RELATIVE STABILITY OF ALICYCLIC COMPOUNDS CONTAINING EXOCYCLIC AND ENDOCYCLIC DOUBLE BOND

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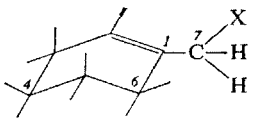
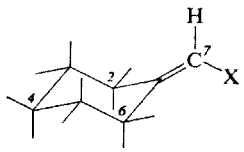
The equilibria between isomers $C_5H_7CH_2X \rightleftarrows C_5H_8CHX$ (C_5H_7 = 1-cyclopenten-1-yl, C_5H_8 = cyclopentylidene) and $C_6H_9CH_2X \rightleftarrows C_6H_{10}CHX$ (C_6H_9 = 1-cyclohexen-1-yl, C_6H_{10} = cyclohexylidene) have been studied and explained on the basis of electron delocalisation data and interactions between substituents on the double bond.

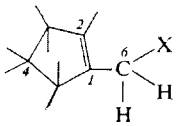
In the present paper we investigate the relative stability of alicyclic compounds containing a double bond *exo* or *endo* relative to a cyclohexane or cyclopentane ring and we try to explain the effect of the substituent X in the side chain on the equilibrium constants.



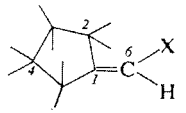
Ia



Ib



IIa



IIb

X = H, CH_3, CN, NO_2, $COCH_3$, $COOC_2H_5$

The *exo–endo* equilibria in the corresponding hydrocarbons (X = H) have been studied by Gil-Av and coworkers[1,2] and by other authors[3–6]. For the equilibrium 1-methyl-1-cyclopentene $\rightleftarrows$ methylenecyclopentane the equilibrium constant K_r (*endo/exo*) was found to be 1140 ± 51 (ΔG_{25} −4·17 kcal mol^{-1}, ΔH_{isom} −3·9 kcal mol^{-1}), for the equilibrium 1-methyl-1-cyclohexene $\rightleftarrows$ methylenecyclohexane K_r (*endo/exo*) = 240 ± 13 (ΔG_{25} −3·24 kcal mol^{-1}, ΔH_{isom}

$-2{\cdot}4$ kcal mol^{-1}, ΔS $+2{\cdot}8$ e.u.). In both equilibria the *endo*-isomer by far predominates, particularly in the five-membered ring compounds. These data are not at variance with the generally accepted Brown's rationalisation[7,8] concerning the higher stability of derivatives with exocyclic double bond in compounds with five-membered ring relative to analogous compounds of the cyclohexane series because this generalisation expresses relative comparison with the saturated compounds (compounds with trigonal and tetragonal hybridisation). Compounds with X = CH_3 were isomerised by Herling[9], Levina[10] and Schriesheim and coworkers[11]. Also in this case the *endo*-isomer predominated at 25°C entirely (for the equilibrium *Ia* ⇄ *Ib*, X = CH_3, the found values are K_r (*endo*/*exo*) $8{\cdot}63 \pm 0{\cdot}3$, ΔG $-1{\cdot}28$ kcal mol^{-1}, for the equilibrium *IIa* ⇄ *IIb*, X = CH_3, K_r (*endo*/*exo*)$20{\cdot}3 \pm 0{\cdot}7$, ΔG $-1{\cdot}78$ kcal mol^{-1}). The heats of isomerisation were determined as the difference between the heats of hydrogenation of the corresponding isomers[4,12]; thus, for X = H, in the system *Ia*—*Ib*, ΔH_{hyd} (AcOH) was found to be $2{\cdot}3$ kcal mol^{-1}, in the system *IIa*—*IIb* ΔH_{hyd} $-3{\cdot}9$ kcal mol^{-1}. For X = CH_3, in the system *Ia*—*Ib* the value of ΔH_{hyd} was determined as $-1{\cdot}24$ kcal mol^{-1}, for *IIa*—*IIb* it is $-1{\cdot}34$ kcal mol^{-1}. As evident from these heats of isomerisation, the *endo*-isomers are in both series also thermochemically more stable. For X = H the entropy changes, $\Delta S°$, calculated for the gas phase, are similar (for *Ia*—*Ib* $\Delta S° = 2{\cdot}9$ e.u., for *IIa*—*IIb* $\Delta S° = 3{\cdot}1$ e.u.). Also the acid-catalysed isomerisations isopropylcycloalkene ⇄ isopropylidenecycloalkane have been studied[13] (for the equilibrium isopropylidenecyclopentane ⇄ isopropylcyclopentene $K(endo/exo)_{326K} = 0{\cdot}746$, ΔG $+0{\cdot}19$ kcal mol^{-1}, ΔH $1{\cdot}03$ kcal mol^{-1}; for the equilibrium isopropylidenecyclohexane ⇄ isopropyl-

