

Short Communications

Ring Opening Reactions of
Dispiro [5.0.5.1.]-trideca-1,5,8,12-
tetraone

II.* Reaction with Thiourea

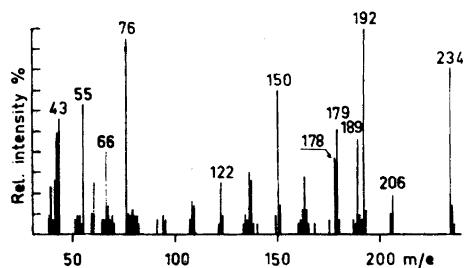
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Fig. 1.

The cyclopropane derivative, dispiro-[5.0.5.1.]-trideca-1,5,8,12-tetraone (*1*),^{2,3} shows an unusually high tendency to undergo ring opening reactions. Methanol and ethanol react with *1* at room temperature in the dark and in the absence of catalyst.¹ The alcohols attack the methylene group of the cyclopropyl ring. Chloride, bromide, and iodide ions, on the other hand, preferentially attack the spiro carbon.⁴

In order to obtain additional information about factors influencing the direction of the ring opening process, the reaction between *1* and thiourea has been studied.

Treatment of *1* in acetone at room temperature with thiourea afforded one major product as shown by TLC. This substance was isolated in 73% yield and was apparently formed by the addition of one molecule of thiourea to *1*.

The mass spectrum of the adduct (Fig. 1), which gave no molecular ion, was closely related to the spectra of thiourea, compound *1*,⁵ and especially its isomer *2*.^{1,4} The major fragmentation sequence starts with elimination of thiourea to give *m/e* 76 and *m/e* 234, the

latter fragment formulated as a mixture of the molecular ions of *1* and *2*. A closely related breakdown pattern is shown by the methanol and ethanol adducts.¹ This suggests structure *3* for the product, formed by attack of thiourea on the methylene group. The alternative point of attack, the spiro carbon, would yield compound *4* which would be expected to give a mass spectrum closely related to that of the cyclic enol ether *5*.^{2,5}

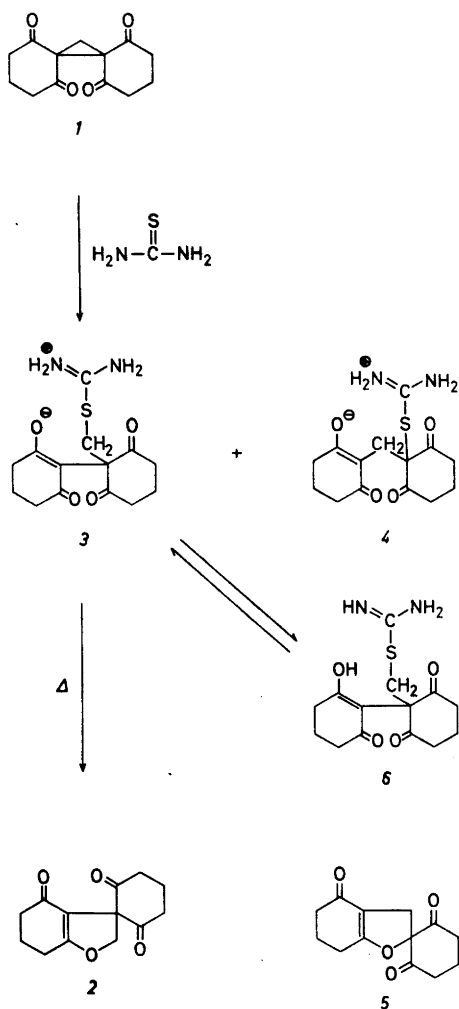
Since it is known⁶⁻⁸ that *S*-alkylthiourea derivatives are at least as strong bases (pK_B ca. 7-9) as 1,3-cyclohexanedione anions (pK_B ca. 8-9), it is reasonable to assume that the adduct exists as the internal thiuronium salt *3* rather than as the tautomer *6*.

Support for structure *3* was given by the UV, IR, and NMR spectra. The UV spectrum (EtOH) gave maxima at 225 nm (ϵ 9800) and 286 nm (ϵ 16 000). The lower maximum was ascribed to the thiuronium group whereas the wavelength and extinction coefficient of the higher maximum correspond to the values of the anion of a 2-substituted 1,3-cyclohexanedione.^{3,9} The latter maximum was shifted to 264 nm (ϵ 10 300) on the addition of acid.

The IR spectrum of the adduct was similar to that of the benzyl thiuronium salt of dimedone and showed a strong and

* No. 1 of this series, see Ref. 1.

