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UNUSUAL EXTRUSION OF THE ELEMENTS OF CARBON MONOXIDE FROM THIOXANTHEN-9-ONES

O.F. Bennett* and J. Collins
Department of Chemistry, Boston College,
Chestnut Hill, Mass. 02167

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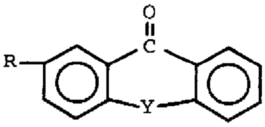
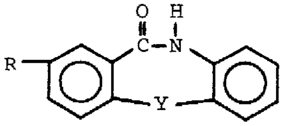
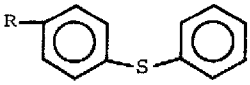
It is known that in the case of thioxanthen-9-one 10,10-dioxides(I) the carbonyl bridge, unlike that of benzophenones, does not undergo Haller-Bauer Cleavage with amide ion.[1] Instead a unique insertion of the NH moiety occurs upon treatment of I with amide ion leading to dibenzo[b,f][1,4]thiazepin-11(10H)-one 5,5-dioxides(II).[2] Since certain derivatives of dibenzo[b,f][1,4]thiazepin-9-one(IIa) are potentially useful therapeutic agents which often require lengthy preparative procedures, this recent discovery of the conversion of I to II prompted us to extend our investigation of the action of amide ion to Ia with the expectation that, in similar fashion to I, the corresponding dibenzo[b,f][1,4]thiazepin-9-one, IIa, would be formed.



I, $Y=SO_2$, R=H
Ia, Y=S, R=H
Ib, Y=S, $R=CH_3$
Ic, Y=S, $R=OCH_3$



II, $Y=SO_2$, R=H
IIa, Y=S, R=H



III, R=H
IIIa, $R=CH_3$
IIIb, $R=OCH_3$

Surprisingly, the course of reaction of amide ion with Ia has been found to be completely different from what has been observed with both I and the benzophenones. Treatment of Ia with $NaNH_2$ in toluene at reflux temperature for 18 hours led to the extrusion of the elements of carbon monoxide and afforded diphenyl sulfide(III) in 50-60% yield. Similar behavior was observed with 2-methylthioxanthen-9-one (Ib) and 2-methoxythioxanthen-9-one (Ic) leading to 4-methyldiphenyl sulfide (IIIa) and 4-methoxydiphenyl sulfide (IIIb),[3] respectively. Interestingly, when Ia was treated with $NaNH_2$ in toluene at lower temperature a trace amount of IIa was isolated, but the major product was III. This observation suggests that the formation of the diaryl sulfides may involve intermediates such as IIa.

This unusual reaction of thioxanthen-9-ones yielding diaryl sulfides does not occur in liquid ammonia nor in the absence of amide ion. It appears at this time that the loss of the elements of carbon monoxide from the heterocyclic ring involves the formation of urea since aqueous extracts of the reaction solution give a positive test with urease.[4]

Investigation of additional examples of this novel reaction and a study of its reaction pathway are in progress.

We are indebted to R. Coogan and D. Harris for the preparation of authentic samples of IIIa and IIIb.

*Author to whom correspondence should be addressed.

References

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(2) O.F. Bennett, J. Johnson and S. Galletto, J. Heterocyclic Chem., In Press.

(3) The structures of compounds III, IIIa, and IIIb were confirmed by comparison of their ir and nmr spectra with the corresponding spectra of authentic samples.

(4) F. Feigl, Spot Tests in Organic Analysis, Elsevier Publ. Co., New York, N.Y., 1966, p. 530.