

REACTIONS OF ELECTRON-DEPLETED THIOCARBONYL COMPOUNDS
WITH DIAZOALKANES

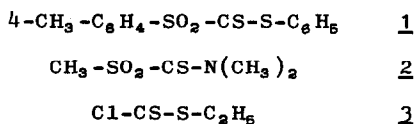
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A large variety of thiocarbonyl compounds have been treated with different diazo compounds¹⁻⁸ and, according to the circumstances, thiadiazoles, dithiolanes, thiranes, or alkenes were observed as reaction products.

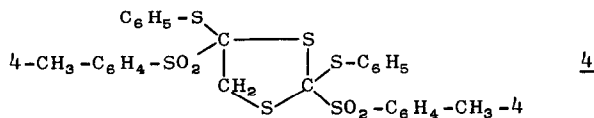
We wished to examine the trithiocarbonate S,S-dioxide system⁹ and the C-sulfonylthioformamide system¹⁰ with respect to their behavior towards diazoalkanes and treated 1⁹, 2¹⁰, and 3¹¹ with diazomethane, phenyldiazomethane, and diphenyldiazomethane. 3 was included in the study because the literature does



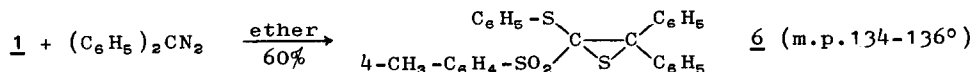
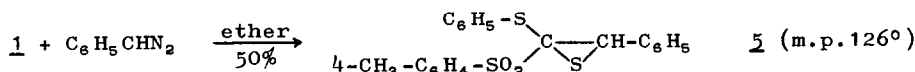
not appear to contain reports about the reactions of chlorodithioformates with diazomethane and because it could be expected that the thiocarbonyl groups of 1 and 3 might have rather similar chemical properties.

All products were purified by recrystallization and/or column chromatography or TLC on silica gel and gave satisfactory elemental analyses, NMR, and IR spectra.

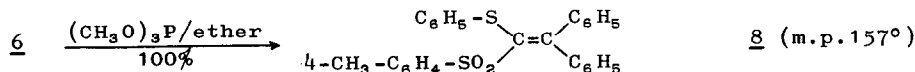
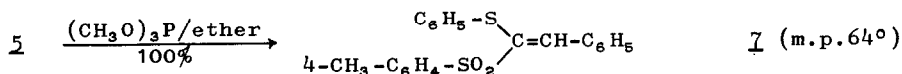
In ether solution, 1 reacts immediately with diazomethane yielding the dithiolane 4 in 8% yield. Upon heating to 125°, the solid colorless 4 turns red violet and thereafter melts at approximately 154°. The structure of 4 can be deduced from the NMR spectrum in which the two methyl groups are non-equivalent and the methylene signal appears as a quartet.



1 reacts equally readily with phenyldiazomethane and diphenyldiazomethane, respectively. Here, thiiranes 5 and 6 are formed which contain the novel functional group of a trithioorthocarboxylate S,S-dioxide. (The same functional group can also be obtained from trithiocarbonate S,S-dioxides and dienes or electron-rich alkenes¹²). 5 and 6 can be converted to the corresponding alkenes



7 and 8 in quantitative yield by treatment with trimethyl phosphite in ether. 1-Thio-1-sulfonylalkenes like 7 and 8 do not seem to have been prepared previously and thus constitute a novel type of compound.



Compounds 4, 5, and 7 can exist as either E or Z isomers. We seem to have obtained single isomers, but have not yet determined which.

The behavior of 2 and 3 towards diazomethane does not resemble that of 1, but instead the isomeric thiadiazoles 9 and 10 and 11 and 12 are formed. In both cases elimination of sulfinic acid or hydrogen chloride leads to aromati-

zation of the ring system. The structure of 9 was proven by comparison with an authentic sample^{1,3} and the structure of 10 could be inferred from this. The structural assignments of the thiadiazoles 11 and 12, which appear less secure, rest upon the assumption that the relative chemical shifts of the ring protons fall into the same sequence as is the case for 9 and 10.

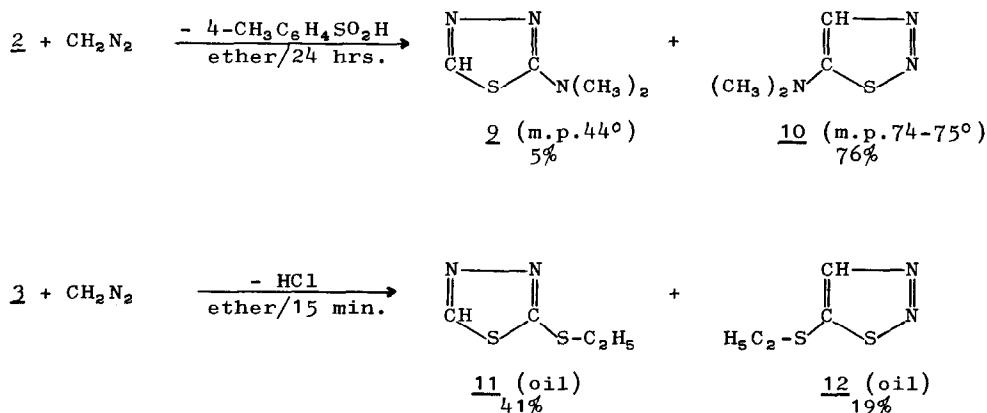


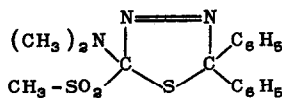
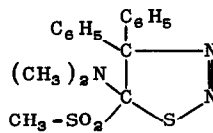
Table 1

Chemical shifts of the ring protons of 9, 10, 11, and 12
(CDCl₃, TMS)

Compound	δ	Compound	δ
<u>9</u>	8.42	<u>11</u>	9.14
<u>10</u>	7.58	<u>12</u>	8.42

The reaction of 2 with diphenyldiazomethane follows the same pattern as that with diazomethane, but only one product is isolated. The lack of mobile hydrogen atoms precludes, of course, the aromatization of the thiadiazoline system. We have at present no strict proof for the structure of the product

(obtained after 24 hours reaction time in ether, yield 52%, m.p.144°), but considering the well-known instability of diazosulfides it is more likely that it is the Δ^3 -1,3,4-thiadiazoline 13 than the Δ^2 -1,2,3-thiadiazoline 14.

1314

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