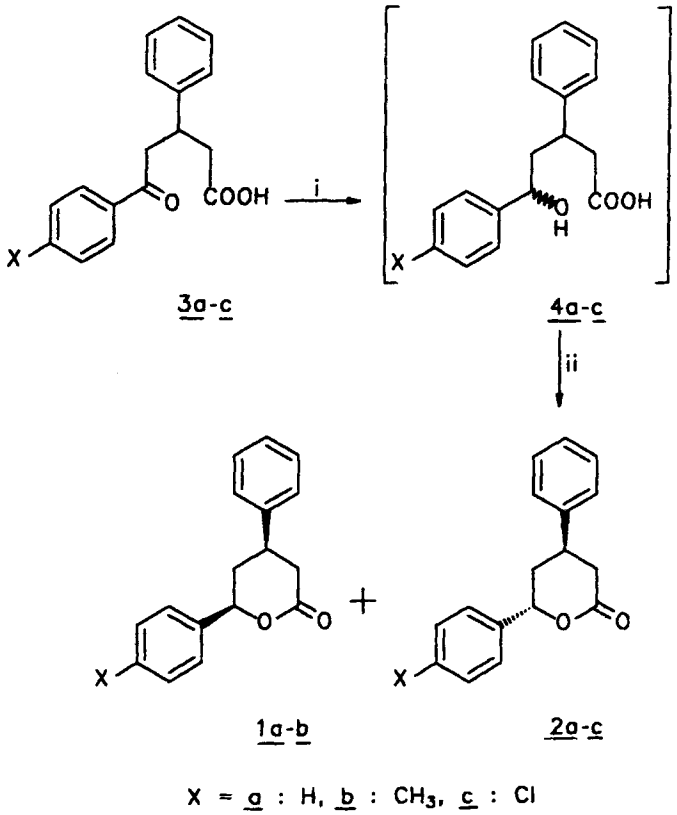
1. Introduction

Studies on the synthesis and stereochemistry of 4,6-disubstituted tetrahydropyran-2-ones attract the attention of organic chemists since they occur as structural moieties in several secondary metabolites (Ohloff 1978; Brand *et al* 1979) such as rhizoxin (Keck *et al* 1993), compactin (Brown *et al* 1976) and mevinolin (Alberts *et al* 1980). The relationship between the structure and conformation of substituted tetrahydropyran-2-ones has been elucidated with spectroscopic techniques such as ultraviolet (UV); (Closson *et al* 1967), infrared (IR) (Cheung *et al* 1965), proton nuclear magnetic resonance (^{1}H NMR); (Stanley *et al* 1990, 1991), optical rotatory dispersion (ORD) and circular dichroism (CD) (Wolf 1966). There is general agreement that the O–CO–C moiety in tetrahydropyran-2-one tends to maintain coplanarity (McConnell *et al* 1962; Cheung *et al* 1965). However, steric and torsional interactions in the molecule dictate the actual conformation (Philip *et al* 1981). Unsubstituted tetrahydropyran-2-one (δ-valerolactone) adopts a half-chair conformation in preference to a boat conformation (Fronza *et al* 1982). Earlier it has been found that both *cis*- and *trans*-4,6-dimethyltetrahydropyran-2-ones also stabilise in half-chair conformation with the latter being slightly flattened (Allinger and Chang 1977). Recently there has been renewed interest in the synthesis and stereochemistry of aryl-substituted tetrahydropyran-2-ones (Stanley *et al* 1990, 1991; Bennett *et al* 1991; Takano *et al* 1992) many years after Meerwein (1918) had originally prepared some of them. We report herein our studies on the synthesis and stereochemistry of hitherto unreported *cis*- (1a-b) and *trans*- (2a-c) 4,6-diaryltetrahydropyran-2-ones.

2. Results and discussion

Synthesis of tetrahydropyran-2-ones (1a-b, 2a-c) is given in scheme 1. Sodium borohydride reduction of the keto group of 3,5-diaryl-5-oxopentanoic acid (3a-c) in methanol and subsequent dehydration at elevated temperature and reduced pressure

*For correspondence



Scheme 1. Reagents and conditions: (i) $NaBH_4$, MeOH, 0 °C, H^+; (ii) 120 °C, 2 mm.