TABLE I
Equilibration Data

X	*T*, K	% *Ib*	*K*(*endo*/*exo*)	ΔG_T, kcal mol^{-1}	ΔH, kcal mol^{-1}
		Equilibria *Ia* ⇄ *Ib*			
H[a]	303	0·4	240 ± 13	−3·24	−2·4
H[a]	303	0·4	198 ± 8	−3·15	—
CH_3[a]	298	10·4	8·63 ± 0·3	−1·28	—
CN	304	89·2 ± 0·3	0·121	+1·27	−1·3
NO_2	293	15 ± 3	5·67	−1·03	−3·4
$COCH_3$	293	15·3 ± 0·5	5·58	−1·0	−2·3
$COOC_2H_5$	304	30·8 ± 1	2·33	−0·47	−0·52
		Equilibria *IIa* ⇄ *IIb*			
H[a]	298	0·09	1 144	−4·17	−3·9
H[a]	298	0·09	1 084	−4·13	—
CH_3[a]	298	4·6	20·3	−1·78 ± 0·02	−1·34
CN	304	89·8 ± 0·3	0·113	+1·32	−2·6
NO_2	293	14·5 ± 3	5·89	−1·05	−2·4
$COCH_3$	304	73·2 ± 0·5	0·366	+0·67	−2·9
$COOC_2H_5$	313	81·0 ± 0·5	0·235	+0·90	−0·54

[a] Taken from ref.[1–14].

cyclohexene $K(endo/exo)_{326K} = 7{\cdot}25$, ΔG $-1{\cdot}28$ kcal mol^{-1}, ΔH $-0{\cdot}73$ kcal mol^{-1}). The position of the equilibrium is therefore a function of the ring size, as well as of the nature of the substituent. Data are also known[14-20] concerning the compounds with X = $COCH_3$, COOR and COOH; however isomerisations of these derivatives were carried out under hardly comparable conditions. The considerable differences in results are due to different analytical methods, side-

TABLE II

Cis–trans Equilibria in Isomers CH_3—CH=CH—X

X	% *cis*	*K* (*trans*/*cis*)	*T*, K	ΔG, kcal mol^{-1}	Ref.
H	50	1·0	300	0·0	—
CH_3	22	3·54	298	−0·74	36
CH_3	26·8	2·73	298	−0·59	37
C_2H_5	26·5	2·77	298	0·60	38, 39
CN	58·8	0·705	303	+0·21	40
CN	57	0·765	418	+0·24	23
CN	65	0·538	298	+0·36	41
$COCH_3$	0·7	142	308	−3·0	42
NO_2	2·8–3·1	34·7	297	−2·06 to −2·1	43, 44
NO_2	5	19	293	−1·70	45
$COOC_2H_5$	15	5·66	305	−1·11	41

TABLE III

Equilibria R—CH_2—CH=CH—X ⇄ R—CH=CH—CH_2X

R	X	% Isomer	*T*, K	$K\frac{\sum\alpha\beta}{\sum\beta\gamma}$	ΔG, kcal mol^{-1}	Ref.
CH_3	H	—	298	0·029	2·08	36
CH_3	H	—	303	0·016	2·47	37
C_2H_5	H	—	328	0·032	2·23	39
CH_3	CH_3	50	300	1·0	0·0	—
CH_3	CN	71	303	2·45	−0·54	40
R	$COCH_3$	—	—	—	—	—
C_4H_9	$COOCH_3$	—	386	2·44	−0·68	33
CH_3	COOH	75·4	470–500	3·08	−1·05	46
C_2H_5	COOH	68	470	2·12	−0·70	47
CH_3	NO_2	86	413	6·14	−1·48	48
CH_3	NO_2	89	293	8·09	−1·21	45

reactions and undefined purity of starting material. For instance, in the acid-catalysed isomerisation *Ia* ⇄ *Ib* (X = COOH) at 180°C the equilibrium mixture contains 25·5% of the isomer *Ib* (ref.[15]), whereas the autocatalysed isomerisation[16] leads to only 14—19% of *Ib*. In the *I* series, X = $COO^{(-)}$, the equilibration with aqueous KOH at 100°C is reported[17,18] to lead to 11—12% of the conjugated isomer *Ib*; equilibration with sodium ethoxide in ethanol affords 38% of this isomer. Ingold and coworkers[21] measured isomeristisation equilibria *Ia* ⇄ *Ib*, X = CN, and found at 25°C 99·2—100% of the conjugated isomer, Descotes and Laconche[22] report 60% at 165°C. The isomerisation *Ia* ⇄ *Ib*, X = NO_2, catalysed by diethylamine, afforded[23] at 5°C the isomer *Ib* in 35% yield.

