The Circular Dichroism of 3-Alkylthio- and 3-Arylthio-cyclohexanones: an Analysis of Through Bonds and Dynamic Coupling Contributions to the Optical Activity

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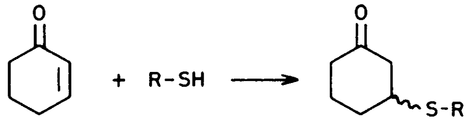
The c.d. spectra of a series of 3-alkylthio- and 3-arylthio-cyclohexanones were recorded and interpreted by means of MO calculations and dynamic coupling approximations. From the analysis, the absolute configurations of the compounds were deduced.

MICHAEL addition of thiols to cyclohex-2-enones, in the presence of catalytic amounts of chiral β-hydroxyamines, affords 3-arylthiocyclohexanones of considerable optical purity.[1] Alternatively, the reaction can be performed under phase transfer conditions, catalysed by the corresponding quaternary ammonium fluoride.[2] Using these methods, 3-ethylthiocyclohexanone and a series of 3-arylthio-derivatives bearing different substituents on the aromatic ring were easily synthesized.



(I) R = Et
(II) R = Ph
(III) R = p-ClC_6H_4
(IV) R = p-$Bu^tC_6H_4$
(V) R = p-MeC_6H_4
(VI) R = p-$MeOC_6H_4$
(VII) R = CH_2Ph

The c.d. spectra of these molecules are of interest as they allow one to test the relative importance of the through bond[3a,b] and dynamic coupling[4] mechanisms for the optical activity of ketones.

A detailed study of the c.d. spectrum of 3-ethylthiocyclohexanone and the influence of the substituents on the phenyl ring on the c.d. of arylthio-derivatives should provide evidence on the relative importance of the different mechanisms and also lead to elucidation of the stereochemistry.

RESULTS

The c.d. and u.v. spectra of the aliphatic derivative (I) are reported in Figure 1. The c.d. spectrum shows a structured transition at *ca.* 300 nm ($n \longrightarrow \pi^*$) and a band of opposite sign corresponding to a weak absorption at *ca.* 240 nm where alkyl sulphides show the first $n \longrightarrow \sigma^*$ transition. At higher energies the u.v. spectrum is similar to those displayed by aliphatic sulphides.[5a,b]

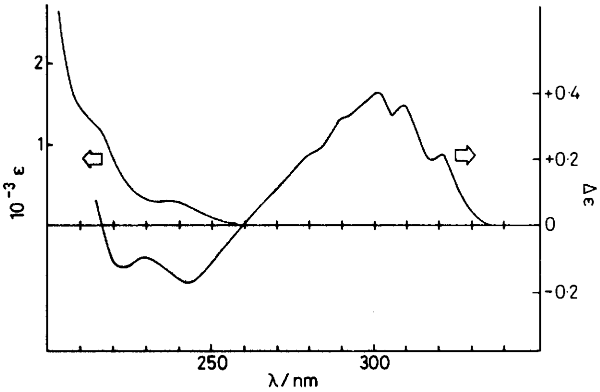


FIGURE 1 The absorption and c.d. spectra of (+)-3-ethylthiocyclohexanone in n-hexane

The u.v. and c.d. spectra of 3-(p-t-butylphenylthio)-cyclohexanone (IV) are shown in Figure 2. The spectra of other aryl derivatives are qualitatively similar and show only intensity variations. The c.d. in these cases is dominated by two bands of opposite sign at *ca.* 300 ($n \longrightarrow \pi^*$) and *ca.* 230—240 nm; however, both bands are considerably more intense than those displayed by the alkyl derivatives.

