Optically Active Bis-β-keto Sulfonium Ylid

Sir:

Tri-ligated sulfoxides, sulfilimines and sulfonium salts have been known to be optically active when the ligands on the sulfur atom are constitutionally different. This is also the case with tetra-covalent sulfoximines and more recently it was shown by the actual resolution that oxosulfonium ion can exist in stable enantiomeric forms.

It was reasonably expected that sulfonium ylids could be likewise optically active as the parent sulfonium salts and this has been evidenced by the case of carbonyl-stabilized sulfonium ylid in which the chirality on sulfur atom is retained in the ylid state.

It seemed of interest to undertake the exploratory synthesis of chiral bis-β-keto sulfonium ylids for the purpose of elucidating their physico-chemical properties as well as their applications to organic synthesis. A priori, bis-sulfonium ylids are capable of existing in inherently optically inactive meso form and enantiomeric pairs because of the two chiral centers of hetero-atoms involved in a molecule and are of potential interest from the viewpoint of simultaneous asymmetric transfer from chiral sulfur to trigonal carbon atoms.

We wish, at this time, to report the first example of optically active bis-β-keto sulfonium ylid and the reactions thereof.

The reaction of 4,4′-bis-bromoacetyl biphenyl with ethyl methyl sulfide in acetone gave the corresponding p, p′-biphenacyl-bis-(ethylmethylsulfonium) bromide (I), which was isolated pure from the reaction mixture by recrystallizations from hot water; (mp 165°C; yield 51%). The optical resolution of bis-sulfonium salt I was achieved by converting the bromide salt to (+)-α-bromocamphor-π-sulfonate II and subsequent repeated fractional recrystallizations from water. The optically active p, p′-biphenacyl-bis-(ethylmethylsulfonium) perchlorate (III) obtained, after replacing bromocamphor sulfonate with perchlorate, showed the rotation [α]D25 = -7.7° (c=2.9, DMSO) and melted at 253–4°C.

The optically active bis-sulfonium salt III was converted into the corresponding bis-(ethylmethylsulfonium) p,p′-biphenacyl ylid (IV) by treating the perchlorate salt with 5% aqueous sodium hydroxide and was extracted with chloroform. The stable bis-sulfonium ylid IV isolated pure was characterized by the following spectroscopic evidence. The IR-spectrum showed a delocalized carbonyl absorption band at 1500 cm⁻¹, and UV-spectrum indicated λmax=320 nm (ε 32,800). The NMR-spectral data fully substantiated the proposed structure of the bis-ylid IV: the NMR-spectrum of the ylid showed the large values of magnetic non-equivalence of diastereotopic methylene protons (δ 2.75 and 3.70), which may result from the effect of the steric interactions upon the weighting of possible conformers. There were observed a triplet at δ 1.2 (6H, SCH₂CH₃), a singlet at δ 2.8 (6H, SCH₃), a broad singlet at δ 4.1 (2H, -CHS–) and a double doublet centered at δ 7.6 and 7.9 (8H, aromatic protons).

The bis-ylid thus identified had the levorotation [α]D25 = -13.4° (c=0.76, DMSO). The
reaction of this chiral ylid with olefin substrate as a Michael acceptor is exemplified by the following. A solution of 0.9 g (2.4 mmole) of the ylid IV, having $\left[\alpha\right]_{D}^{25} -9.2^\circ$ in DMSO, and 0.9 g (4.8 mmole) of 3-benzylidenacetylacetone (V) in 30 ml of DMSO were stirred at room temperature under nitrogen atmosphere for two days. The reaction was quenched with water and the reaction mixture was extracted with chloroform and after the removal of solvent, the product was recrystallized from benzene-hexane to give the bis-cyclopropane derivative VII, mp 235-6°C; (Anal. Found: C, 78.40; H, 5.75; C$_{40}$H$_{34}$O$_6$ requires C, 78.67; H, 5.61), yield 0.6 g (41%): $\left[\alpha\right]_{D}^{25} -4.6^\circ$ (c=3.4, chloroform).

In the same manner, the reaction with dibenzoylethylene (VI) yielded the corresponding bis-cyclopropane compound VIII in a 42% yield; mp 270-2°C; (Anal. Found: C, 81.28; H, 4.93; C$_{45}$H$_{34}$O$_6$ requires C, 81.57; H, 4.85). $\left[\alpha\right]_{D}^{50} -1.5^\circ$ (c=1.6, CF$_3$COOH).

It is concluded by the present work that the chirality on the two sulfur atoms in the parent bis-sulfonium salt is retained in the bis-ylid, as manifested in its optical activity, and, upon the reaction with olefin substrates, is transferred to trigonal carbon atoms at the expense of the former, to afford optically active bis-cyclopropane products. This constitutes a variant asymmetric double induction of the self-immolative type.

The assignment of stereochemistry to bis-sulfonium salt, bis-ylid and bis-cyclopropane products is currently in progress and will be described elsewhere in detail.

REFERENCES

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