We determined the equilibrium positions together with the equilibration rates for both series where X = CN, $COCH_3$, NO_2, $COOC_2H_5$, working with compounds of defined purity. The isomerisation was catalysed by potassium tert-butoxide or triethylamine in tert-butyl alcohol and equilibrium was approached from both sides. The results of the isomerisations are given in Table I. The ΔH values were determined from the gradient of plots of log K against $1/T$. Since already these values are of considerable error, the ΔS values are not given. The analyses of the equilibrium mixtures were performed using gas–liquid chromatography and ^{1}H-NMR spectroscopy.

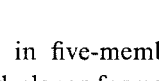
The relative stability of the isomers depends on the difference of non-bonding interactions and torsion tensions on the one side, and on the electron delocalisation (σ and π-electron stabilisation) on the other. The calculation of the non-bonding interactions in cycloalkenes and alkylcyclopentenes, using approximate potential functions for bonds C—C, C—H and H—H was described[24]. For cyclohexene and cyclopentene the approximate values of all interactions have been determined[25] using a model, simulating rehybridisation of carbon atoms. The agreement of theory with experiment depends significantly on the chosen assumptions. Owing to the small ΔG values, the calculation for the systems given in Table I is not yet promising. In order to calculate the differences of the non-bonded interactions and the electron delocalisation, we used the ΔG values derived from constants, characterising the differences in the mentioned series.

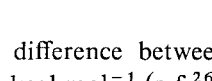
TABLE IV
Resulting Substituent Effect

X	ΔG^{cis}_{trans}	ΔG_{isom}	$\sum \Delta G$, kcal mol^{-1}
H	0·0	+2·2 ± 0·2	2·2
CH_3	0·65 ± 0·1	0·0	0·65
CN	−0·25 ± 0·05	−0·54	−0·79
$COCH_3$	3·0	—	—
COOR	1·1	−0·7	0·4
NO_2	1·85 ± 0·1	−1·3 ± 0·1	0·55

Using Dreiding models, we estimated the differences between interactions in the given systems. It can be deduced that for the isomers *Ia* and *Ib* (X = H) the diaxial interactions H_3-H_5 and H_4-H_6 in *Ia* can be compensated by the interactions H_4-H_6 and H_2-H_4 in the isomer *Ib* because the distances between the atoms in question are the same. Since in the isomer *Ib* there is no H_6-H_2 interaction (trigonal hybridisation $C_{(1)}$), the main difference between *Ia* and *Ib* is one diaxial interaction H_3-H_5, which favours energetically *Ia* against *Ib*. The cyclohexane ring was assumed to exist only in the chair form because it is known[25,26] that the boat form which represents the rotation barrier between the both chair forms, is by about 6·4–7 kcal mol^{-1} less stable.

In the *Ia* isomer the free rotation of the CH_2X group can be hindered by the interaction of the pseudoequatorial hydrogens H_7-H_6 in the case X = H; in the case of another substituent it is necessary to consider a hindrance, caused by mutual influence of the substituent X and the hydrogens on $C_{(2)}$ and $C_{(6)}$ in all the studied molecules. The hindrance, caused by the rotation of the $C_{(7)}$-COR or $C_{(7)}$-COOR bond, is about the same in both isomers *Ia* and *Ib*. Because of the hindered rotation of C—C bonds in the ring, the isomers *Ia* and *Ib* differ in the energy of the interaction.





It is known that in five-membered rings the difference between the non-planar (C_s symmetry) and planar forms amounts to 0·4 kcal mol^{-1} (ref.[26]), one atom of the ring being placed 0·3 Å apart from the plane of the ring, as shown by ^{1}H-NMR data and microwave spectra[27]. As a result, isomers *IIa* and *IIb* differ in 2 synperiplanar interactions H—H ($\tau \sim 10-15°$) and further in the double bond interactions, mentioned above. Both these factors contribute to the higher energy content of the *IIb* isomer. The maximum value of the interaction H—H ($\tau = 0°$), as derived from the barrier to rotation of ethane[28], is 0·9 kcal mol^{-1}, the CH_3—H interaction, estimated on the basis of the barrier of propane (3·3 kcal mol^{-1}) is 1·5 kcal mol^{-1}, under assumption of constant H—H interactions and neglecting other, unimportant, interactions. The dependence of the interaction energy on the distance or angles is, however, very steep[29–31].