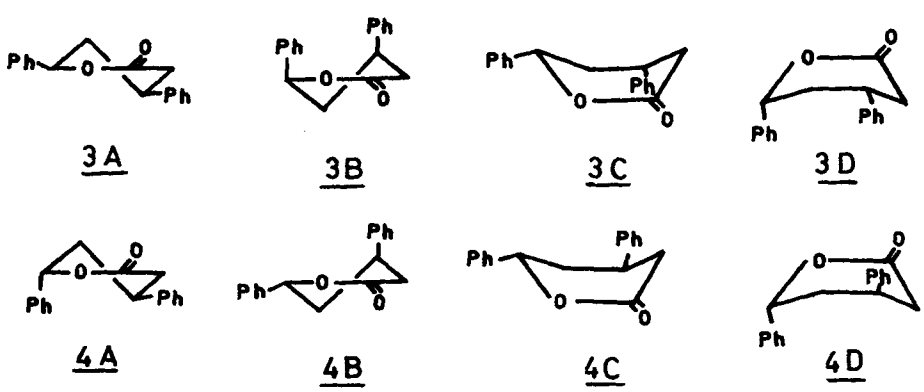


Figure 1. Possible half-chair and boat conformations of 1a and 2a.

resulted in the required tetrahydropyran-2-ones which were chromatographically separated and analysed.

Assignment of the configurations and conformations for 1a-b and 2a-c depends mainly on the analysis of their first order 400 MHz ^{1}H NMR spectra. Possible half-chair and boat conformations (3A-D, 4A-D) for *cis*- and *trans*-tetrahydropyran-2-ones (1a, 2a) are shown in figure 1.

The ^{1}H NMR spectrum of *cis*-4,6-diphenyltetrahydropyran-2-one (1a) indicated that C_4–H was a triple double doublet (*tdd*), with coupling constants (J), $J_{4ax,3ax}$ and $J_{4ax,5ax} = 11{\cdot}7$ Hz; $J_{4ax,3eq} = 5{\cdot}9$ Hz; $J_{4ax,5eq} = 3{\cdot}9$ Hz, and C_6–H a double doublet (*dd*), with $J_{6ax,5ax} = 11{\cdot}7$ Hz, $J_{6ax,5eq} = 2{\cdot}9$ Hz. These data indicate that both C_4–H and C_6–H are in axial positions and consequently, the two phenyl rings occupy equatorial positions. A long range coupling of 2·0 Hz between C_{3eq}–H and C_{5eq}–H indicates that these two hydrogens are present in near planar W configuration (Jackman and Sternhell 1969). A geminal coupling constant of 18·1 Hz seen between C_{3eq}–H and C_{3ax}–H indicates that the C_3-methylene group bisects the adjacent carbonyl (Barfield and Grant 1963). These data are consistent with the half-chair conformation for tetrahydropyran-2-one, 1a. The carbonyl absorption at 1730 cm^{-1} also supports a half-chair conformation for 1a (Cheung *et al* 1965; Herz *et al* 1970; Lindsay and Overton 1973). A global minimum energy conformation of 1a generated by molecular mechanics calculations utilising PCMODEL version 1·0 software gives theoretical coupling constants, which agree well with experimental values (table 1). Interestingly, the C_4-carbon having a phenyl substituent in tetrahydropyran-2-one, 1a, resonates upfield (37·63 ppm), compared to C_5 (38·93 ppm) in ^{13}C NMR spectra. This can be attributed to the γ-gauche effect of the ring oxygen atom (Atta-ur-Rahman 1986).