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broad band at 1480 cm^{-1} , which suggested the presence of an enolate anion.¹⁰ N—H stretching frequencies at 3280 and 3040 cm^{-1} and bands in the region 1640 – 1690 cm^{-1} (C=N)^{11,12} gave further evidence for structure 3. The adduct also exhibited a band at 1721 cm^{-1} assigned to the isolated carbonyl groups. It is noteworthy that it did not give the doublet typical for many 2,2-disubstituted 1,3-cyclohexanediones.^{2,13}

The NMR spectrum (DMSO- d_6) showed signals from the methylene protons of the cyclohexanedione rings in the region δ 1.6–2.9. The remainder of the spectrum

which consisted of six singlets at δ 4.80, δ 5.03, δ 5.23, δ 5.65, δ 5.81, and δ 7.00 (2:14:10:15:11:56) suggests an equilibrium between 3 and 6. The signals from the methylene protons adjacent to the sulfur atom in both 3 and 6 as well as from the protons attached to nitrogen and oxygen are expected to fall in the above region, but no complete interpretation can be given without further investigation. If the adduct had the alternative structure 4, the methylene bridge protons should give a signal in a very narrow region δ 3.1–3.2.⁴ A weak singlet found in that region in the spectrum of the crude reaction mixture indicates that the thiourea to a minor extent may also attack the spiro carbon.

When the adduct was distilled at 155°C , 10^{-3} mm Hg, two main products were obtained, thiourea and a compound which had the same TLC properties as 2 (R_F value, UV absorption at 250 nm, and reaction with 2,4-dinitrophenyl hydrazine). The mass spectrum of the crude distillate was virtually identical with the superimposed spectra of thiourea and 2.

The results presented show that the dispiro cyclopropane derivative 1 already at room temperature undergoes a ring opening addition reaction with thiourea which preferentially attacks the methylene group of the cyclopropyl ring, *i.e.* in the same way as the alcohols.¹ Evidence for the alternative attack on the spiro carbon was given only by the NMR spectrum of the crude product.

Further studies on the ring opening reactions of 1 are in progress.¹⁴

Experimental. Compound 1 (135 mg, 0.58 mmol) and thiourea (76 mg, 1 mmol) were stirred in acetone (10 ml) for 63 h at room temperature. The precipitate formed was collected and dried to yield 131 mg, 73 % of 3, m.p. 152 – 154°C , ν_{max} (KBr) 3280 , 3040 , 1721 (s), 1690 , 1640 , 1580 , 1510 , 1480 (s), 1395 , 1188 cm^{-1} . (Found: C 53.7; H 5.73; N 9.02; O 21.3; S 10.3. $\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_4\text{S}$ requires: C 54.2; H 5.83; N 9.02; O 20.6; S 10.3).

The benzyl thiuronium salt of dimedone was prepared from benzyl thiuronium bromide and the sodium salt of dimedone in ethanol. ν_{max} (NaCl discs) 3100 (br), 1650 , 1490 (s, br), 1380 , 1265 , 1230 , 1145 cm^{-1} .

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Studies on the Chemistry of Lichens

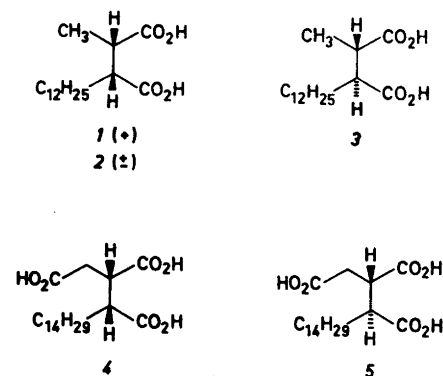
28. *Additional Evidence for the *erythro* Configuration of Roccellic Acid

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In order to establish beyond doubt the absolute configuration of roccellic acid (1), *erythro*-2-methyl-3-dodecylsuccinic acid (2) was synthesised from *erythro*-2-allyl-3-methylsuccinic acid.¹ Since the melting points of the synthetic racemic acid (2) and

the optically active roccellic acid differed by a few degrees, we tried to resolve the *erythro*-allylmethylsuccinic acid. Unfortunately, the early attempts were completely unsuccessful. However, the IR-spectra of the *erythro* acid (2) (Fig. 1:1) and roccellic acid were superimposable.¹ The work with nor-rangiformic acid (5) had shown that while the IR-spectra of the racemic and optically active forms of (5) were superimposable, as were the spectra of active and inactive *erythro* forms (4), there were substantial differences between the spectra of



the *threo* (5) and *erythro* (4) forms (Fig. 1: 3,4).^{2,3} It therefore seemed safe to conclude that roccellic acid had the *erythro* configuration. However, some additional evidence seemed to be desirable.

Roccellic acid was therefore epimerised with concentrated sulfuric acid to give one isomer, m.p. 136–138°, identical with synthetic *erythro*-2-methyl-3-dodecylsuccinic acid (2), and one isomer, m.p. 81–83°, which must be *threo*-2-methyl-3-dodecylsuccinic acid (3). The IR-spectrum of the *threo* acid (3) was different from that of roccellic acid, particularly in the region 1150–1300 cm^{-1} , (Fig. 1:1,2). Roccellic acid therefore most probably has the *erythro* configuration and, consequently, the (2*S*:3*R*) configuration as suggested earlier.^{1,4} The *erythro* forms (2) and (4) of roccellic and nor-rangiformic acid both have two fairly distinct IR absorption peaks at about 1200 and 1260 cm^{-1} (presumably C–O stretching of the carboxyls; Fig. 1: 1, 3). By contrast the *threo* forms have one broad band with some fine structure at about 1200 cm^{-1} (Fig. 1: 2,4). The 1,2-diisopropyl, di-*t*-butyl and dicyclohex-

* Part 27: Ref. 2.