Thione Photochemistry: Cyclopropanethiol (Homothioenol) Formation by β-Hydrogen Abstraction

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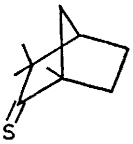
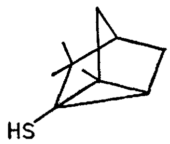
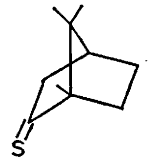
Summary Irradiation of thiofenchone and thiocamphor leads to the formation of cyclofenchyl thiol and tricyclyl thiol respectively; on heating, these homothioenols revert to thiocarbonyl compounds.

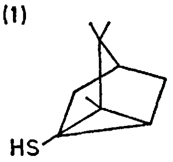
Previous studies on the photochemistry of non-aromatic thiones were restricted to observations of dimerisation, cycloaddition, and reduction in adamantanethione.[1] We report here a new class of reaction for which there is little analogy in ketone photochemistry.

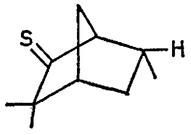
Irradiation of thiofenchone[2] (**1**) in n-pentane at 254 nm gave the tricyclic thiol (**2**)† and the corresponding disulphide (**3**). Compound (**2**) was characterised chemically by the preparation of a 3,5-dinitrobenzoate thiol ester. That the extra double-bond equivalent contained in the molecule was present as a cyclopropane ring was shown chemically by desulphurisation with Raney nickel to cyclofenchane,[3] identical with an authentic specimen prepared from fenchone.


(**1**)


(**2**)


(**4**)


(**5**)


(**6**)

The structure of (**3**) followed from its mass spectrum and other spectroscopic data, and was confirmed chemically by its preparation from (**2**) by oxidation with ferric chloride and acid.[4]

Similar irradiation of thiocamphor (**4**) gave the thiol (**5**) and the corresponding disulphide; the structures of these were demonstrated as for thiofenchone. The Raney nickel desulphurisation of (**5**) gave tricyclene.[3]

The thiols (**2**) and (**5**) are the sulphur analogues of the homoenols shown to be intermediates in the β-deuterium exchanges and related transformations first reported by Nickon in the bicycloheptane ring system.[6] It was, therefore, of interest to see whether a homothioketonisation could be induced. In fact, the thiol (**2**) when heated (sealed tube) at 135° gave (**1**) and (**6**) ($>80\%$) in about a 3 : 2 ratio. The new thione was characterised spectroscopically and identified by conversion, with mercuric acetate in $HOAc–CHCl_3$ to the corresponding ketone. This, the *endo* methyl isomer, was identified by comparison with an authentic specimen.[7] The thiol (**5**) on the other hand, as far as could be detected, gave only the original thioketone (**4**). The *exo* protonation of the homothioenol is in accord with the observations of Nickon on the homoketonisation of 1-acetoxynortricyclene in non-electrophilic media,[6] but since the conditions are different we make no implications with regards mechanism.

We have been able to find only three methods reported for the preparation of cyclopropanethiols. One, the insertion of sulphur atoms into the C–H bond has been applied only to the formation of cyclopropanethiol itself.[8] Neither of the other two methods, the rearrangement of thietan oxides,[9] and the reduction of cyclopropyl thioacetals,[10] could be applied to the preparation of (**2**) or (**5**). It seems most probable that these are formed by β-hydrogen abstraction by the excited thione. Such a reaction does not, apparently, occur in the ketonic equivalents (with spontaneous thermal opening of the cyclopropane) since the n.m.r. and mass spectra of fenchone irradiated in CD_3CN and D_2O showed that no deuterium had been incorporated.

Although β-hydrogen abstraction appears to be of very rare occurrence in carbonyl photochemistry giving precedence to the Norrish Type II, intermolecular hydrogen abstraction, or simply other photochemical reactions, instances have been reported.[11]

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† Adequate analyses and appropriate spectra have been recorded for all new compounds.

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