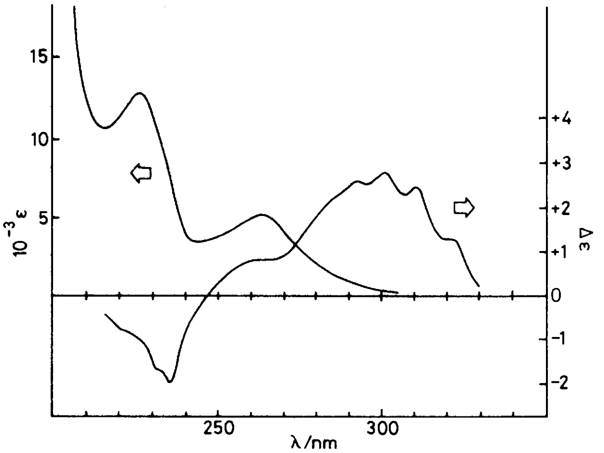


FIGURE 2 The absorption and c.d. spectra of (+)-3-(p-t-butylphenylthio)cyclohexanone in n-hexane

The absorption spectra of 3-arylthiocyclohexanones are very similar to those of alkyl aryl sulphides;[6a,b] the $n \longrightarrow \pi^*$ absorption of the carbonyl chromophore is not clearly detectable. The absorption at *ca.* 260 nm corresponds to the *p*-benzene-like transition which is ' long axis ' polarized in thioanisole.[6b] The second more intense transition at *ca.* 230 nm corresponds to the β-component which in thioanisole is ' short axis ' polarized.[6b]

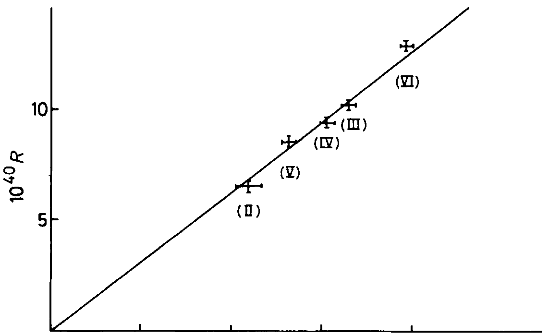


FIGURE 3 Plot of the rotational strengths (R) of the $n \longrightarrow \pi^*$ carbonyl transition of derivatives (II)—(VI) *versus* $\mu/\Delta\nu$. μ is the electric dipole moment of a thioaromatic chromophoric transition observed at *ca.* 230 nm. $\Delta\nu$ is the energy separation between the $n \longrightarrow \pi^*$ and the aromatic transition

It is worth noting that in the c.d. spectra, the *p*-transition (long axis polarized) gives rise to weak c.d. of the same sign as the $n \longrightarrow \pi^*$, while the transition at *ca.* 230 nm (short axis) is of opposite sign to the $n \longrightarrow \pi^*$ band and considerably more intense.

In particular, it is possible to obtain an excellent correlation between the rotational strength of the $n \longrightarrow \pi^*$ carbonyl transition and the dipole strength for the transition of the thioaromatic moiety at *ca.* 230 (Figure 3).

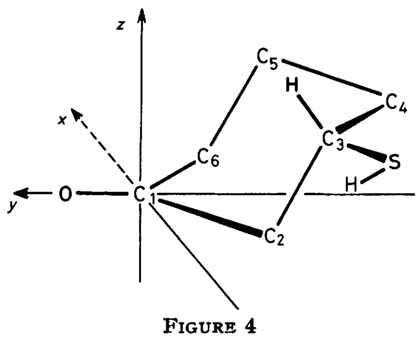


FIGURE 4

Reduction of the carbonyl group causes the disappearance of the strong c.d. at *ca.* 230 nm as well as of the $n \longrightarrow \pi^*$ transition.

MO–CI Computation and Localized MO Analysis of Rotational Strengths.—We have reported MO–CI computations of natural c.d. activities to allow the assignment of the lowest electronic transitions for a number of organic molecules.[5a,7a,b] Conversely, theoretical estimates of the rotational strength of a given electronic transition can be used to establish the absolute molecular configuration.

To this purpose, we have obtained MO and CI wavefunctions, energies, and rotational strengths for the *S* absolute configuration of 3-mercaptocyclohexanone. The geometry in Figure 4 was adopted for the S–H bond to connect the two lone pairs of the molecule by a favourable coupling path.