The ^{1}H NMR spectrum of *trans*-4,6-diphenyltetrahydropyran-2-one (2a) showed that C_4–H was a doublet of quartets (*dq*, broad), with $J_{4ax,3ax} = 9{\cdot}3$ Hz, $J_{4ax,5ax}$, $J_{4ax,3eq}$ and $J_{4ax,5eq} \simeq 6{\cdot}3$ Hz, and C_6–H a doublet (*dd*) with $J_{6eq,5ax} = 6{\cdot}9$ Hz, $J_{6eq,5eq} = 4{\cdot}9$ Hz. These data indicate that C_4–H and C_6–H occupy axial and equatorial positions respectively and, consequently, C_4-phenyl and C_6-phenyl groups are in equatorial and axial positions respectively. ^{1}H NMR also revealed large geminal

Table 1. ^{1}H NMR spectral data with observed and calculated coupling constants for *cis*-4,6- diphenyltetrahydropyran-2-one 1a and *trans*-4,6-diphenyltetrahydropyran-2-one, 2a.

Proton splitting pattern	J values, 1a (*cis*-isomer)		Proton splitting pattern	J values, 2a (*trans*-isomer)	
	Observed	Calculated		Observed	Calculated
$H_{3ax} = 2{\cdot}68$, *dd*,	$J_{3ax,3eq} = 18{\cdot}1$		2·80, *dd*	$J_{3ax,3eq} = 17{\cdot}6$	
	$J_{3ax,4ax} = 11{\cdot}7$	(11·9)		$J_{3ax,4ax} = 9{\cdot}3$	(11·07)
$H_{3eq} = 3{\cdot}05$, *ddd*,	$J_{3eq,3ax} = 18{\cdot}1$		2·90, *dd*,	$J_{3eq,3ax} = 17{\cdot}6$	
	$J_{3eq,4ax} = 5{\cdot}9$	(4·7)		$J_{3eq,4ax} = 6{\cdot}4$	(5·0)
	$J_{3eq,5eq} = 2{\cdot}0$			$J_{3eq,5eq} =$ --	
$H_{4ax} = 3{\cdot}39$, *tdd*,	$J_{4ax,3ax} = 11{\cdot}7$	(11·9)	3·28, *dq*,	$J_{4ax,3ax} = 9{\cdot}3$	(11·7)
	$J_{4ax,5ax} = 11{\cdot}7$	(12·3)		$J_{4ax,5ax} = 7{\cdot}2$	(12·3)
	$J_{4ax,3eq} = 5{\cdot}9$	(4·7)		$J_{4ax,3eq} = 4{\cdot}9$	(5·0)
	$J_{4ax,5eq} = 3{\cdot}9$	(2·6)		$J_{4ax,5eq} = 5{\cdot}9$	(2·4)
$H_{5ax} = 2{\cdot}05$, *dt*,	$J_{5ax,5eq} = 14{\cdot}2$		2·37, *ddd*,	$J_{5ax,5eq} = 14{\cdot}0$	
	$J_{5ax,4ax} = 11{\cdot}7$	(12·3)		$J_{5ax,4ax} = 7{\cdot}2$	(12·3)
	$J_{5ax,6ax} = 11{\cdot}7$	(11·6)		$J_{5ax,6eq} = 6{\cdot}9$	(5·3)
$H_{5eq} = 2{\cdot}42$, *dddd*	$J_{5eq,5ax} = 14{\cdot}2$		2·32, *ddd*,	$J_{5eq,5ax} = 14{\cdot}0$,	
	$J_{5eq,6ax} = 2{\cdot}9$	(2·1)		$J_{5eq,6eq} = 4{\cdot}9$	(1·3)
	$J_{5eq,4ax} = 3{\cdot}9$	(2·6)		$J_{5eq,4ax} = 5{\cdot}9$	(2·4)
	$J_{5eq,3eq} = 2{\cdot}0$			$J_{5eq,3eq} =$ ---	
$H_{6ax} = 5{\cdot}47$, *dd*	$J_{6ax,5ax} = 11{\cdot}7$	(11·6)	5·52, *td*,	$J_{6eq,5ax} = 6{\cdot}9$	(5·3)
	$J_{6ax,5eq} = 2{\cdot}9$	(2·1)	(H_{6eq})	$J_{6eq,5eq} = 4{\cdot}9$	(1·3)
Ar–H = 7·2–7·6, (*m*, 10 H)			Ar–H = 7·2–7·4, (*m*, 10 H)		