The systems *I* and *II* are similar, the *endo*-isomer being more favoured in the second series. If we compare the non-bonded interactions, hindering the free rotation of the $C_{(7)}$—X or $C_{(6)}$—X bond, then in the *exo*-isomer of the five-membered ring compounds the rotation is free whereas in certain conformations of the *endo*-isomer the rotation is hindered. As a result, the presence of sterically demanding substituents —$COCH_3$, —COOR will shift the equilibrium towards the higher concentration of the *exo*-isomer in the series *II* as compared with series *I*. It is also necessary to consider the stabili-

sation of the conjugated isomer by ±M effect and its destabilisation by −I effect of the substituent X, as shown by isomerisations of aliphatic unsaturated acids[32], sulphoxides[33] and sulphones[34,35]. The resulting effect of the substituent X can be derived from the ΔG value of the *cis-trans* isomerisation of the system R-CH= =CH-X and ΔG of the prototropic isomerisation of the system R-CH_2-CH=CH-X. The first value comprises following interaction energies:

$$\Delta G\,(cis/trans) = I_{H-H} + I_{RCH_2-X} - (I_{RCH_2-H} + I_{H-X})\,.$$

The interactions I_{H-H} and I_{RCH_2-H} are constant throughout the whole series of studied compounds, and the interaction I_{H-X} changes only negligibly, as follows from the values of barriers to rotation of compounds CH_3-CH_2X (ref.[28]). Therefore, the ΔG value can be regarded to be an approximate measure of the interaction I_{RCH_2-X}. Only incomplete data on the ΔG values for both isomerisations are available (Tables II and III).

TABLE V
Conditions of Analytical and Preparative Gas–Liquid Chromatography

Compound	Analytical[a]				Preparative[a]			
	Column[b]	°C	l cm/r mm	kp/cm^2	Column[b]	°C	l cm/r mm	kp/cm^2
I, X = CN	A	158	180/4	0·4	A	160	360/10	0·3
	B	133	150/4	0·3				
I, X = COOR	C	185	100/4	0·3	D	170	300/10	2
	D	180	150/4	0·3				
	E	160	180/4	0·2				
I, X = $COCH_3$	F	110	180/4	0·2				
I, X = NO_2	D	150	200/6	0·25				
II, X = CN	C	185	60/6	0·3	G	160	300/10	2
	H	130	100/6	0·3				
	G	160	100/4	0·2				
II, X = COOR	E	155	200/6	0·15	D	160	300/10	3
	D	152	160/4	0·2				
II, X = $COCH_2$	B	112	180/4	0·2	B	120	360/10	0·3

[a] The analyses were performed on a Chrom 3 (Laboratorní přístroje, Prague) chromatograph, the preparative separations were carried out on a chromatograph built by Vývojové dílny, Czechoslovak Academy of Sciences, Prague. [b] A 15% Carbowax 20M, Chromaton NAW; B 20% diethylene glycol succinate, Chromosorb 80–100 mesh; C 6% trinitrofluorenone, ground porous tile 0·2–0·3 mm; D 20% Apiezon L, ground porous tile 0·2–0·3 mm; E 10% Versamide 900, Chromaton NAW; F 6% OV101, Chromosorb 80–100; G 10% diethylene glycol adipate, ground porous tile 0·2–0·3 mm; H 15% dinonyl phthalate, ground porous tile 0·2–0·3 mm.

The resulting effect of the substituent X($\Sigma\Delta G$) is obtained as a sum of the free energy of the prototropic isomerisation and the *cis-trans* isomerisation (Table IV).

We may expect a linear dependence of $\Sigma\Delta G$ on ΔG (*endo*/*exo*) for substituents without any further steric interactions (Fig. 1). In the series *I*, the correlation coefficient for the linear dependence is 0·99, in the series *II* the coefficient is 0·92. In this case the disturbing factor is the value for $COOC_2H_5$ because its neglecting results in an increase of the correlation coefficient to 0·99. As seen from these dependences, for X = H the predominance of the *endo*-isomer is conditioned first of all by a different number of substituents attached to the multiple bond (zero-energy differences between the isomers); for X = CH_3 the *endo*-isomer predominates as a result of a *cis*-2-butene type interaction. In the case of X = CN the contribution of conjugation, as well as the interaction $I_{R...CN}$, favours the *exo*-isomer in both series. When X = NO_2, the effect of $I_{R...NO_2}$ predominates over the delocalisation energy and the *endo*-isomer is the more stable one in both series. In compounds with X = COR and COOR the *endo*-isomer predominates in the series *I*, whereas in the series *II*, where both the effects compensate each other to a great extent, the *exo*-isomer predominates, presumably as the result of the energy differences due to the hindered rotation.

