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NEW THIOCARBONYL YLIDES FROM THIOBENZOPHENONE

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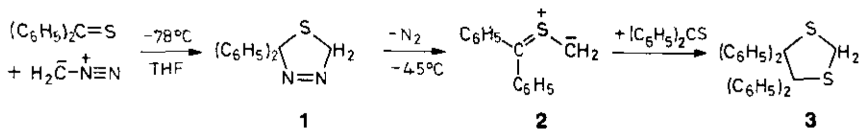
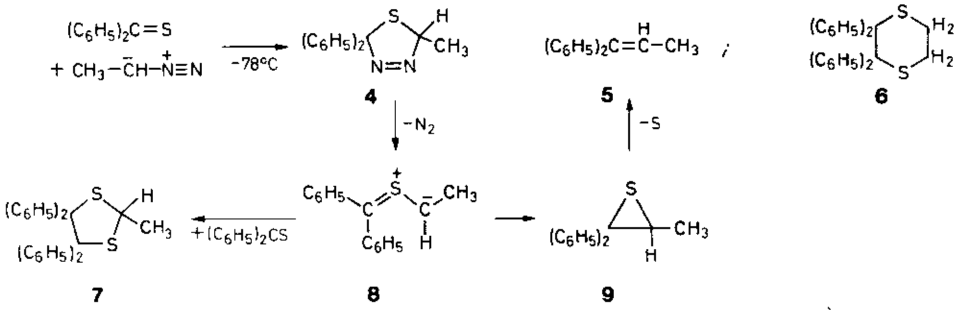
Abstract - Thiobenzophenone is converted to 1,3,4-thiadiazolines by reaction with diazoethane, phenyldiazomethane or diphenyldiazomethane at -78°C. Extrusion of nitrogen from the thiadiazolines furnishes thiocarbonyl ylides which, in turn, undergo electrocyclic ring closure to form thiiranes. Thiobenzophenone *S*-ethylide and *S*-benzylide can be intercepted by suitable dipolarophiles to provide 5-membered 1,3-cycloadducts.

Bergmann et al.[1] and Schönberg et al.[2] discovered in 1930/31 that the 1,3-dithiolane 3 is formed from thiobenzophenone with diazomethane at 0°C. A mechanism via the thiadiazoline 1 and thiobenzophenone *S*-methylide (2) was recently secured.[3] The thiadiazoline 1 is prepared at -78°C; it loses nitrogen at -45°C with a half-life of 55 min. Addition of an electrophilic dipolarophile at -78°C and generation of 2 at -45°C made a plethora of cycloadducts accessible.[4] With a second molecule of thiobenzophenone adopting the role of the dipolarophile, the mentioned 1,3-dithiolane 3 was produced at 96% yield.[3]



Analogously, Schönberg[2] obtained the 2:1-product 7 from thiobenzophenone and diazoethane. On adding 1 equiv. of diazoethane to thiobenzophenone in dichloromethane at -78°C, we observed decolorization within seconds. 5-Methyl-2,2-diphenyl-1,3,4-thiadiazoline (4) crystallized from a sufficiently concentrated solution; the colorless solid exploded on warming to room temperature. The addition direction is the "thiophilic" one, i.e., the carbanionic center of the diazoalkane is bonded to the thione sulfur.

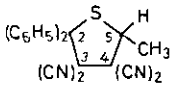
At -45°C in THF solution, the nitrogen evolution from 4 followed the first order with a half-life of 18 min, i.e., 3 times faster than for 1. The ^{1}H-nmr spectrum (CDCl$_3$) indicated 96% of 2-methyl-1,1-diphenylthiirane (9): δ 1.24 (d, J = 6.0 Hz, CH$_3$), 3.62 (q, CH). The thiirane slowly lost sulfur at 20°C (half-life $\sim$ 400 hr in CDCl$_3$) and furnished 1,1-diphenylpropene (5); the sulfur elimination did not obey a simple rate law.



In the exclusive electrocyclization, 8 → 9, the behavior of the intermediate thiocarbonyl ylide 8 differs from that of 2 which, under the same conditions (-45°C), afforded the 1,4-dithiane 6 as the head-head dimer.[3] Only at low concentration and/or higher temperature, 2 is partially converted to 1,1-diphenylthiirane.