coupling constant of 17·6 Hz for C_3-methylene group which indicates that it is bisected by the adjacent carbonyl (Barfield and Grant 1963). Therefore, it can be concluded that *trans* isomer 2a is stabilised in a half-chair conformation rather than in the boat conformation. The IR spectrum of 2a showed carbonyl stretching frequency at 1730 cm^{-1}, confirming a chair conformation for the molecule (Cheung *et al* 1965; Herz *et al* 1970; Lindsay and Overton 1973). However, since the ^1H NMR spectrum did not reveal any long range W coupling (Jackman and Sternhell 1969) between C_{3eq}–H and C_{5eq}–H, we favour a dynamic twisted half-chair conformation for 2a with C_4–Ph in an equatorial position and C_6–Ph in an axial position. The location of the C_6–Ph in an axial position may relieve dipole interactions with the neighbouring oxygen atom. A twisted half-chair conformation may decrease unfavourable 1,3-diaxial interactions between C_6–Ph and C_{4ax}–H. However, vicinal coupling constants generated by theoretical calculations for the half-chair conformation of 2a do not agree well with the experimental values (table 1), indicating the dynamic behaviour of 2a.

A few more *cis*- (1b) and *trans*- (2b-c) tetrahydropyran-2-ones having electron-withdrawing and-donating substitutents at the para position of the C_6-phenyl ring were synthesised to study the effect of substituents in a reduction-cyclisation sequence. Interestingly, when 5(4-chlorophenyl)-3-phenylpentanoic acid (3c) was subjected to the reduction-cyclisation sequence only *trans*-6(4-chlorophenyl)-4-phenyltetrahydropyran-2-one (2c) resulted from the reaction. However, the NMR spectrum of the crude reduction product of the ketoester precursor revealed the presence of two diastereomeric alcohol esters (like and unlike, Juaristi 1991) in the ratio of 85:15. Since the single product 2c resulted from the reaction, we believe that the cyclization step may go through a benzylic carbocation intermediate leading to the formation of the thermodynamically more stable isomer. NMR spectra of tetrahydropyran-2-ones 1b, 2b and 2c show expected patterns.

In conclusion, we have reported spectral and stereochemical properties of hitherto unknown *cis*- and *trans*-4,6-diaryltetrahydropyran-2-ones.

3. Experimental section

Thin layer chromatography (TLC silica gel, Qualigens, India) was used to monitor the progress of the reactions. Chromatographic separations were carried out on silica column using 5% ethyl acetate in hexane as the eluent. The organic extracts were dried over anhydrous sodium sulphate. Solvents were reagent grade. Melting points are uncorrected and were taken using a Gallenkamp melting point apparatus. Infrared spectra were recorded on a Perkin–Elmer spectrometer. ^1H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ solvent on a JEOL GSX 400 MHz instrument. Mass spectra were recorded on a Finnigan Mat 8320 mass spectrometer with 70 ev ionisation energy.

3.1 *General procedure for the synthesis of cis- and trans-4,6-diaryltetrahydropyran-2-ones*

To a magnetically stirred solution of 3,5-diphenylpentanoic acid 3a (536 mg, 2 mmol) in MeOH (15 ml) at 0°C was added $NaBH_4$ (74 mg, 2 mmol) portionwise. The reaction mixture was stirred for an hour and acidified with conc. hydrochloric acid. Stirring was continued for an hour at room temperature; methanol was then removed under reduced pressure. The residue was extracted with chloroform and the organic solution was washed with water and brine, dried over anhydrous sodium sulphate and

concentrated. The residue after removal of solvent *in vacuo* was heated to 120 °C under reduced pressure (2 mm) for an hour to yield a mixture of *cis*- and *trans*-tetrahydropyran-2-ones. They were separated and purified by column chromatography on silica gel (elution with 95:5 hexane-ethyl acetate) to afford 210 mg (42%) of *cis*-isomer 1a and 267 mg (53%) of *trans*-isomer 2a as colourless solids.