EXPERIMENTAL

Synthesis of Compounds

1-Cyclopenten-1-ylacetonitrile (*IIa*, X = CN) and cyclopentylideneacetonitrile (*IIb*, X = CN) were prepared by condensation[48] of cyanoacetic acid (30 g; 0·30 mol) with cyclopentanone (30 g; 0·35 mol) in the presence of piperidine (4 ml) and acetic acid (4 ml), followed by thermal decarboxylation. This procedure afforded 25·6 g (80%) of a mixture of *IIa* and *IIb* (37 : 63), b.p. 69–73°C/10 Torr (ref.[49] states b.p. 90–92°C/25 Torr). The isomer *IIa*, b.p. 191·8°C/753 Torr, was obtained in 99% purity, isomer *IIb* b.p. 193·7°C/753 Torr, was contaminated with 8·5% of *IIa*.

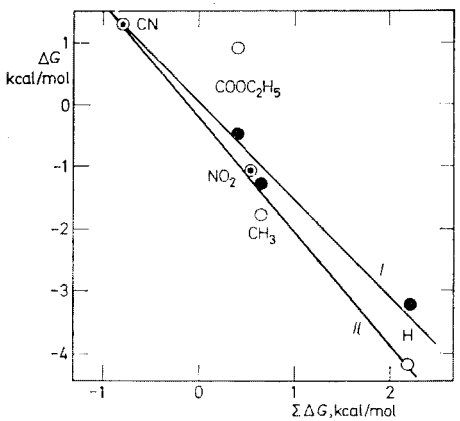


FIG. 1

Dependence of ΔG of Isomerisation on the Value of $\Sigma\Delta G$

Ethyl 1-*cyclopenten*-1-*ylacetate* (*IIa*, X = $COOC_2H_5$) *and ethyl cyclopentylideneacetate* (*IIb*, X = $COOC_2H_5$) were prepared using following two procedures. *a*) Dehydration of ethyl 1-hydroxy-1-cyclopentylacetate[50] (40 g) in boiling benzene (3 hours) in the presence of phosphorus pentoxide (40 g). Distillation afforded 30 g (83%) of a mixture of unsaturated esters, boiling at 74–84°C/10 Torr, which contained 35% of *IIa* and 65% of *IIb*. *b*) Reaction of cyclopentanone (7·2 g; 0·085 mol), triethyl phosphonoacetate[51] (19 g; 0·085 mol) and sodium hydride (2 g; 0·082 mol) in 1,2-dimethoxyethane afforded 7·2 g (55%) of a mixture of 88% *IIa* and 12% *IIb*. Separation of the isomers by gas–liquid chromatography gave *IIb* of 99·5% purity, b.p. 72·5°C/10 Torr, n_D^{20} 1·4542 (ref.[52] reports b.p. 82–82°C/11 Torr) and *IIa* of 99% purity, b.p. 83·5 to 84°C/10 Torr, n_D^{20} 1·4718 (ref.[52] states b.p. 88°C/10 Torr).

1-*Cyclopenten*-1-*ylacetone* (*IIa*, X = $COCH_3$) and cyclopentylideneacetone (*IIb*, X = $COCH_3$) were prepared using following procedures. *a*) Reaction of cyclopentanone (6·5 g; 0·077 mol), diethylphosphonoacetone (15 g; 0·077 mol) and sodium hydride (1·8 g; 0·077 mol) in 1,2-dimethoxyethane gave 5·5 g (57%) of a 63 : 37 mixture of *IIa* and *IIb*, b.p. 67·5–69°C/11 Torr. *b*) Treatment of 1-cyclopenten-1-ylacetyl chloride[53] with dimethyl cadmium(from 10·7 g–0·13 mol of cadmium chloride and 0·26 mol of methylmagnesium iodide) in benzene afforded 30 g (38%) of a mixture of *IIb* and *IIa* (75 : 25), b.p. 65–66°C/11 Torr.

1-*Cyclopenten*-1-*ylnitromethane* (*IIa*, X = NO_2) and *cyclopentylidenenitromethane* (*IIb*, X = NO_2) were prepared by condensation of cyclopentanone (42 g; 0·5 mol) and nitromethane (58 g; 0·95 mol) in the presence of piperidine (2·5 mol) and anhydrous magnesium sulphate (14 g). The resulting mixture of isomers (12 g; 19%), b.p. 84–85°C/13 Torr, was not separable into components. The composition of the mixture was determined by IR and NMR spectroscopy according to Descot[54]; it contained 84% of the isomer *IIa* and 16% of the isomer *IIb*.

1-*Cyclohexen*-1-*ylacetonitrile* (*Ia*, X = CN) and *cyclohexylideneacetonitrile* (*Ib*, X = CN) were prepared analogously to the preparation of the five-membered ring nitriles. Decarboxylation of cyclohexylidenecyanoacetic acid at 160°C afforded in 70% yield a mixture of *Ia* (62·5%) and *Ib* (37·5%), boiling at 75–77°C/8 Torr. The isomer *Ia*, b.p. 209°C/754 Torr, was obtained in 99% purity (ref.[55] gives b.p. 105°C/22 Torr).