At room temperature the product palette shows a remarkable dependence on the mode of addition. When 0.5 M diazoethane in ether was dropwise introduced into 0.7 M thiobenzophenone in THF, 86% of the dithiolane 7, the interception product of 8 with thiobenzophenone, was isolated, and ^{1}H-nmr showed 5% 9 and 5% 5 in the mother liquor. The reverse procedure, dropping of ethereal 0.35 M thiobenzophenone into the stirred 0.2 M solution of diazoethane in ether, procured 68% 9 + 5 and 28% dithiolane 7. Thus, electrocyclization of 8 takes precedence, and it is astounding that even at such a low stationary concentration of thiobenzophenone 28% of 8 are still intercepted by cycloaddition.

Not the thiirane 9, but its precursor 8 smoothly combines with suitable dipolarophiles in 1,3-dipolar cycloadditions. After titration of thiobenzophenone with diazo-



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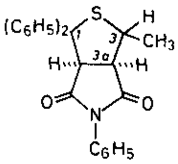

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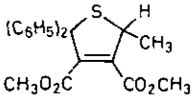

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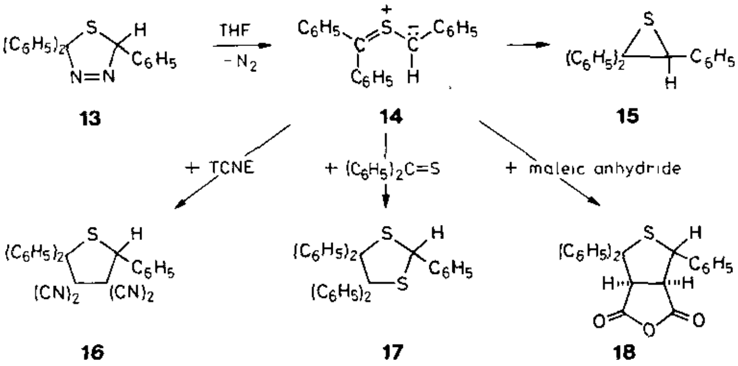
ethane in THF at -78°C, 1.3 equiv. of tetracyanoethylene (TCNE) was added; the reaction at -45°C provided 75% of cycloadduct 10 [7] according to ^1H-nmr analysis with standard; 66% 10, mp 159.5 - 161°C, was isolated. Whereas the ^1H-nmr spectrum would likewise be compatible with an 8-adduct to a cyano group of TCNE, the ^{13}C-nmr ($CDCl_3$) corroborated 10; in addition to the q(CH_3) at δ 18.5 and the d(C-5) at 47.3, three singlets appeared for the quaternary ring carbons at 53.3, 57.3, and 73.1.

The same technique allowed the trapping of the intermediary thiocarbonyl ylide by *N*-phenylmaleimide yielding 90% of 11, mp 207.5 - 209°C. Spectra and elementary analysis confirm 11. Only one of two conceivable diastereomers was found; $J_{3,3a}$ = 8.0 Hz is insufficient to assign the configuration. Analogously, thiobenzophenone *S*-ethylide (8) reacted in situ with dimethyl acetylenedicarboxylate at -45°C to give 12 in 59% yield, mp 115.5 - 117°C. The occurrence of 25% 9 + 5 demonstrated the lower dipolarophilic activity of the acetylenic ester. The methyl-free thiocarbonyl ylide 2 combines 170 times faster with *N*-phenylmaleimide than with acetylenedicarboxylic ester.[6]

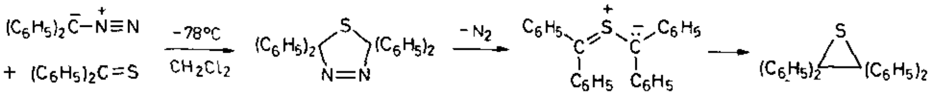
Schönberg, König, and Singer [7] stated that any combination of thione + diazoalkane gives rise either to a 1,3-dithiolane (2:1-product) or a thiirane (1:1 product), but never both side by side. This claim requires modification for the reactions of thiobenzophenone with diazoethane and phenyldiazomethane, respectively. According to Schönberg et al.,[7] the system thiobenzophenone + phenyldiazomethane furnished 80% 15 in ether at 20°C.[7] We observed that the reaction of thiobenzophenone with 1 equiv. of phenyldiazomethane in THF at -78°C is finished in 2-3 min, but evolution of N_2 from 13 started before the blue color of the thioketone had disappeared. At -100°C in ether, the cycloaddition giving 13 required 60 min, and slow elimination of N_2 became visible after 40 min. With a half-reaction time of 17 min at -81°C and ca. 0.5 min at -65°C, the loss of N_2 from 13 in THF is substantially faster than that from 1 and 4. The transition state of the 1,3-dipolar cycloreversion which affords the thiocarbonyl ylide 14 + N_2 appears to profit from the stabilization by the additional phenyl group.



