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REACTION OF BIS(α-BROMOALKYL) SULFIDE WITH DIIRON NONACARBONYL

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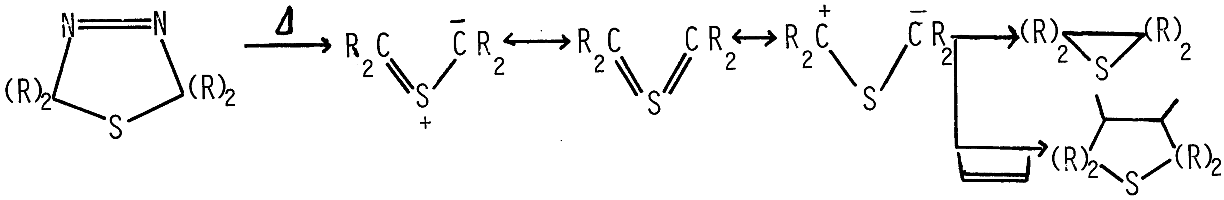
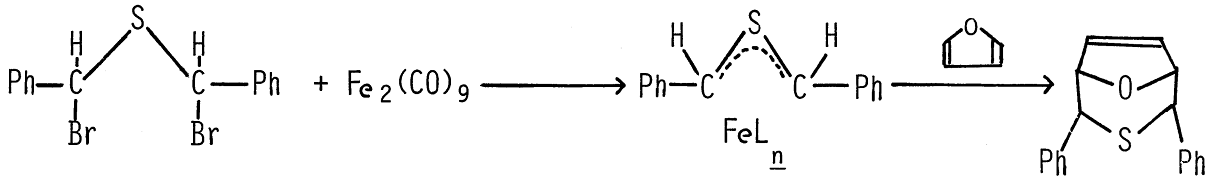
An iron-stabilized thiocarbonyl ylide was generated by the reaction of bis(α-bromobenzyl) sulfide with diiron nonacarbonyl. This species was not a typical 1,3-dipole, but underwent a [2+4] type addition reaction with furan.

Recently S-heterocumulenes have attracted much attention for their unique reactivity. Compounds classified as S-heterocumulenes include azasulfines, sulfur diimides, and sulfines.1) "Thiocarbonyl ylide" generated by the pyrolysis of 1,3,4-thiadiazoline is also a species which has a structure analogous to S-heterocumulenes. This intermediate combines as 1,3-dipole with olefinic dipolarophile.2)



The authors wish to report here that an iron-stabilized thiocarbonyl ylide can be generated by the reaction of bis(α-bromobenzyl) sulfide (1) with diiron nonacarbonyl, and that this species undergoes [2+4] cycloaddition reaction with furan.



(1) (2) (3)

On addition of diiron nonacarbonyl to the benzene solution of 1, the color of the solution turned to red, and the presence of the iron-stabilized thiocarbonyl ylide (2) could be revealed by observing this species in a pmr spectrum. The pmr absorptions of the methine protons3) shifted to lower field, overlapping with that of aromatic protons [Fig. 1].

This complex was stable at low temperature (0 °C) for at least several hours. The color rapidly faded away on addition of furan with concomitant precipitation of iron salts, and [2+4] adduct 3 was formed immediately. This is the first example that the species of type 2 was detected.

When 1 was added to the mixture of diiron nonacarbonyl and furan, the same [2+4] adduct was isolated. In a typical experiment, 1 (0.8 mmol) in dry benzene (5 ml) was added to the benzene solution (15 ml) of diiron nonacarbonyl (1 mmol) and furan (10 mmol) at 0 °C and the mixture was stirred for 30 min. After usual work-up, a crude product was purified by column chromatography (silica gel, benzene) to give the pure adduct in 85% yield. Spectral data were in good agreement with structure of 3.[4)]

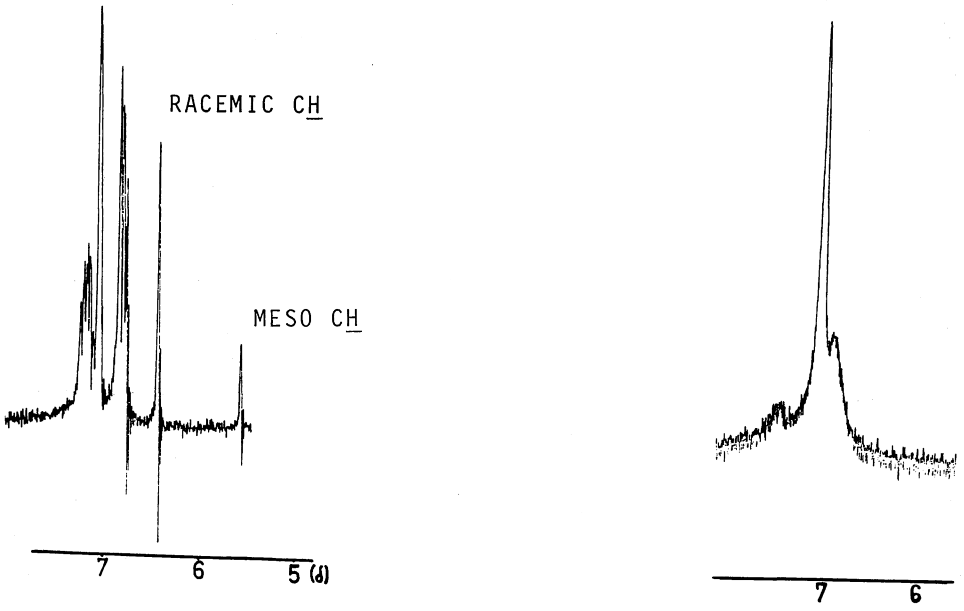
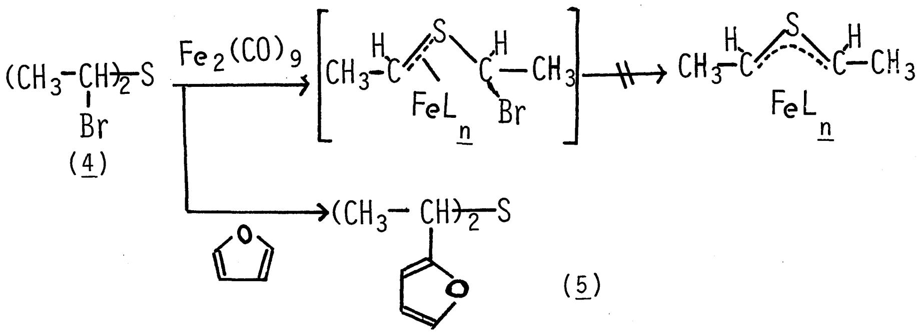