3.2 *cis-4,6-diphenyltetrahydropyran-2-one (1a)*

Yield = 42%; m.p. = 88–89 °C; IR 3020, 2960, 2920, 1730, 1600, 1540, 1260, 1225, 1065, 1055, 960 cm^{-1}; ^1H NMR (400 MHz) δ 2·05 (*dt*, 1H, J = 14·2, 11·7 Hz, C_{5ax}–H), 2·42 (*dddd*, 1H, J = 14·2, 3·9, 2·9, 2·0 Hz, C_{5eq}–H), 2·68 (*dd*, 1H, J = 18·1, 11·7 Hz, C_{3ax}–H), 3·05 (*ddd*, 1H, J = 18·1, 5·9, 2·0 Hz, C_{3eq}–H), 3·4 (*tdd*, 1H, J = 11·7, 5·9, 3·9 Hz, C_{4ax}–H), 5·47 (*dd*, 1H, J = 11·7, 2·9 Hz, C_{6ax}–H), 7·2–7·6 (*m*, 10 H, Ar–H); ^{13}C NMR (100 MHz) δ 37·63 (*d*, C_4), 37·99 (*t*, C_5) 38·93 (*t*, C_3), 81·83 (*d*, C_6), 125·71, 126·43, 127·34, 128·49, 128·53, 128·69 (*d*, Ar–C), 139·45, 142·53 (*s*, Ar–C), 170·55 (*s*, C_2); LRMS 252 (M^+, 10), 212 (27), 195 (18), 194 (92), 193 (21), 149 (35), 107 (100), 105 (25), 104 (27), 91 (37), 78 (28), 77 (48), HRMS m/z (M^+) calculated for $C_{17}H_{16}O_2$ 252·1150, observed 252·1138.

3.3 *trans-4,6-diphenyltetrahydropyran-2-one (2a)*

Yield = 53%; m.p. = 68–69 °C; IR 3040, 2970, 1745, 1730, 1605, 1265, 1250, 1070, 965 cm^{-1}; ^1H NMR (400 MHz) δ 2·32 (*ddd*, 1H, J = 14·0, 5·9, 4·9 Hz C_{5eq}–H), 2·37 (*ddd*, 1H, J = 14·0, 7·2, 6·9 Hz, C_{5ax}–H), 2·8 (*dd*, 1H, J = 17·6, 9·3 Hz, C_{3ax} – H) 2·9 (*dd*, 1H, J = 17·6, 6·4 Hz, C_{3eq}–H), 3·28(*dq*, 1H, J = 9·2, 6·3 Hz, C_{4ax}–H), 5·52 (*dd*, 1H, J = 6·9, 4·9 Hz, C_{6eq}–H), 7·2–7·4 (*m*, 10 H, Ar–H); ^{13}C NMR (100 MHz) δ 34·11 (*d*, C_4), 36·31 (*t*, C_5), 37·23 (*t*, C_3), 78·70 (*d*, C_6), 125·49, 126·58, 127·17, 128·13, 128·64, 128·98 (*d*, Ar–C), 139·53, 142·62 (*s*, Ar–C), 171·36 (*s*, C_2); LRMS 252 (M^+, 40), 234 (35), 224 (23), 192 (12), 146 (23), 132 (100), 120 (40), 105 (60), 104 (58), 91 (11), 78 (15), 77 (10); HRMS m/z calculated for $C_{17}H_{16}O_2$ 252·1150, observed 252·1186.