Canonical MOs (CMOs) were computed by a modified version of the Gaussian 70 system of programs using standard atomic orbitals (STO/3G).[8] The highest occupied CMOs and the lowest antibonding CMOs, which are relevant for the description of the lowest excited molecular states are, in order of increasing orbital energies, the lone pair orbitals of the oxygen $(n)_O$ and sulphur $(n)_S$ atoms, the π^* orbitals of the carbonyl group $(\pi^*)_{CO}$ and the antibonding orbital of the C–S–H chromophore $(\sigma^*)_{CSH}$.

Localized MOs (LMOs) have been useful for analysing the various contributions to the optical activity.[9-12] For this reason, the LMOs for 3-mercaptocyclohexanone were computed by the Boys–Foster procedure.[13] Since this method does not make any distinction between the σ and π components of the two-centre bonding or antibonding orbitals, we have obtained two equivalent bonding and two antibonding orbitals for the CO group $[(\sigma + \pi)_{CO}{}^i, (\sigma^* + \pi^*)_{CO}{}^i\ (i = 1 \text{ or } 2)]$ and two equivalent lone pair orbitals for oxygen and sulphur $[(l)_O{}^i, (l)_S{}^i\ (i = 1 \text{ or } 2)]$.

For all other bonds in the molecule, the localization procedure provided one occupied bonding and the corresponding virtual antibonding MO.

Ground and excited state molecular wavefunctions have been obtained by the configuration interaction (CI) and random phase (RPA) methods. The advantages of the latter procedure to allow *a priori* predictions of c.d. intensities have been discussed in detail by Bouman and Hansen.[14] One example of its applications is given in ref. 15. Since only a subset of electronic excitations have been included in the CI and RPA expansion, the descriptions based on CMOs and LMOs are not necessarily equivalent. For this reason, both types of orbitals have been used to obtain the CI and the RPA energies and rotational strengths.

With both types of orbitals, the lowest transitions of the molecule are described as $(n)_O \longrightarrow (\pi^*)_{CO}$ and $(n)_S \longrightarrow (\sigma^*)_{CSH}$. The rotational strengths computed for the two lowest transitions from the dipole velocity representation of the electric dipole operator are given in Table 1. The values computed from the dipole length representation of the operator are similar and have identical signs.

Based on the values given in Table 1, the following points appear relevant. (i) The lowest energy calculated transition has, as expected, largely $(n)_O \longrightarrow (\pi^*)_{CO}$ character and shows for the *S* absolute configuration negative rotational strength in agreement with the octant rule.

TABLE 1

Rotational strengths computed with the CI (a, c) and RPA (b, d) expansion based on canonical (a, b) and localized (c, d) MOs. Experimental rotational strength of (+)-3-ethylthiocyclohexanone (exp.). Values are in 10^{-38} c.g.s.

	a	b	c	d	Exp.
$S_0 \longrightarrow S_1$	−0.046	−0.009	−0.066	−0.073	+0.012
$S_0 \longrightarrow S_2$	+0.038	+0.037	+0.044	+0.065	−0.0035

(ii) The next calculated transition has positive rotational strength and dominant $(n)_S \longrightarrow (\sigma^*)_{CSH}$ character. This transition, which is typical of alkyl sulphides, is the best candidate for the second transition of the c.d. absorption at *ca.* 240 nm in the spectrum of 3-ethylthiocyclohexanone.

The $(n)_O \longrightarrow (\pi^*)_{CO}$ and $(n)_S \longrightarrow (\sigma)_{CSH}$ transitions are magnetically allowed, with a large component of the transition magnetic dipole along the y direction (Figure 4). Therefore, analysis of the c.d. in this molecule is most easily performed by inspecting the CI and the RPA expansion over LMOs of the y components of the electric transition dipoles of the two transitions. These are written as equation (1) where a_{rs} are fixed coefficients for a given ij

$$\mu_{ij}^{y} = \sum_{rs} a_{rs}\mu_{rs}^{y} \qquad (1)$$

electronic transition and μ_{rs}^{y} are local transition bond dipoles or charge transfer dipoles. We have performed the above analysis and found that most of the terms in equation (1) mutually cancel. For the $(n)_O \longrightarrow (\pi^*)_{CO}$ transition the surviving terms are −0.0143 45, $(l)_O^1$–C(2)C(3)*; −0.0166 46, C(1)C(2)–C(2)C(3)*; and −0.0237 06, C(2)C(3)–C(2)C(3)*.

