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THE REACTION OF DIAZOACETIC ESTER WITH THIOBENZOPHENONE

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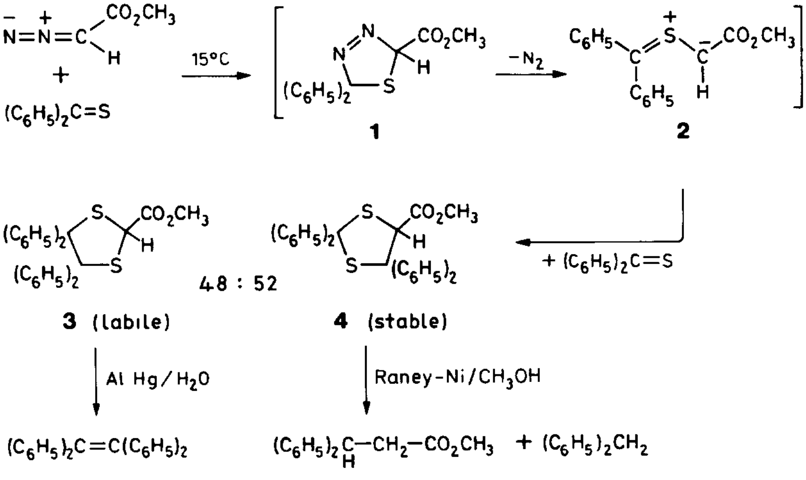
Summary Methyl diazoacetate reacts with two equivalents of thiobenzophenone to furnish two isomeric 1,3-dithiolanes and nitrogen; the intermediate thiocarbonyl ylide is intercepted by 1,3-dipolar cycloaddition or undergoes electrocyclic ring closure.

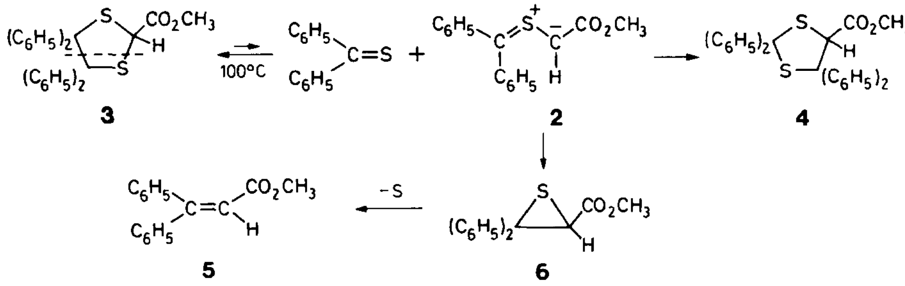
Nitrogen is eliminated during the reaction of aliphatic diazo compounds with thiobenzophenone at room temperature. The N_2 evolution is induced; the diazo compounds are stable at 25°C. Whereas diphenyldiazomethane produces tetraphenylthiirane in a 1:1 reaction,[1] two moles of thiobenzophenone are consumed in the interaction with diazoacetic ester [2] or diazomethane.[2,3] Schönberg, Černik, and Urban [2] have assigned structure 3, C_2H_5 instead of CH_3, to the product from ethyl diazoacetate and thiobenzophenone.



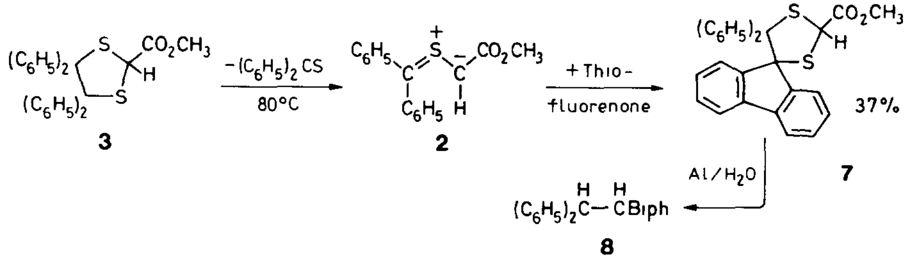
When we repeated the Schönberg reaction with methyl diazoacetate and 2.5 equiv. of thiobenzophenone in ether at 15°C, the N_2 evolution was finished after 30 min and two isomeric 1,3-dithiolanes, 3 and 4, in a 51 : 49 ratio (86% yield) were obtained in colorless crystals. The "labile isomer" 3, mp 147.5 - 148.5°C,[4] remained undissolved in boiling acetone, whereas the "stable isomer" 4, mp 156.5 - 157.5°C, was isolated from the acetone phase and recrystallized.

The reduction of 3 with aluminium amalgam and water in ether afforded tetraphenylethylene (93%). The same product was obtained in 96% yield from 3 in refluxing methanolic KOH; the pathway is unclear. Treatment of 4 with Raney nickel in refluxing methanol gave diphenylmethane and - after alkaline hydrolysis - 3,3-diphenylpropionic acid (83%). The ^{1}H-NMR spectra ($CDCl_3$, δ) support the structures. The ring proton of 3 appears at 4.59, that of 4 at 5.19. The ester methyl singlet of 4 (3.29) reveals a deshielding by the cis-vic-phenyl compared with the normal OCH_3 value of 3 (3.67). In the ^{13}C-NMR spectrum of 3 C-4 and C-5 are equivalent (s, δ 78.8) and C-2 gives rise to a doublet at 47.5, whereas in 4 the three ring C-atoms are different (C-2 and C-4 73.1 and 77.0, C-5 d 63.0). In the MS of 3, two fragmentation pathways become evident: m/e = 270 (2^+, 22%), 198 (thiobenzophenone$^+$, 100%), 332 (tetraphenylethylene$^+$, 56%). Instead of the latter signal, the MS of 4 shows m/e = 230, $(C_6H_5)_2CS_2^+$, 100%.

