

REACTION OF GROUP IV ORGANOMETALLIC KETIMINES WITH NITROSYL CHLORIDE.

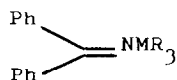
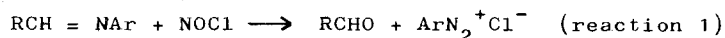
COMMENT ON THE THERMOLYSIS OF THE PRODUCT N-NITROSOKETIMINES

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The known¹ conversion of aldimines to diazonium salts by nitrosyl chloride² (reaction 1) and the availability³ of related group IV organometallic derivatives (e.g. I a-e) prompted an investigation of a possible synthetic entry into the hitherto unknown diazonium ions of type $R_3MN_2^+$ or $Ar_3MN_2^+$ (M = Si, Sn, Pb).



I

a; M = Si; R = Me

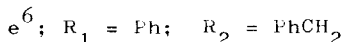
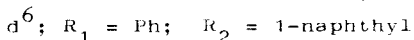
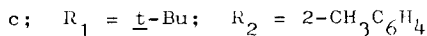
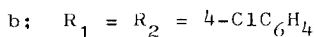
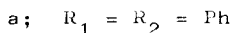
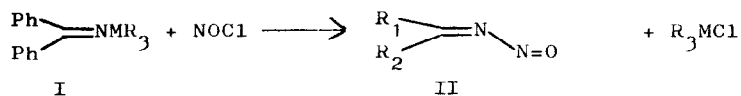
b; M = Si; R = Ph

c; M = Sn; R = Me

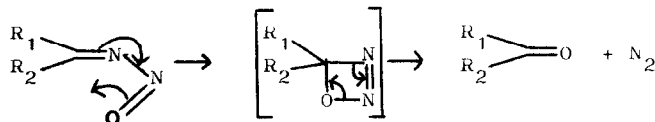
d; M = Sn; R = Ph

e⁴; M = Pb; R = Et

Addition of 10% solutions of NOCl in Et₂O to 25% solutions of I in Et₂O at room temperature immediately produces deep violet solutions with λ_{\max} 516 nm; on exposure to air they slowly decolourise (e.g. for Ia) to produce a mixture of benzophenone (45%), benzophenoneimine hydrochloride (20%) and trimethylchlorosilane. Careful work up and unambiguous synthesis⁵ of the violet product indicates that the initial reaction is an almost quantitative cleavage of the metal-nitrogen bond to give the N-nitrosoketimine (IIa);

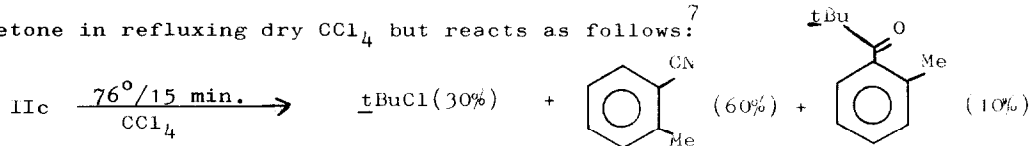


Recently Thoman and Humsberger³ reported the first definitive investigation of N-nitrosoketimines which were prepared by reaction of nitrosyl chloride with the parent imine. They found that sterically unhindered compounds (e.g. IIa and IIb) decomposed under anhydrous conditions at room temperature or below to give the parent ketone and nitrogen; kinetic data suggested a cyclic mechanism:

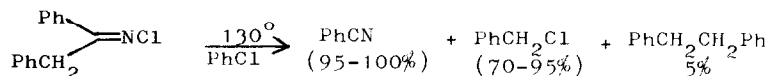


The hindered ketone (IIc), however, was reported to be stable at room temperature for several days and is decomposed in carbon tetrachloride under reflux to give the ketone.

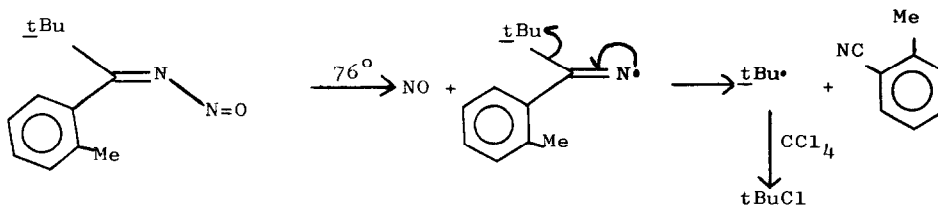
The present work indicates that the thermal behaviour of (II, a-e) is as reported; in our hands, however, IIc does not decompose entirely to the ketone in refluxing dry CCl₄ but reacts as follows:⁷



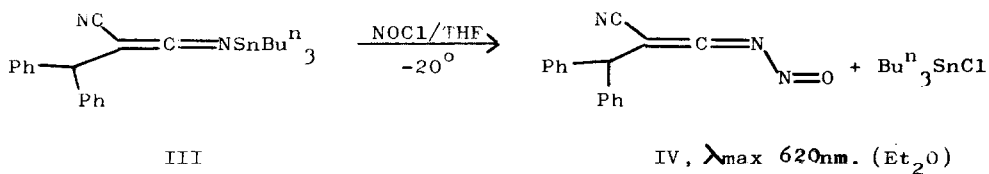
The reaction is closely related to the recently noted⁸ thermolysis of N-chloroketimines, e.g.:



Apparently for the hindered IIc decomposition by the cyclic process is minimised; presumably a free radical decomposition mode predominates:



The cleavage of group IV metal-nitrogen bonds with nitrosyl chloride may be general (e.g. $\text{Ph}_3\text{SiNEt}_2$ and Ph_3SnEt_2 give N-nitrosodiethylamine) and may prove useful for the synthesis of unsaturated N-nitrosimines where the parent imine is unstable. Preliminary studies indicate that (III)⁹ produces a new class of compound (IV, an N-nitrosoketenimine) the chemistry of which is presently under investigation.



REFERENCES

1. J. Turcan, Bull.Soc.Chim. 2,627,(1935)
2. In our hands organic ketimines also react with NOCl to give the appropriate diazonium compound.
3. Lui-Heung Chan and E.G. Rochow, J.Organometal.Chem. 9,231,(1967)
4. Ie is a new compound, b.p. 138°/0.5mm; I.R. C=N str. 1610 cm⁻¹; λ_{max} 232 nm. prepared as described in ref. 3.
5. C.J. Thoman and I.M. Hunsberger, J.Org.Chem.,33,2852,(1968)
6. IIId and IIe were prepared by the method described in ref. 5.
7. Yields are estimated from g.l.c. analysis: the conversion of IIc to products is almost quantitative.
8. M.L. Poutsma and P.A. Ibarbia, J.Org.Chem.,34,2848,(1969)
9. E. Müller, W.P. Neumann and R. Sommer, Ann., 718,1,(1968)