This is easily explained by expressing the $(n)_O$ and the $(\pi^*)_{CO}$ CMOs as linear combinations of the LMOs as shown in Figure 5. As found for similar molecules,[3a,16] the lone pair orbital $(n)_O$ is largely delocalized, leading to partial delocalization of the excitation over the entire molecule. The chromophore (C=O) and the substituent (S) do not interact directly, but *via* a ' through bond mechanism '.[3a,16,17]

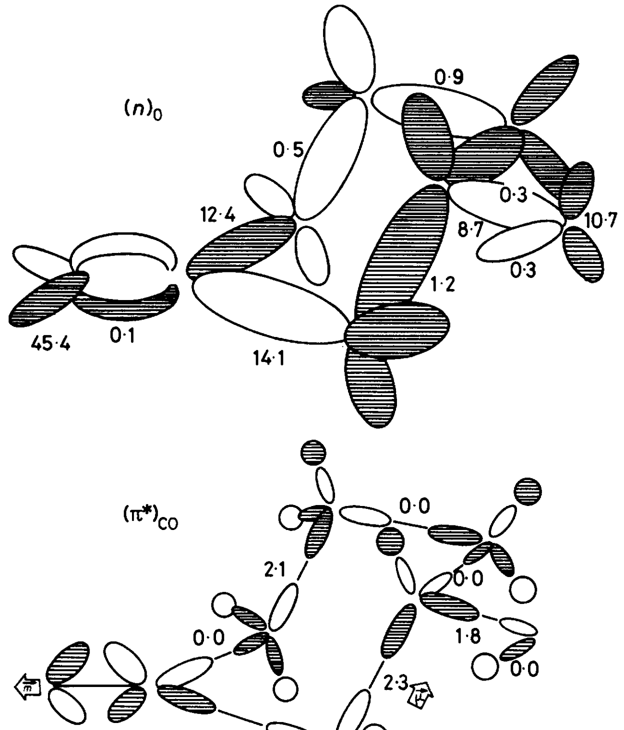


FIGURE 5 Sketches of the ground $(n)_O$ and the excited $(\pi^*)_{C\text{–}O}$ localized MOs of (*S*)-3-mercaptocyclohexanone. $\vec{m}$ and $\vec{\mu}$ are the principal magnetic and electric moments of the transition, as deduced from the phases of the orbitals. The figures represent the relative weight of the coefficients

As shown in Figure 5, a zig-zag-shaped[3a,11,16] sequence of bonds enhances the delocalization and favours the ' through bond mechanism '.

Our results indicate that the electric transition dipole does not arise from the mixing of the n and π orbitals [17] and that the delocalization of the $(\pi^*)_{CO}$ orbital provides essential contributions to the c.d. of this molecule. As shown in Figure 5, the delocalization of the $(n)_O$ and of the $(\pi^*)_{CO}$ orbitals enhances the polarizability of the C(2)–C(3) bond and generates an electric dipole antiparallel to the magnetic dipole, thus explaining the negative rotational strength for this transition.