Ethyl 1-*cyclohexen*-1-*ylacetate* (*Ia*, X = $COOC_2H_5$) and *ethyl cyclohexylideneacetate* (*Ib*) X = $COOC_2H_5$) were prepared by the following methods. *a*) Dehydration of ethyl 1-hydroxycyclohex-1-ylacetate[50] with phosphorus pentoxide in benzene afforded in 76% yield a mixture of the isomeric esters, b.p. 88–94°C/9 Torr, containing 92% of *Ib* and 8% of *Ia*. *b*) Dehydration of the above hydroxyester (60 g, 0·33 mol) by thionyl chloride (47 g; 0·4 mol) in pyridine (71 ml) under cooling yielded 25 g (45%) of a mixture consisting of 79% *Ia* and 21% *Ib*, b.p. 100–104°C/14 Torr. *c*) Using the Wittig method (according to ref.[51]), a mixture of triethyl phosphonacetate (18·6 g; 0·083 mol), cyclohexanone (8·1 g; 0·083 mol) and sodium hydride (1·95 g; 0·08 mol) afforded 1·5 g of a mixture of *Ia* (95%) and *Ib* (5%), boiling at 97–101°C/11 Torr. The isomers were separated by preparative gas–liquid chromatography: *Ia*, b.p. 88·5–89°C/10 Torr, n_D^{20} 1·4626, *Ib*, b.p. 93·5–94°C/10 Torr, n_D^{20} 1·4797. The reported boiling points are: for *Ia* b.p. 98–105°C/12 Torr[56] and 104–105°C/15 Torr[57], for *Ib* b.p. 110–114°C/15 Torr.

1-*Cyclohexen*-1-*ylacetone* (*Ia*, X = $COCH_3$) and cyclohexylideneacetone (*Ib*, X = $COCH_3$) were prepared by condensation of cyclohexanone (98 g; 1 mol) with acetone (58 g; 1 mol) in 5% ethanolic sodium ethoxide (500 ml); yield 43 g (32%) of a mixture of 80% *Ia* and 20% *Ib*, b.p. 75–77°C/10 Torr. It was not possible to separate the isomers either by distillation or by preparative gas–liquid chromatography. The isomer *Ia* is reported to boil at 202°C[58] and 90°C/15 Torr[59], the isomer *Ib* is reported to be 95°C/17 Torr[60,61].

1-*Cyclohexen*-1-*ylnitromethane* (*Ia*, X = NO_2) and cyclohexylidenenitromethane (*Ib*, X = NO_2) were prepared by dehydration of 1-hydroxycyclohex-1-ylnitromethane[62] by the following procedures. *a*) Treatment of the above-mentioned nitro alcohol (16 g; 0·1 mol) with acetyl chloride (16 g; 0·2 mol) in chloroform (30 ml) afforded 16·5 g (82%) of 1-acetoxycyclohex-1-ylnitromethane, b.p. 119°C/3 Torr[23]. Boiling of this compound (10 g; 50 mmol) with sodium acetate (0·5 g) in benzene (70 ml) gave the mixture of *Ib* (67%) and *Ia* (33%), b.p. 106–107°C/10 Torr. *b*) The nitro alcohol (25 g; 0·15 mol) was treated with thionyl chloride (20 g; 0·17 mol) in pyridine (25 g; 0·32 mol) using a procedure analogous to that described in ref.[63]. The mixture of *Ia* (91%)

TABLE VI
Isomerisation Results

Compound	°C	Equilibrium composition, %		K_r	ΔG	ΔH, kcal mol^{-1}
		Isomer *b*	Isomer *a*			
I, X = CN	31	89·6 ± 0·2	10·4	8·26	1·265	1·31
	40	88·5	11·5	7·69	1·270	
	53	87·7	12·3	7·13	1·273	
I, X = $COOC_2H_5$	20	30·8 ± 1	69·2	0·445	0·47	0·52
	32	30·0	70·0	0·428	0·51	
	70	27·9	72·1	0·383	0·64	
I, X = $COCH_3$	20	15·2 ± 0·5	84.8	0·179	0·90	2·30
	40	12·0	88·0	0·136	0·99	
	50	11·0	89·0	0·124	1·32	
I, X = NO_2[a]	20	15 ± 7	85	0·176	1·03	5·0
	40	9 ± 4	91	0·092	1·49	
	70	5 ± 4	95	0·049	2·0	
II, X = CN	31	89·5 ± 0·3	10·5	8·81	1·30	2·6
	40	88·0	12·0	7·33	1·24	
	53	86·9	13·1	6·63	1·23	
II, X = $COOC_2H_5$	40	81 ± 0·5	19	4·26	0·90	0·54
	53	80·4	19·6	4·1	0·91	
II, X = $COCH_3$	30	73·2 ± 0·5	26·8	2·73	0·58	2·9
	50	72·7	27·3	2·66	0·43	
	70	72·4	27·6	2·62	0·64	
II, X = NO_2[a]	20	14·5 ± 4	85·5	0·165	1·05	2·5
	40	12	88	0·136	1·25	
	70	8	92	0·088	1·66	

