

ON THE GEOMETRIC CONFIGURATIONS OF  $\beta$ -THIODICROTIC ACID

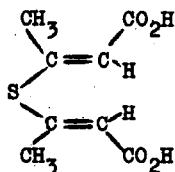
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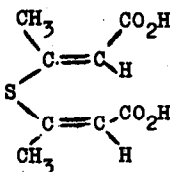
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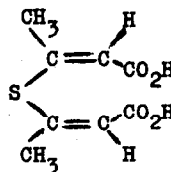
Of the three possible isomers of  $\beta$ -thiodicrotonic acid only one has so far been reported (1). This compound (I), which is obviously the thermodynamically most stable isomer, has a m.p. of  $215^{\circ}$  and was assigned the structure (c) solely on the basis of its reaction with acetic anhydride to form a cyclic anhydride from which the acid could be regenerated (1). This assignment appears, however, to be wrong and we now wish to



(a)



(b)



(c)

present evidence for the assignment of structure (a) to this compound and also report a new isomer (II) with m.p. 164° which we have assigned structure (b). The isomer with structure (c) was, however, not obtained.

The NMR spectrum of I (in methanol) showed two resonance peaks, at  $\delta = 5.6$  and 2.0 ppm. respectively, with an intensity ratio of 1:3. The second peak was distinctly split into a doublet with a coupling constant of about 1.5 cps. The spectrum of II (in methanol) showed two badly resolved peaks at  $\delta = 5.75$  and 5.65 ppm. and two well separated doublets at  $\delta = 2.05$  and 1.8 ppm. respectively. The intensity ratio between these two doublets was 1:1. An intensity ratio of 1:3 between the sum of the peaks at low field and the sum of the two doublets at higher field was also obtained. The chemical shifts were measured from TMS as an external reference.

It has been shown earlier for  $\beta$ -alkylthiocrotonic acids, that the methyl group resonance occurs at the lowest field when this group is cis-related to the carboxyl group (2). On this basis it is evident from our results that II is the unsymmetrical isomer, i.e. II has structure (b), and also that I is the symmetrical isomer with structure (a), because in this case the resonance peak, which originates from the two magnetically

equivalent methyl groups, occurs at the higher  $\delta$ -value ( $\delta = 2.0$  ppm.) corresponding to the lowest field.

This assignment of configurations was also supported by results obtained from IR and UV spectra of the two isomers I and II.

The sulfoxides corresponding to I and II (III and IV respectively; III: m.p.  $183^{\circ}$ , IV: m.p.  $170^{\circ}$ ) were also prepared and their reactions in acidic iodide solution were studied. Earlier, a very great difference in the rates of reduction by means of iodide for the two geometric isomers of a  $\beta$ -alkylsulfinylcrotonic acid has been observed (3, 4). This is obviously due to neighbouring group participation in those isomers where the sulfoxide and carboxyl groups are cis-related to each other, resulting in fast reduction of the sulfoxide group in these cases.

III and IV were studied under identical conditions (2.7 M hydrochloric acid and  $\sim 0.5$  M potassium iodide in aqueous solution at room temperature). IV immediately began to liberate iodine and after approximately 40 min the reaction was complete. The liberated iodine was titrated with sodium thio-sulfate and an equivalent weight could be determined in this way. (Found: 107.7. Calc.: 109.1). In the case of III, no

reaction at all could be observed, even after two days. Thus, these results confirm the configuration assignments based on the other methods, and it also seems to us that the last method offers an easy way of determining the geometric configurations of  $\alpha,\beta$ -unsaturated sulfide acids and that it has a general applicability.

The NMR-spektra were recorded with a Varian A-60 high resolution spektrometer.

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