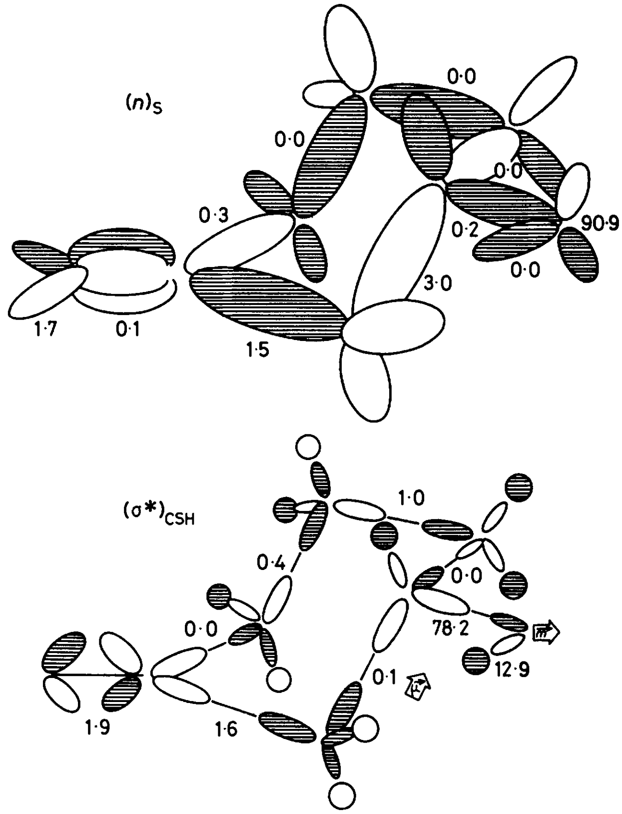


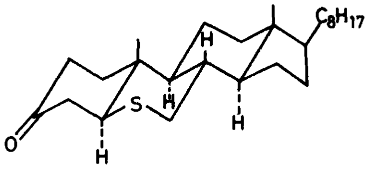
FIGURE 6 Sketches of the ground $(n)_S$ and excited $(\sigma^*)_{CSH}$ localized MOs for (*S*)-3-mercaptocyclohexanone. Conventions as for Figure 5

The circular dichroism of the second electronic transition $(n)_S \longrightarrow (\sigma^*)_{CSH}$ may be similarly explained. The surviving contributions to the electric dipole of this transition are found to be −0.0252 88, C(2)C(3)–C(2)C(3)*; −0.0292 04, C(2)C(3)–C(3)S*; and −0.0115 156, $(l)_S^1$–C(2)C(3)*. The dominant bonding interactions for this transition are shown in Figure 6.

The dependence of the $n \longrightarrow \pi^*$ optical activity on the conformation of the S–H group as studied at the CNDO/2 level.[3b] Calculations were carried out on four different rotamers of 3-mercaptocyclohexanone obtained from the conformer depicted in Figure 4 by successive clockwise rotation of 90° around the C(3)–S bond. The results indicate octant contributions for all conformations except that obtained from the first 90° rotation (S–H perpendicular) which gives an antioctant contribution of very nearly zero.

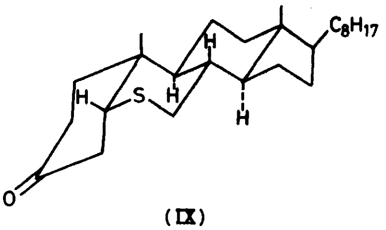
DISCUSSION

From the results of the MO calculations, the absolute configuration of (−)-3-ethylthiocyclohexanone turns out to be *S*, in agreement with the octant rule.[18] We have confirmed the assignment by two independent methods. (i) *R*-(+)-3-Methylcyclohexanone, dissolved in the nematic liquid crystal MBBA, induces a *P* cholesteric helix and its twisting power β is 0.25. (+)-3-Ethylthiocyclohexanone, dissolved in the same nematic solvent, induces a cholesteric phase of the same handedness; its twisting power is *ca.* 2. This is a strong indication that (+)-3-ethylthiocyclohexanone has the *R* absolute configuration.[19] (ii) From a comparison of the c.d. spectrum of (+)-3-ethylthiocyclohexanone with those of [20] the steroidal derivatives (VIII) and (IX) one can similarly deduce an *R* absolute configuration for (+)-3-ethylthiocyclohexanone.



(VIII)

λ 292 nm Δε $+2{\cdot}06 \times 10^{-40}$ (EtOH)



(IX)

λ 292 nm Δε $-4{\cdot}94 \times 10^{-40}$(EtOH)

The experimental data for the optical activity of the arylthio-derivatives clearly indicate interactions between the keto and the arylthio chromophores. In particular, the correlation of Figure 3 shows that the c.d. intensity of the $n \longrightarrow \pi^*$ transition depends on the isotropic intensity of the *short axis polarized* transition of the arylthio-chromophore at *ca.* 230 nm.