3.4 *cis-4-phenyl-6-p-tolyltetrahydropyran-2-one (1b)*

Yield = 47%; m.p. = 82–83 °C; IR 3040, 2960, 2930, 1730, 1600, 1515, 1410, 1380, 1260, 1070, 1060 cm^{-1}; ^1H NMR (400 MHz) δ 2·05 (*dt*, 1 H; J = 13·7, 11·7 Hz, C_{5ax}–H), 2·36 (*s*, 3H, Ar–CH_3), 2·38 (*dddd*, 1 H, J = 13·7, 3·9, 2·9, 2·0 Hz, C_{5eq}–H), 2·66 (*dd*, 1 H, J = 18·1, 11·7 Hz, C_{3ax}–H), 3·04 (*ddd*, 1 H, J = 18·1, 5·9, 2·0 Hz, C_{3eq}–H), 3·37 (*tdd*, 1 H, J = 11·7, 5·9, 3·9 Hz, C_{4ax}–H), 5·43 (*dd*, 1 H, J = 11·7, 2·9 Hz, C_{6ax}–H), 7·2–7·5 (*m*, 9 H, Ar–H); ^{13}C NMR (100 MHz) δ 21·16 (Ar–CH_3), 37·61 (*d*, C_4), 37·96 (*t*, C_5) 38·83 (*t*, C_3), 81·82 (*d*, C_6), 125·71, 126·41, 127·29, 129·00, 129·31 (*d*, Ar–C), 136·48, 138·33, 142·61 (*s*, Ar–C), 170·67 (*s*, C_2); LRMS 266 (M^+, 100), 188 (11), 118 (28), 104 (35), 91 (10), 77 (10); HRMS m/z calculated for $C_{18}H_{18}O_2$ 266·1306, observed 266·1342.

3.5 *trans-4-phenyl-6-p-tolyltetrahydropyran-2-one (2b)*

Yield = 50%; m.p. = 63 °C; IR 3060, 3040, 2830, 1735, 1730, 1605, 1456, 1380, 1245, 1155, 1070, 975 cm^{-1}; ^1H NMR (400 MHz) δ 2·31 (*ddd*, 1 H, J = 14·2, 6·8, 4·4 Hz C_{5eq}–H), 2·35 (*s*, 3 H, Ar–CH_3), 2·38 (*dt*, 1 H, J = 14·2, 7·3, C_{5ax}–H), 2·81 (*dd*, 1 H, J = 17·6, 8·8 Hz, C_{3ax}–H), 2·91 (*dd*, 1 H, J = 17·6, 6·4 Hz, C_{3eq}–H), 3·29 (*m*, 1 H, C_{4ax}–H), 5·51 (*dd*, 1 H, J = 7·3, 4·4, C_{6eq}–H), 7·2–7·5 (*m*, 9 H, Ar–H); ^{13}C NMR (100 MHz) δ 21·10 (Ar–CH_3), 34·14 (*d*, C_4), 36·38 (*t*, C_5), 37·25 (*t*, C_3), 78·72 (*d*, C_6), 125·47, 126·61,

127·17, 128·99, 129·33 (*d*, Ar–C), 136·54, 137·93, 142·73 (*s*, Ar–C), 171·40 (*s*, C_2); LRMS 266 (M^+, 5), 209 (10), 134 (12), 121 (35), 120 (18), 119 (65), 118 (18), 115 (20), 104 (100), 103 (18), 91 (58), 77 (46); HRMS *m/z* calculated for $C_{18}H_{18}O_2$ 266·1306, observed 266·1294.

3.6 *trans-6(4-Chlorophenyl)-4-phenyltetrahydropyran-2-one* (2c)

