Tetrahedron Letters, Vol.22, No.30, pp 2909 - 2912, 1981
Printed in Great Britain

0040-4039/81/302909-04$02

THE REACTION OF DIAZOMETHANE WITH CHLOROAZIRINES :
A NEW ROUTE TO 1,2,3-TRIAZINES

T.C. Gallagher and R.C. Storr*

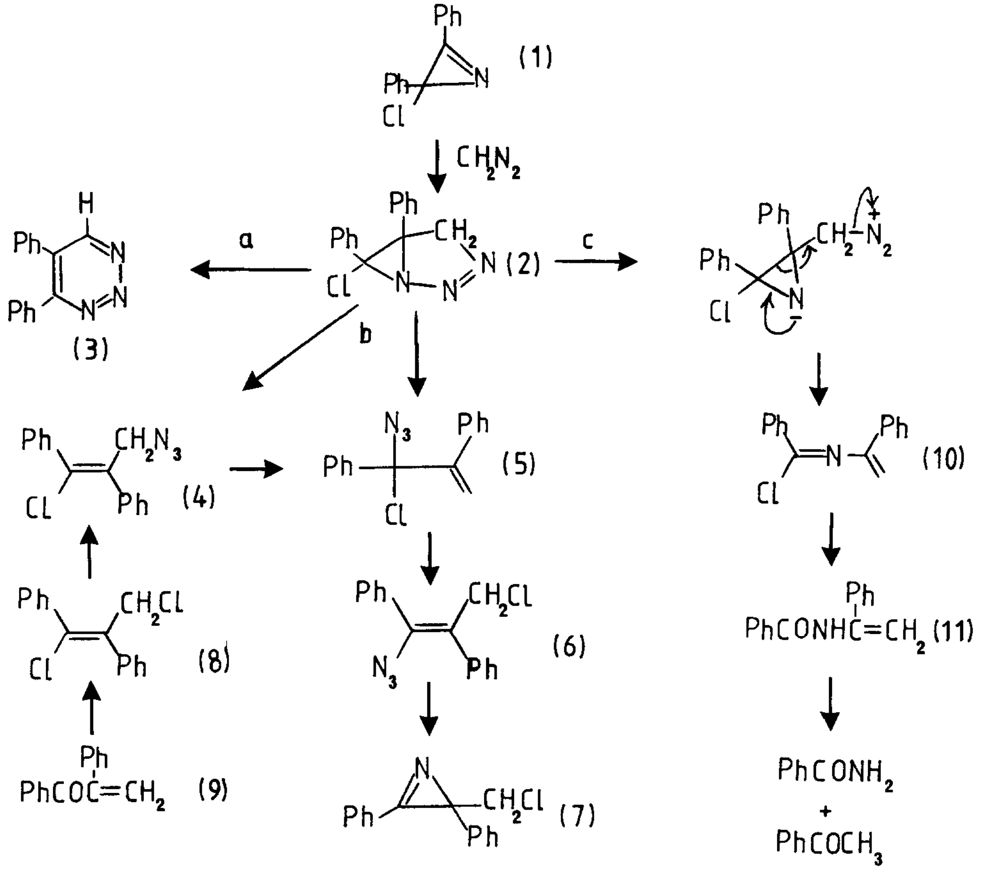
Robert Robinson Laboratories, Liverpool University, P.O. Box 147, Liverpool L69 3BX

Summary : The reaction of diazomethane with chloroazirines gives 1,2,3-triazines and chloromethylazirines.

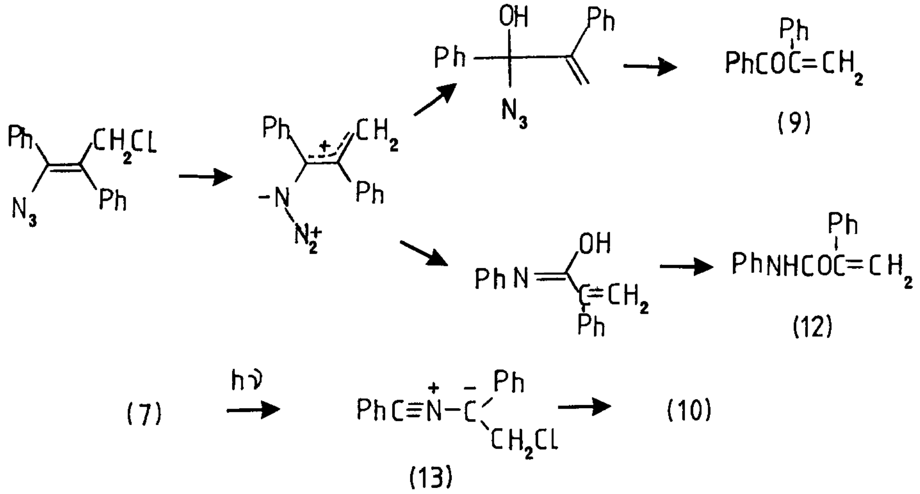
The reaction of cyclopropenyl halides with diazocompounds gives pyridazines probably by cycloaddition followed by ring expansion and loss of hydrogen chloride.[1] As part of our investigation of azacyclopropenium systems we have therefore studied the reaction of diazocompounds with chloroazirines in anticipation that this might provide a new route to either 1,2,3- or 1,2,4-triazines.