[a] Concentration determined by ^{1}H—NMR spectroscopy.

and *Ib*(9%), b.p. 98·5—101°C/9 Torr, thus obtained, weighed 7·2 g (32%). *c*) The nitro alcohol (6·4 g; 40 mmol) was heated with phthalic anhydride (10 g; 65 mmol) at 40 Torr for 15 min, affording 3 g (53%) of a mixture of the nitro olefins, b.p. 112—113°C/11 Torr, consisting of 10% *Ia* and 90% *Ib*. Heating with phthalic anhydride for 40 min gave a mixture containing 60% *Ib*. *d*) Reaction of cyclohexanone (47 g; 0·48 mol) with nitromethane[63] (58 g; 0·95 mol) afforded 33 g (48%) of a mixture of *Ia* (89%) and *Ib* (11%), b.p. 91—93°C/9 Torr. Reported boiling points: for *Ia*, b.p. 95—96°C/12 Torr[63], for *Ib*, 92—95°C/1 Torr (ref.[23]).

Isomerisations

The isomerisations were performed in tert-butyl alcohol with potassium tert-butoxide as catalyst. A solution (1—3 ml) of a known concentration of the studied isomer was allowed to attain the bath temperature and then a chosen amount of the butoxide was added. The samples, taken at given time intervals, were neutralized with an equivalent amount of acetic acid (2M acetic acid in tert-butyl alcohol). The concentration of the compounds and catalyst was 0·02M and 0·05M, respectively, the ketones were isomerised either in a solution 1M with respect to the ketone and 0·1M with respect to the butoxide, or in a 0·1M triethylamine solution in tert-butyl alcohol. The found equilibria were identical within the experimental error. The analyses were performed by gas–liquid chromatography (Table V). In the case of nitro olefins which were isomerised in 0·01M solution in the presence of 1 mol% triethylamine, the mixture was neutralised with an equivalent of 5% aqueous sulphuric acid, the nitro olefins were taken into ether, the solution dried over magnesium sulphate and the solvent was evaporated on a rotatory evaporator at 15°C, the recovery of the nitro olefins being 85—90%. The mixture was analysed by gas–liquid chromatography and NMR spectroscopy.

REFERENCES

1. Gil-Av E., Herling J.: Tetrahedron Lett. *1961*, 27.
2. Shabtai J., Gil-Av E.: J. Org. Chem. *28*, 2893 (1963).
3. Cope C. A., Ambros D., Ciganek E., Howell Ch. F., Jacura L.: J. Amer. Chem. Soc. *82*, 1750 (1960).
4. Turner R. B., Garner R. H.: J. Amer. Chem. Soc. *80*, 1424 (1958).
5. Benkeser R. A., Hazdra J. J.: J. Amer. Chem. Soc. *81*, 228 (1959).
6. Turkshma H., Steinberg H., de Boer T. J.: Rec. Trav. Chim. Pays-Bas *82*, 1057 (1963).
7. Brown H. C., Brewster J. H., Shechter H.: J. Amer. Chem. Soc. *76*, 467 (1954).
8. Brown H. C.: J. Org. Chem. *22*, 439 (1957).
9. Herling J., Shabtai J., Gil-Av E.: J. Amer. Chem. Soc. *87*, 4107 (1965).
10. Levina R. J., Mezencova N. N., Akišin P. A.: Zh. Obshch. Khim. *23*, 562 (1953).
11. Schriesheim A., Muller R. J., Rowe C. A.: J. Amer. Chem. Soc. *84*, 3164 (1962).
12. Turner R. B.: *Theoretical Organic Chemistry*, IUPAC Kekulé Symposium p. 79. Butterworths, London 1959.
13. Bigley D. B., May R. W.: J. Chem. Soc. *1970*, 1761.
14. Linstead R. P., Noble E. G.: J. Chem. Soc. *1934*, 610.
15. Kon G. A. R., Nargund K. S.: J. Chem. Soc. *1934*, 623.
16. Linstead R. P.: J. Chem. Soc. *1930*, 1063.
17. Goldberg A. U., Linstead R. P.: J. Chem. Soc. *1928*, 2343.
18. Linstead R. P.: J. Chem. Soc. *1927*, 2579.
19. Kon G. A. R., Linstead R. P., Maclennan G. W. G.: J. Chem. Soc. *1932*, 2454.
20. Kon G. A. R.: J. Chem. Soc. *1931*, 248.