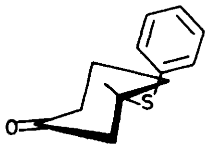
In the electric dipole–magnetic dipole coupling mechanism for the optical activity of ketones,[4] the magnetically allowed $n \longrightarrow \pi^*$ carbonyl transition interacts, *via* its associated electric quadrupole, with the electric moments of the substituent transitions. As a consequence, the magnetically allowed transition of the carbonyl acquires a collinear component of the electric moment and the electric transitions of the substituent acquires a component of the magnetic moment.

Restricting the case to a single appropriate transition of the substituent, the rotational strengths are given by equation (2) [21] when *V* is the dipole–quadrupole interaction energy, Δε the energy separation of the $n \longrightarrow \pi^*$ and the substituent transition, and $\vec{m}$ and $\vec{\mu}$ the magnetic and electric transition moments respectively. The coupled transitions have opposite rotational strengths of equal intensity. Equation (2) is the theoretical expression of the experimental correlation reported in Figure 3.

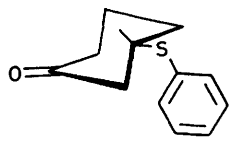
$$R_{n\rightarrow\pi^*} = -\frac{V}{\Delta\varepsilon}\vec{m}_{n\rightarrow\pi^*}\cdot\vec{\mu}_{\text{subst.}} = -R_{\text{subst.}} \quad (2)$$

In our case coupling occurs only between the $n \longrightarrow \pi^*$ transition and the *short-axis polarized* β-component of the thioaromatic chromophore. Assuming an equatorial conformation of the S–Ar group, as reported [22] for phenylthiocyclohexane, this indicates that the preferred rotamer of the equatorial S–Ar group is one in which the long axis of the phenyl group is nearly perpendicular to the C–O bond (direction m_y of the magnetic moment of the $n \longrightarrow \pi^*$ transition); furthermore the short axis of the phenyl group must be roughly parallel to the C–O bond.

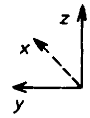
The two possible limiting conformations fulfilling these requirements are (a) and (b). In these conformations the phenyl plane is roughly perpendicular to the C–S–C plane in agreement with the preferred conformation recently proposed by Heilbronner *et al.*[23] for alkyl aryl sulphides having a bulky alkyl group.



(a)



(b)



Of the two conformations, (a) gives, for the configuration depicted, a negative contribution to the c.d. for the $n \longrightarrow \pi^*$ transition (upper right octant) and (b) a positive (lower right) contribution opposite to the alkyl derivative.

Molecular models clearly indicate conformation (a) as the less hindered. This leads to the prediction of *S* absolute configuration for the derivative displaying negative c.d. by analogy with the alkylthio-derivative. Indeed, there is no reason to predict an inversion of the enantiomeric excess in the asymmetric synthesis on passing from alkane- to arene-thiols.[1]

Conclusions.—In alkylthio-derivatives the ' through bond mechanism ' seems to play a dominant role in determining the c.d. of the $n \longrightarrow \pi^*$ carbonyl transition. This contribution is octant-like. The absolute configuration deduced is *S* for the derivative displaying negative c.d. at *ca.* 300 nm. This assignment is confirmed by comparison with known models and by the liquid crystal experiment. In arylthio-derivatives, the presence of the phenyl chromophore introduces dynamic coupling affecting the optical activity in addition to the ' through bond ' contributions. From the short axis polarization of the coupled aromatic transition one can deduce two possible conformations important in determining the dynamic optical activity. Disregarding the

TABLE 2

Experimental data of the addition of thiols to cyclohex-2-enone to give sulphides (I)—(VII)