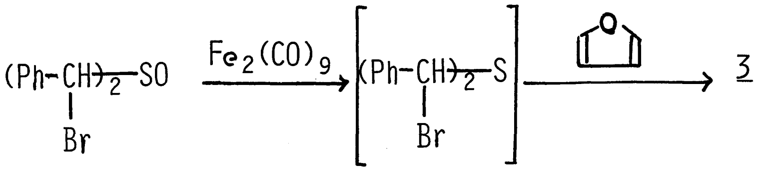
Fig. 1 Change of pmr spectrum on the formation of the iron complex (2)
(LEFT) 1 in C_6D_6 (RIGHT) 1 with diiron nonacarbonyl in C_6D_6

Dipolarophile, such as dimethyl acetylenedicarboxylate, gave no reaction product with 2. Heating the benzene solution of 2 at 80 °C produced no 2,3-diphenyl episulfide.[5)] These observations suggest that the iron-stabilized complex formed in this reaction hardly behaves as a 1,3-dipole, and therefore, is quite different from thiocarbonyl ylide generated by the pyrolysis of 1,3,4-thiadiazoline.

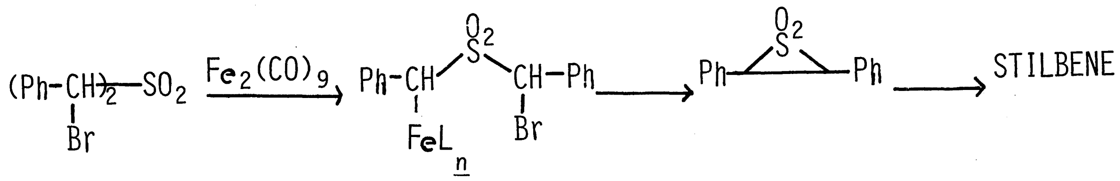
On the other hand, under the same conditions, bis(α-bromoethyl) sulfide (4) gave no cycloaddition product with furan. The Friedel-Crafts type substitution reaction took place instead.[6)] Such a behavior can be explained in terms of a lack of the stabilization by the benzene moiety, thus making the formation of the iron-stabilized complex less feasible.[7)]



By treating bis(α-bromobenzyl) sulfoxide under the same reaction condition, 3 was isolated as the product. Obviously bis(α-bromobenzyl) sulfide should be the precursor of the adduct 3. Deoxygenation by diiron nonacarbonyl prior to the debromination is plausible.[8)]



Reaction with bis(α-bromobenzyl) sulfone gave stilbene as the only product. One of the plausible explanations is as follows : two-electron transfer from diiron nonacarbonyl results in a carbanion formation, which in turn undergoes an intramolecular displacement reaction to produce episulfone. The expulsion of sulfur dioxide gives stilbene. This process is essentially the analogue of the Ramberg-Bäcklund reaction.



These results suggest the participation of the sulfur atom in stabilizing the ligand in the iron complex. This stabilizing effect is lost in sulfones. The formation of a stable two-electron system seems to be the major driving force of [2+4] type addition.

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References and Notes

1) G. Kresze and W. Wucherpfennig, Angew. Chem., 79, 109 (1967).

2) J. Buter, S. Wassenaar, and R. M. Kellogg, J. Org. Chem., 37, 4045 (1972).

3) Starting material 1 was obtained as a mixture of the meso and the racemic form, and was used without the separation into pure diastereomers. A pmr spectrum of 1, as the mixture of the diastereomers, shows different absorptions for methine proton corresponding to the meso and the racemic isomer. Tentative assignment was made according to Bordwell.[3a)]
Line-broadening and the slight decrease in the intensity were observed in the pmr spectrum of 2, that may suggest the presence of paramagnetic iron in the system.

3a) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, J. Am. Chem. Soc., 90, 5298 (1968).

4) Yellow liquid, pmr (CCl_4) : δ 7.10 (10H, aromatic), 6.16 (d, 2H, olefinic), 5.82 (d, 2H, bridgehead), and 5.70, 5.30 (d, 2H).

5) 2,3-Diphenyl episulfide did not react with furan in the presence of diiron nonacarbonyl.

6) Yield 50%, Yellow liquid, pmr (CCl_4) : δ 7.24, 6.16, 6.04 (6H, furan), 3.92 (q, 2H, methine), and 1.52 (d, 6H, methyl).

7) 5 might be produced by the action of iron salts($FeBr_3$, etc.), which could be formed by the decomposition of iron complex. Blank experiment showed that with no Friedel-Crafts catalysts added the formation of 5 was very sluggish.

8) W. Storohmeier, J. F. Guttenberger, and G. Popp, Chem. Ber., 98, 2248 (1965).

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