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ENANTIOFACE-DIFFERENTIATION IN FREE RADICAL ADDITION OF THIOLACETIC ACID TO (Z)-2-OCTENE IN THE PRESENCE OF CHIRAL SUBSTANCES

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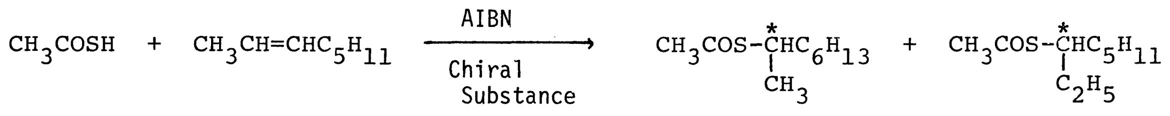
The free radical addition of thiolacetic acid to (Z)-2-octene in the presence of ℓ-menthol or deoxycholic acid using 2,2'-azobisisobutyronitrile (AIBN) gave optically active 2-acetylthio-n-octane and 3-acetylthio-n-octane.

During the course of our investigations[1-3] on radical copolymerizations of styrene with polar vinyl monomers such as 2,6-dimethylpyridazine-3-one, methyl methacrylate, and N,N-dimethylacrylamide, such protic solvents as phenol and carboxylic acid were found to accelerate the reaction due apparently to the hydrogen bonding to the partially polarized growing radicals, eventually stabilizing the transition state. Meanwhile, we also found that the radical copolymerization of styrene with maleic anhydride in ℓ-menthol results in the formation of an optically active copolymer which is devoid of ℓ-menthol.[4] Although the copolymer thus obtained is believed to be an asymmetrically induced product, there is no definite proof to substantiate that the asymmetric induction is taking place in the addition of a free radical to the particular olefin in the presence of such a chiral solvent as ℓ-menthol. Thus we have carried out the free radical addition of thiolacetic acid to (Z)-2-octene in the presence of either ℓ-menthol or deoxycholic acid (DCA) together with AIBN, and found that the addition products, i.e., 2-acetylthio-n-octane (I) and 3-acetylthio-n-octane (II), are highly asymmetrically induced (nearly 30% in the case of I).

A typical run is as follows; to a stirred n-hexane (100 ml) solution of (Z)-2-octene (0.04 mol), ℓ-menthol (0.04 mol) and AIBN (0.12 mmol), was added dropwisely thiolacetic acid (0.04 mol) at 45°C in nitrogen atmosphere and the whole mixture was stirred for 6 h. After evaporation of n-hexane and unreacted components under reduced pressure, the residue was chromatographed on silica gel TLC and then the isolated products were purified further by gas chromatography to obtain 45% of 2-acetylthio-n-octane and 40% of 3-acetylthio-n-octane which were identified by means of IR, NMR, and GC-MS.



$$CH_3COSH + CH_3CH{=}CHC_5H_{11} \xrightarrow[\text{Chiral Substance}]{\text{AIBN}} CH_3COS\text{-}\underset{CH_3}{\overset{*}{C}}HC_6H_{13} + CH_3COS\text{-}\underset{C_2H_5}{\overset{*}{C}}HC_5H_{11}$$

(I) (II)

Table. Enantioface-Differentiating Radical Addition of Thiolacetic Acid to (Z)-2-Octene in the Presence of Chiral Substances Using AIBN.

Chiral Substance	Thiolester	Yield(%)	$[\alpha]_D^{25}$ (C, Benzene)
ℓ-Menthol	I	45	-1.82° (5.5)
	II	40	-0.84° (5.3)
DCA[a]	I	40	-0.46° (4.3)
	II	38	-0.61° (3.6)

[a] Ethanol was used as a reaction solvent.

The reactions were found to be inhibited completely by the addition of a small amount of hydroquinone, implying these reactions to proceed via a free radical process. The values of specific rotations of these optically active thiolesters were determined and listed in the Table. Based on the reported rotation of -6.4° for (S)-(-)-I,[5] the optical yield (i.e., e.e.) of I was estimated to be 28% in the presence of ℓ-menthol and 7% with DCA, respectively. Since the absolute configuration of II has not been determined, the optical yield of this compound II thus obtained was not estimated. Thiolacetic acid is quite acidic enough to form hydrogen bonding with chiral ℓ-menthol and the addition of acetylthiyl radical formed from the hydrogen bonded complex between thiolacetic acid and ℓ-menthol to the olefin in the vicinity would still recognize the original chirality. Studies on the mechanistic details of this and related reactions are now underway in this laboratories.

We believe that this is the first example of the free radical addition of an achiral thiol to a prochiral olefin to give an optically active thiolester.

References

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