If the unimolecular electrocyclization, 14 → 15, and the bimolecular cycloaddition to thiobenzophenone yielding 17 were to compete, one would expect the higher temperature coefficient for the first-order process. Only the formation of 17 should be burdened by a negative $\Delta S^{\ddagger}$ - usually -25 to -35 e.u. for 1,3-dipolar cycloadditions; for $\Delta G^{\ddagger}$ values to be of the same magnitude for both processes, the activation enthalpy must be *higher for the first-order than for the* second-order reaction. This reasoning turned out to be correct. The reaction of 3 equiv. of thiobenzophenone in THF *at -78°C* was complete after 3 hr; ^{1}H-nmr analysis (with *N*,*N*-dimethylaniline as weighed standard) indicated 70% 2,4,4,5,5-pentaphenyl-1,3-dithiolane (17) and 14% triphenylthiirane (15). *At 0°C*, however, 16% 17 and 67% 15 were obtained. Properties of 17: mp 134 - 136°C (blue melt suggests cycloreversion); δ(2-H) 5.15 ($CDCl_3$); δ-^{13}C($CDCl_3$): 51.4 (d, C-2), 79.8 (s, C-4 and C-5).

After reacting thiobenzophenone with phenyldiazomethane (1:1 ratio) in THF at -100°C for 70 min, we added 1.2 equiv. of TCNE and kept the mixture at -70°C for 2 h. Evaporation and treatment with methanol provided 66% of adduct 16; mp 189 - 191°C, δ(5-H) 5.33 ($CDCl_3$). The ^{1}H-nmr spectrum of the mother liquor registered 6% 16, 14% 17, and 4% 15. Analogously, the maleic anhydride adduct 18, mp *265 - 269°C (dec.)*, was attained in 61% yield along with 24% 17 and 7% 15. The competing electrocyclization, 14 → 15, limits the applicable dipolarophiles; an adduct of 14 and dimethyl acetylenedicarboxylate was not to be obtained. The k_{rel} values of ylide 2 are 33,000,000 for tetracyanoethylene, 1,150,000 for thiobenzophenone, 290,000 for maleic anhydride, and 340 for dimethyl acetylenedicarboxylate.[6]

In 1920, Staudinger and Siegwart [8] described the formation of tetraphenylthiirane



19 **20** **21**

(21) from thiobenzophenone and diphenyldiazomethane; the stability of the latter at 20°C suggested an induced loss of N_2. 1,3-Cycloadditions of diphenyldiazomethane are by 10^2 slower than those of diazomethane.[9] We observed decolorization of thiobenzophenone in the 1:1 reaction with diphenyldiazomethane in dichloromethane at -78°C within 24 h; the virtually insoluble, colorless crystals of the thiadiazoline 19 precipitated. A seemingly high solvent dependence of the decomposition rate at -45°C was unmasked to be due to the slow process of dissolving 19. In methanol the extrusion of N_2 is fast even at -78°C.

Astonishingly, 20 mg samples of crystalline 19 can be stored for a short time at room temperature. Correct C,H analyses were achieved; the N analysis requires longer handling, and 6.36% N resulted instead of 7.14%. The loss of N_2 from the crystals of 19 takes place in the solid state without melting. After 1 hr at 20°C, the nitrogen had disappeared and the mp 177 - 179°C of thiirane 21 was found. Larger samples of 19 blow up due to the exothermicity of the N_2 elimination.

All endeavors to intercept thiobenzophenone *S*-diphenylmethylide (20) in the cycloreversion of 19 failed. Neither methanol in the presence of trifluoroacetic acid[4] nor thiobenzophenone or maleic anhydride combined with the tetraphenyl-substituted thiocarbonyl ylide 20. Electrocyclization giving 21 was the only reaction observed.

Another limitation in the synthetic application of cycloadditions of thiocarbonyl ylides is encountered in the system thiobenzophenone + methyl diazoacetate.[10] The formation of the thiadiazoline - even at low temperature - is not significantly faster than its cycloreversion yielding N_2 + thiobenzophenone *S*-methoxycarbonylmethylide. The separation of the formation and decomposition of the thiadiazoline in time and temperature is mandatory for the interaction with the electrophilic dipolarophile. Otherwise the aliphatic diazo compound would combine with the olefinic or acetylenic dipolarophile.

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