Yield = 95%; m.p. = 116–117 °C; IR 3055, 2915, 1739, 1730, 1600, 1540, 1250, 1085, 1030 cm^{-1}; ^1H NMR (400 MHz) δ 2·34 (*t*, 2 H, J = 6·4, C_{5eq}–H & C_{5ax}–H), 2·85 (*dd*, 1 H, J = 17·6, 8·8 Hz, C_{3ax}–H), 2·93 (*dd*, 1 H, J = 17·6, 6·4 Hz, C_{3eq}–H), 3·31 (*dq*, 1 H, J = 8·8, 6·4 Hz, C_{4ax}–H), 5·5 (*t*, 1 H, J = 6·3, C_{6eq}–H), 7·2–7·4 (*m*, 9 H, Ar–H); ^{13}C NMR (100 MHz) δ 34·11 (*d*, C_4), 36·31 (*t*, C_5), 37·23 (*t*, C_3), 78·70 (*d*, C_6), 126·59, 126·94, 127·34, 128·90, 129·10 (*d*, Ar–C), 134·06, 138·08, 142·38, (*s*, Ar–C), 170·92 (*s*, C_2); LRMS 288 (10), 286 (25, M^+, 10), 270 (25), 268 (51), 260 (13), 258 (29), 245 (13), 243 (30), 210 (16), 208 (41), 180 (26), 156 (21), 154 (50), 132 (42), 104 (64), 91 (41), 77 (10); HRMS *m/z* calculated for $C_{17}H_{15}O_2Cl$ 286·0760, observed 286·0776.

Acknowledgement

HSPR thanks the Council of Scientific and Industrial Research, New Delhi for financial support. BB thanks the Government of Pondicherry for study leave. We also thank the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras for recording the spectra.

References

Alberts A W, Chen J, Kuron G, Hunt V, Huff J, Hoffmann C, Rothrock J, Lopez M, Joshua H, Harris E, Patchett A, Monaghan R, Currie S, Stapley E, Albers-schonberg G, Hensens O, Hirshfield J, Hoogsteen K, Liesch J and Springer J 1980 *Proc. Natl. Acad. Sci. USA* **77** 3957

Allinger N L and Chang S H M 1977 *Tetrahedron* **33** 1561

Atta-ur-Rahman 1986 *Nuclear magnetic resonance, Basic principles* (New York): Springer Verlag) p. 143

Barfield M and Grant D M 1963 *J. Am. Chem. Soc.* **85** 1899

Bennett F, Knight D W and Fenton G 1991 *J. Chem. Soc., Perkin Trans. 1* 133

Brand J M, Young J C and Silverstein R M 1979 *Fortschr. Chem. Org. Naturst.* **37** 1

Brown A G, Smale T C, King T J, Hasenkamp R and Thompson R H 1976 *J. Chem. Soc., Perkin. Trans. 1* 1165

Cheung K K, Overton K H and Sim G A 1965 *J. Chem. Soc., Chem. Commun.* 634

Closson W D, Orenski P J and Goldschmidt B M 1967 *J. Org. Chem.* **32** 3160

Fronza G, Fuganti C and Grasselli P 1982 *J. Chem. Soc., Perkin Trans. 1* 885

Herz W, Aota K, Holub M and Samek Z 1970 *J. Org. Chem.* **35** 2611

Jackman L M and Sternhell S 1969 *Nuclear magnetic resonance spectroscopy in organic chemistry* 2nd edn (Elmsford, NY: Pergamon) p. 334

Juaristi E 1991 *Introduction to stereochemistry and conformational analysis* (New York: Wiley) p. 52

Keck G E, Park M and Krishnamoorthy D 1993 *J. Org. Chem.* **58** 3787

Lindsay G A and Overton K H 1973 *J. Chem. Soc., Perkin Trans. 1* 389

McConnell J F, Mathieson A McL and Schoenborn B P 1962 *Tetrahedron Lett.* 445

Meerwein H 1918 *J. Prakt. Chem.* **97** 225

Ohloff G 1978 *Fortschr. Chem. Org. Naturst.* **35** 431

Philip T, Cook R L, Mallory T B Jr, Allinger N L, Chang S and Yuh Y 1981 *J. Am. Chem. Soc.* **103** 2151

Stanley J, Matallona A and Kingsbury C A 1990 *J. Phys. Org. Chem.* **3** 419

Stanley J A, Dakin S, Szabo L, Posaw L, Lee C and Hou W M 1991 *Org. Prep. Proced. Int.* **23** 193

Takano S, Kamikubo T, Sugihara T and Ogasawara K 1992 *Tetrahedron Asym.* **3** 853

Wolf H 1966 *Tetrahedron Lett.* 5151