21. Ingold C. K., de Salas E., Wilson Ch. L. J.: J. Chem. Soc. *1936*, 1328.
22. Descotes G., Laconche P.: Bull. Soc. Chim. Fr. *1968*, 2149.
23. Eckstein Z., Urbanski T., Wojnowska H.: Rocz. Chem. *31*, 1177 (1957).
24. Coppeus P., Gil-Av E. Herling J., Shabtai J.: J. Amer. Chem. Soc. *87*, 4111 (1965).
25. Allinger N. L., Sprague J. T.: J. Amer. Chem. Soc. *94*, 5734 (1972).
26. Bucourt R., Hainaut D.: Bull. Soc. Chim. Fr. *1965*, 1366.
27. Lawrenson I. J., Rushworth F. A.: Proc. Phys. Soc. (London) *72*, 791 (1958).
28. Lowe J. P.: Progr. Phys. Org. Chem. *6*, 36 (1968).
29. Tichý M., Vašíčková S., Arakelian S. V., Sicher J.: This Journal *35*, 1529 (1970).
30. Tichý M., Sicher J.: This Journal *33*, 68 (1968).
31. Tichý M., Kniežo L.: This Journal *38*, 1537 (1973).
32. Damico R.: J. Org. Chem. *33*, 1550 (1968).
33. O'Connor D. E., Broaddus C. D.: J. Amer. Chem. Soc. *86*, 2267 (1964).
34. O'Connor D. E., Lynass W. J.: J. Amer. Chem. Soc. *86*, 3840 (1964).
35. Frey F. E., Huppke W. F.: Ind. Eng. Chem. *25*, 54 (1933).
36. Haag W. O., Pines H.: J. Amer. Chem. Soc. *82*, 387 (1960).
37. Kilpatrick J. E., Prosen D. G., Pitzer K. S., Rossini F. D.: J. Res. Nat. Bur. Stand. *36*, 559 (1946).
38. Bank S., Rowe C. A., Schrieshiem A.: J. Amer. Chem. Soc. *85*, 2115 (1963).
39. Procházka M., Zelinka J., Černý J. V., Vilím A.: This Journal *35*, 1224 (1970).
40. Mialhe Y., Vessiere R.: Bull. Soc. Chim. Fr. *1968*, 4181.
41. Sváta V.: Unpublished results.
42. Hesse G., Jäger V.: Ann. *740*, 79 (1970).
43. Hesse G., Jäger V.: Ann. *740*, 85 (1970).
44. Kochany J., Piotrowska H.: Bull. Acad. Pol. Sci. *21*, 75 (1973).
45. Goldberg A., Linstead R. P.: J. Chem. Soc. *1928*, 2345.
46. Linstead R. P., Noble E. G.: J. Chem. Soc. *1934*, 614.
47. Bourillot M., Rostating P., Descotes G.: C. R. Acad. Sci. (C) *262*, 1080 (1966).
48. Nazarov I. N., Kuznecov N. V.: Zh. Obshch. Khim. *29*, 765 (1959).
49. Ming Chien Chiang: J. Chinese Chem. Soc. *18*, 6317 (1951); Chem. Abstr. *46*, 4472 (1952).
50. Charlesworth E. H., Campbell H. J., Stachiw D. L.: Can. J. Chem. *37*, 877 (1959).
51. Wadsworth W. S., Emmons W. D.: J. Amer. Chem. Soc. *83*, 1733 (1961).
52. Dickins A. H., Hugh W. E., Kon G. A. R.: J. Chem. Soc. *1929*, 578.
53. Birch S. F., Kon G. A. R., Norris W. S. G.: J. Chem. Soc. *123*, 1361 (1923.)
54. Descotes G., Bahurel Y., Bourillot M., Pingeon G., Rostaing R.: Bull. Soc. Chim. Fr. *1970*, 292.
55. Kandiah A., Linstead R. P.: J. Chem. Soc. *1929*, 2146.
56. Schnider O., Hellerbach J.: Helv. Chim. Acta *33*, 1437 (1950).
57. Dauben G., Hance P. D.: J. Amer. Chem. Soc. *75*, 3352 (1953).
58. Kon G. A. R.: J. Chem. Soc. *1921*, 826.
59. Quadrat-I-Khuda: J. Chem. Soc. *1929*, 716.
60. Kon G. A. R., Linstead R. P.: J. Chem. Soc. *1929*, 1277.
61. Dickins A. H., Hugh W. E., Kon G. A. R.: J. Chem. Soc. *1928*, 1636.
62. Grob C. A. Tschamer W. von: Helv. Chim. Acta *33*, 1070 (1950).
63. Nightingale D. V., Erikson F. B., Strackelfor J. M.: J. Org. Chem. *17*, 1005 (1952).

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