Tetrahedron Letters No. 21, pp. 1781-1784, 1971. Pergamon Press. Printed in Great Britain.

THE REACTION OF SULFONIUM YLIDES WITH CARBON DISULFIDE

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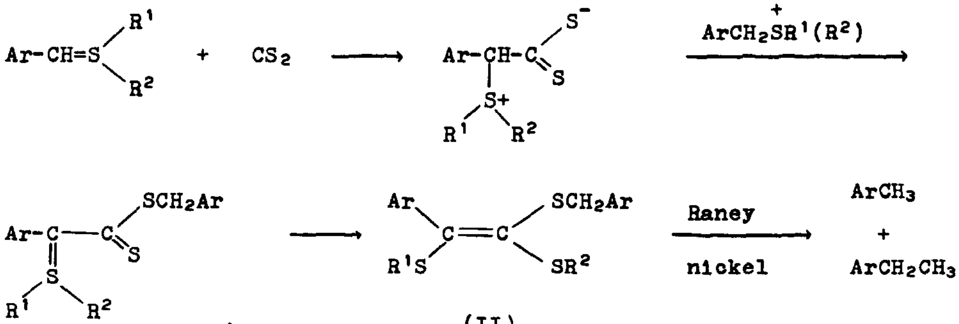
(Received in Japan 5 April 1971; received in UK for publication 16 April 1971)

Recent publications concerned with several different resonance-stabilized sulfonium ylides have covered their preparation and spectral properties and synthetic utility but relatively few of thiocarbonyl-stabilized ylides have been reported$^{1)}$. We wish to report here a synthesis of some dithioformate-stabilized sulfonium ylides and their facile intramolecular nucleophilic substitution and also a new one-step synthesis of a relatively unfamiliar class of compounds, 1,3-dithietanes.

Treatment, at room temperature, of aqueous solution of dimethylbenzylsulfonium chloride with carbon disulfide and powdered sodium hydroxide gave rise to exothermic reaction which afforded new ylide Ia which crystallized from dimethylformamide-ethanol as a colourless microcrystals, mp. 121-122°C, in 82% yield, besides a small amount of dibenzyltrithiocarbonate.
The assignment of structure of the product Ia was made on the basis of elemental analysis($C_{17}H_{18}S_3$); IR; NMR(τ, in $CDCl_3$), 2.8(m,10H), 5.45(s,2H), 7.51(s,6H) and the following series of reactions as shown in Scheme 1.

Scheme 1



(I) a, Ar=Ph, $R^1=R^2=CH_3$

(II)

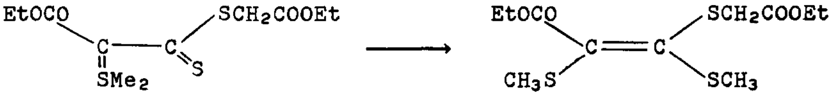
Analogous results were obtained starting from benzylsulfonium chlorides bearing substituents in phenyl ring.

The crystalline ylide Ia then rearranged completely and quantitatively to styrene derivative IIa, mp. 33.5-34°C, on standing at room temperature for several days, as did also a solution of chloroform or methyliodide on standing at ambient temperature for a few hours.

The structure of IIa was demonstrated by elemental analysis; IR; NMR, 2.8-3.3 (m,10H), 6.24(s,2H), 7.55(s,3H), 8.25(s,3H) and desulfurization with Raney nickel to toluene and ethylbenzene quantitatively.

The values of SCH$_3$ in the NMR of IIa suggest that the product is cis isomer[2]. Although the generality of this intramolecular substitution reaction has not been thoroughly investigated, experiments with Ib(Ar=p-Cl-C$_6$H$_4$, R^1=R^2=CH$_3$, mp. 139-141°C, 89% yield) have led to IIb(mp. 84-86°C, 63% yield), with Ic(Ar=Ph, R^1= CH$_3$, R^2=C$_2$H$_5$, mp. 130-132°C, 45% yield) have led to a mixture of CH$_3$-rearranged and C$_2$H$_5$-rearranged product and with Id(Ar=Ph, R^1,R^2= -CH$_2$CH$_2$CH$_2$CH$_2$-, mp. 140-145°C, 61% yield) have led to a gummy mixture.

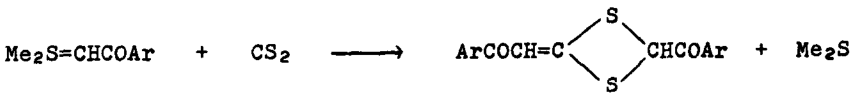
Ethyl (dimethylsulfuranylidene)acetate reacted vigorously with carbon disulfide at -20°C without solvent to yield a colourless crystalline product III, mp. 85.5-86°C, in 75% yield. Proof of structure stemmed from elemental analysis; IR, νC=O, 1645 and 1740cm^{-1}; NMR, 5.71(q,2H), 5.83(q,2H), 5.93(s,2H), 7.03(s,6H), 8.56(t,3H), 8.66(t,3H) and rearrangement to cis and trans mixture of IV, bp. 200-205°C/10.



(III) (IV)

Reaction of (dimethylsulfuranylidene)acetophenone with carbon disulfide in aprotic solvents did not take the same course as benzylides.

Reaction of Va(Ar=Ph) with carbon disulfide in chloroform at room temperature for 20hr gave a 78% yield of yellow 1,3-dithietane VIa, mp. 145-147°C, whose structure was demonstrated by elemental analysis; IR, νC=O, 1610 and 1685cm^{-1}; NMR, 2.0-2.8(m,10H), 2.99(s,1H), 3.94(s,1H) and UV(λmax, logε, in ethanol), 258nm(4.50) and 342nm(4.40).



(V)

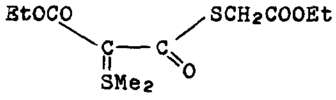
(VI)

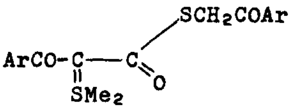
Desulfurization of VIa with zinc-acetic acid gave acetophenone(45%) and propiophenone(15%).
Treatment of ethanol suspension of VIa with equiv. amount of aqueous sodium hydroxide have led to red clear solution(λmax, 518nm, logε, 4.50).
Decomposition of VIa in alkaline ethanol was relatively slow at room temperature, while refluxing the red solution gave benzoic acid and intractable products.

When Va was treated with carbon disulfide in ethanol at room temperature for a day and subsequent crystallization of the precipitate(contaminated with VIa) from dimethylformamide gave yellow product, mp.216-218°C(lit.3) mp.206-207°C). This was found to be insoluble in alkaline ethanol and to analyse correctly for 3,5-diphenacylidene-1,2,4-trithiole. This assignment as a trithiole was confirmed by IR4), NMR, UV4) and elemental analysis.
Desulfurization of 3,5-di-p-methylphenacylidene-1,2,4-trithiole(mp. 219-222°C, 15% yield) with zinc-acetic acid gave p-methylpropiophenone in 76% yield.

Although the reaction of ammonium1) or phosphonium5) ylides with carbon disulfide was known, no analogous products reported here were isolated. Substitution or ring closure to 1,3-dithietanes might be favoured in our reactions owing to the greater ability of R$_2$S as leaving group compared with R$_3$N or R$_3$P.

Preliminary experiments with carbonyl sulfide have also led to stable ylides as shown below.





Further studies of these reactions are in progress and more complete details will be reported later.

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