Treatment of an ethereal solution of diphenylchloroazirine[2] (1) with an excess of diazomethane does indeed give the 1,2,3-triazine (3) although only in moderate yield. The reaction is complex but all products can be accounted for satisfactorily in terms of initial formation of the unstable cycloadduct (2) which breaks down by three different modes (Scheme). The simplest product mixture is obtained by removal of the excess of diazomethane (after 3h at 0°C) and heating of the residue in toluene. Chromatographic work-up on silica gel then gives triazine[3] (3 , 10-20%), chloromethylazirine (7 ; 45-55%) together with acetophenone and benzamide.[4] Triazine (3) arises by loss of HCl and ring cleavage in (2) (mode a); attempts to improve the yield of triazine by performing the reaction in the presence of a number of bases was, however, unsuccessful.

The chloromethylazirine[5] (7) arises by mode b. 1,3-Dipolar cycloreversion in (2), for which there is precedent with other azirine-diazomethane adducts[6] would give the allylic azides (4)[7] and (5). A simple chloride shift (via an ion-pair) in (5) would give the vinyl azide (6), the obvious precursor to (7). Both azides (4) and (6) can be detected by singlet absorptions, δ 4.40 and 4.13ppm respectively, in the 'Hmr spectrum ($CDCl_3$) of the reaction mixture after removal of diazomethane and prior to heating in toluene; on heating, signals due to both (4) and (6) disappear with concomitant growth of the AB quartet due to (7). Chromatographic work-up prior to heating allows the isolation of (4)[8] but not (6); under these conditions the α,β-unsaturated



Scheme



ketone (9)[9] and the amide (12) resulting from decomposition and hydrolysis of (6) are isolated. The azide (4) can be independently prepared from the dichloride (8)[10] obtained by reaction of ketone (9) with phosphorus pentachloride. The more reactive allylic chlorine in (8) is readily replaced by azide ion. On heating in toluene, (4) is converted to chloromethylazirine (7 ; 80%) presumably via the well-known allyl azide isomerisation[11] to give (5) and hence (6) and ultimately (7). This last sequence constitutes a very simple route to this novel type of functionalised azirine from α,β-unsaturated carbonyl compounds.

The final mode (c) of breakdown of adduct (2) accounts for acetophenone and benzamide. The key intermediate[12] (10) can be obtained alternatively by photolysis of (7) via a 1,4-chlorine shift in the nitrile ylide (13)[13] and the two singlets due to the methylene group of (10) can be detected in the 'Hmr spectrum of the reaction mixture both before and after heating in toluene. Chromatography causes hydrolysis of (10) to benzamide and acetophenone.

Thermal rearrangement of cyclopropenyl azides[14] and oxidation of N-aminopyrazoles[15] are the only reported routes to unfused 1,2,3-triazines. Unfortunately this alternative method appears to be of limited generality. Thus while a similar sequence of reactions is observed with diazomethane and chlorodi-p-tolylazirine, diazoethane gave no triazine with (1), modes (b) and (c) being followed exclusively. No reaction was observed between azirine (1) and ethyl diazoacetate or phenyldiazomethane.

References and Notes

1. H.M. Cohen, J.Het.Chem., 1967, 4, 130 ; Y. Yoshida, Jpn.Kakai Tokkyo Koho, 78,103,482 Chem.Abstr., 1979, 90, 87498.
2. Prepared from α-chlorostilbene by treatment with chlorine azide, base and thermolysis of the resulting chlorovinyl azide.
3. H. Neunhoeffer, H.D. Votter and H. Ohl, Chem.Ber., 1972, 105, 3695. In our hands this triazine prepared by either route had m.p. 165-166°C from benzene-hexane.
4. Yields are variable due to losses on work-up and chromatography.
5. M.p. 68-69°C., νmax 1746 cm^{-1}, δ $CDCl_3$ 3.85 (1H, d, J=12Hz), 4.54 (1H,d, J=12Hz), 7.20-7.38 (8H, m) and 7.96 (2H, dd, J=7.2Hz).
6. J. Bowie, B. Nussey and A.D. Ward, Aust.J.Chem., 1973, 26, 2547; A.L. Logothetis, J.Org.Chem., 1964, 29, 3049; V. Nair, ibid., 1968, 33, p.2121.
7. The E-configuration is assumed for compounds (4), (6) and (8).

8. Colourless needles, m.p. 46-48^{0}C from hexane, ν max 2100, 2070 (N$_3$), 1618 cm^{-1}.
9. Identified by comparison with an authentic sample, H. Fiesselmann and J. Ribka, Chem.Ber., 1956, 89, 27.
10. Colourless rods, m.p.77-78^{0}C from hexane, obtained from (9) and phosphorus pentachloride heated under reflux in dichloromethane for 48h. Chromatography on silica gel was necessary to effect separation from a small amount of 2,3-dichloro-2-phenylpropiophenone also formed.
11. A. Gagneux, S. Winstein and W.G. Young, J.Amer.Chem.Soc., 1960, 82, 5956; C.A. van der Werf and V.L. Heasley, J.Org.Chem., 1966, 31, 3534.
12. Irradiation, 254 nm., of (7) in dry benzene gave a moisture sensitive yellow oil, CDCl$_3$ 4.69 (1H,s),5.24(1H,s) and 7.20-8.18(10H, complex m); ν max 1658, 1610, 1595 and 1580 cm^{-1}.
13. A. Padwa, P.H.J. Carlsen and A. Tremper, J.Amer.Chem.Soc.,1978, 100, 4481.
14. H. Neunhoeffer, "Chemistry of Heterocyclic Compounds", Vol 33, Wiley 1978.
15. A. Ohsawa, H. Arai, H. Ohnishi and H. Igeta, J.C.S. Chem.Comm., 1980, 1182.

(Received in UK 27 April 1981)