Sulphide	Catalyst	$[\alpha]_{578}$ (°)	Enantiomeric excess (%)	Yield (%)	Reaction time (h)
(I)	(−)-Quinine	+0.99 [a]	8	62	352
(II)	(−)-Quinine	+29.9 [b]	41.3	90	4
(III)	Quibec	−11.8 [b]	15.3	88	4
(IV)	(−)-Quinine	+25.5 [b]	50.3	98	20
(V)	Quibec	−21.3 [b]	30.4	98	4
(VI)	(−)-Quinine	+20.9,[b] +29.5 [c]	34.3	92	21
(VII)	Quibec	−27.9 [b]	16.3	94	4

[a] *c* 8 (CH_2Cl_2). [b] *c* 2 (C_6H_6). [c] *c* 3 (CCl_4). Quibec = *N*-benzylquininium chloride. 3-Ethylthiocyclohexanone has n_D^{23} 1.5030. 3-(*p*-Methoxyphenylthio)cyclohexanone has n_D^{30} 1.5735.

apparently less favoured rotamer one can deduce the *S* absolute configuration for levorotatory derivatives.

EXPERIMENTAL

C.d. spectra were measured with a JASCO J-500 A spectropolarimeter with a D.P.-500 data processor. U.v. spectra were measured with a Cary 14 spectrophotometer. All the reported c.d. data were corrected to 100% of optical purity.

Thiol Addition.[2]—In a typical experiment, thiophenol (5 mmol) and cyclohex-2-enone (6.25 mmol) were added with magnetic stirring under nitrogen to dry toluene (12.5 ml) containing an 'onium salt (0.02 mmol) and potassium fluoride (7.5 mmol) and the mixture was left for 4 h at room temperature. The product was isolated by diluting the reaction mixture with methylene dichloride; the organic layer was washed with 10% aqueous sodium hydroxide and water and evaporated to dryness. The residue was chromatographed on silica with ether–light petroleum (1 : 9, then 1 : 1).

3-Phenylthiocyclohexanone had b.p. 110 °C at 0.08 mmHg (lit.[24] 110 °C at 0.8 mmHg). Table 2 lists the results of the addition reactions with other mercaptans, together with yields, optical rotations, and enantiomeric excesses.

Reduction of 3-*Arylthiocyclohexanones to a Diastereoisomeric Mixture of* 3-*Arylthiocyclohexanols.*—To the title compound (10 mmol) dissolved in anhydrous ethanol (5 ml), sodium borohydride (10 ml) was added. After 3 days at room temperature, the solvent was evaporated and the residue was diluted with methylene dichloride and washed with water. The organic phase was separated, dried (Na_2SO_4), and evaporated under vacuum; the yields were in the range 90—95%. The diastereoisomeric mixture of alcohols obtained starting from 3-(*p*-t-butylphenylthio)cyclohexanone, $[\alpha]_{578}$ +25.5° (*c* 1.6, C_6H_6), had $[\alpha]_{578}$ +4.584° (*c* 2, C_6H_6). The diastereoisomeric mixture of alcohols obtained starting from 3-(*p*-methoxyphenylthio)cyclohexanone, $[\alpha]_{578}$ +20.9° (*c* 2, C_6H_6), had $[\alpha]_{578}$ +2.60° (*c* 1.6, C_6H_6).

3-(*p*-Chlorophenylthio)cyclohexanone, $[\alpha]_{578}$ −11.8° (*c* 2, C_6H_6), gave a diastereoisomeric mixture of alcohols with $[\alpha]_{578}$ −2.1° (*c* 1.5, C_6H_6). 3-*p*-Tolylthiocyclohexanone, $[\alpha]_{578}$ −18.0° (*c* 2, C_6H_6), gave a diastereoisomeric mixture of alcohols which had $[\alpha]_{578}$ −1.55° (*c* 2.1, C_6H_6).

Enantiomeric Excesses.—The values of the enantiomeric excess for derivatives (II)—(VII) were known from refs. 1 and 2. The value for derivative (I), evaluated by ^{13}C n.m.r. in the presence of $Yb(dpm)_3$ as a chiral shift reagent, was *ca.* 8%.

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