Both 3 and 4 turn blue at the mp, thus signaling the occurence of thiobenzophenone. The dithiolane 3 is designated "labile", because in toluene at 100°C it produces a blue color in contrast to 4. What is the second product of the dissociation?

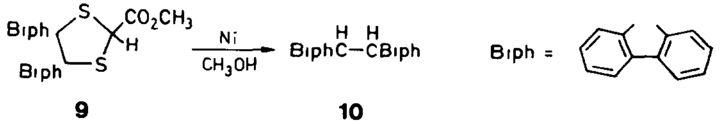


When the labile dithiolane 3 in toluene in the presence of 10 mol% thiobenzophenone was kept 10 h at 100°C, 34% of the stable dithiolane 4 and 66% methyl 3,3-diphenylacrylate (5) were formed. Dithiolane 4 was stable in toluene at 100°C. We propose that the thiocarbonyl ylide 2 occurs in the 1,3-dipolar cycloreversion of 3 as well as in the formation of 3 and 4 from the reactants. The cycloaddition of the 1,3-dipole 2 to thiobenzophenone proceeds in both conceivable directions. The third competing reaction of 2 is the electrocyclic ring closure to the thiirane 6 which loses sulphur to give 5 (vide infra). The ring closure of 2 corresponds to the known behavior of thiocarbonyl ylides; Kellogg et al.[5] demonstrated the conrotatory course of thiirane formation. Carbonyl ylides behave analogously.[6]



Our attempts to intercept the thiocarbonyl ylide 2 in the thermolysis of 3 with olefinic or acetylenic dipolarophiles (dimethyl maleate, N-phenylmaleimide, dimethyl acetylenedicarboxylate) failed. It turned out that thiocarbonyl compounds are the most active dipolarophiles towards thiocarbonyl ylides. When 3 was heated in $CDCl_3$ in the presence of 1 equiv. of thiofluorenone for 70 h at 80°C in the sealed tube, the NMR spectrum (2-methylnaphthalene as an internal standard) indicated 38% of the mixed dithiolane 7 which was isolated, mp 186 - 187°C. The NMR singlet at δ 3.83 is normal and corresponds to that of the labile isomer 3. The C,S hydrogenolysis by aluminium amalgam yielded 8, mp 220°C (aliphatic protons as AB spectrum at δ 4.11 and 4.77, J = 9 Hz), thus confirming 7.

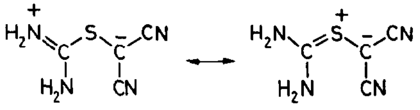
Schönberg, König, and Singer[7] reported in 1967 that each combination of diazoalkane and thiocarbonyl compound affords either thiirane or 1,3-dithiolane, but never both products side by side. The mechanistic elucidation of the dithiolane formation also allows to make the thiirane 6 the main product. In an inverse procedure, thiobenzophenone in $CHCl_3$ was added dropwise in 4 h to 15 equiv. of stirred methyl diazoacetate at 50°C. After removal of the excess diazoacetic ester by high-vacuum distillation, the remaining colorless oil (99%) gave correct analyses and NMR spectrum ($CDCl_3$, δ = 3.37, s, OCH_3; 4.12, s, 2-H) for the episulfide 6. Sulfur elimination from 6 required 12 h in CCl_4 at 60°C, and methyl 3,3-diphenylacrylate (5) was identified. The low stationary concentration of thiobenzophenone, the excess of diazoacetic ester, and the increased temperature favor the electrocyclic ring closure of 2.



Interestingly enough, diazoacetic ester reacted with thiofluorenone in CH_2Cl_2 at 20°C to yield 92% of a single 1,3-dithiolane (9), mp 222 - 224°C;

^1H-NMR ($CDCl_3$): δ 3.86 (s, OCH_3), 5.86 (s, 2-H). Hydrogenolysis with Raney nickel in boiling methanol furnished 9,9-bifluorenyl (10), mp 248 - 249°C, in 96 % yield. It is not clear why thiofluorenone produces only the 1 : 2 product which structurally corresponds to the labile isomer 3 from thiobenzophenone.

How is the thiocarbonyl ylide 2 formed from diazoacetic ester and thiobenzophenone? An initial 1,3-dipolar cycloaddition to give the thiadiazoline 1 and an ensuing 1,3-dipolar cycloreversion to 2 + N_2 is plausible. Not in this case, but in the analogous reactions of diazomethane [8] and diphenyldiazomethane [9] at low temperature the 1,3,4-thiadiazolines can be isolated.



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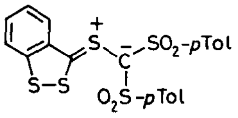

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Thiocarbonyl ylides do not constitute a hypothetical class of compounds. Push-pull substitution at the terminal carbon atoms can bring the energy level of the thiocarbonyl ylide below that of the corresponding thiirane; 11 [10] and 12 [11] are examples of stable crystalline thiocarbonyl ylides. Of course, the central sulfur atom in these stable representatives holds only a fraction of the positive charge.

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