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# THE CHEMISTRY OF 2,2-DICHLORO-3-p-NITROPHENYL-1-PHENYL AZIRIDINE, **6**. PREPARATION OF A STABLE AZIRIDINYL C- ANION, **3**.

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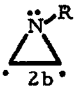
Although the chemistry of $\Delta^1$- azirine **1** is well documented[1], the $\Delta^2$- azirine system **2**, is as yet unknown. The failure of attempted syntheses of structures of type **2**[2] has been rationalized by noting that the $\Delta^2$- azirine has antiaromatic character[3]. That is, the $2_pz$ system of two contains $4\pi$ electrons.

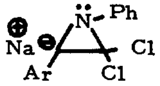
**1**

**2a**

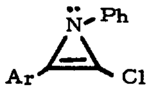


**2b**

The following account presents evidence for the sodium salt of 2,2-dichloro-3-p-nitrophenyl-1-phenylaziridine, **3**, a possible precursor of **4**, a $\Delta^2$- azirine[4].



**3**

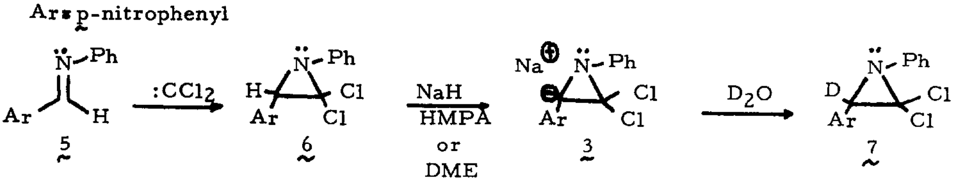


**4**

Ar = p-nitrophenyl

Treatment of imine **5**[5] with ethyl trichloroacetate afforded the aziridine **6** in 70% yield[6]. When **6** was allowed to react with sodium hydride in aprotic hexamethylphosphoramide (HMPA) or dimethoxyethane (DME), the bright purple anion **3** resulted. Quenching of **3** in HMPA with $D_2O$ afforded **7**, mp 101-101.5°, mass spectrum m/e 309.0180 (parent ion), calculated for $C_{14}H_9N_2O_2DCl_2$: 309.0192, nmr: no ring proton, in 80% yield with no trace of **6**[7], thereby verifying the formation of **3**, the first stable aziridinyl C- anion. These reactions are summarized below in Scheme I:

Scheme I

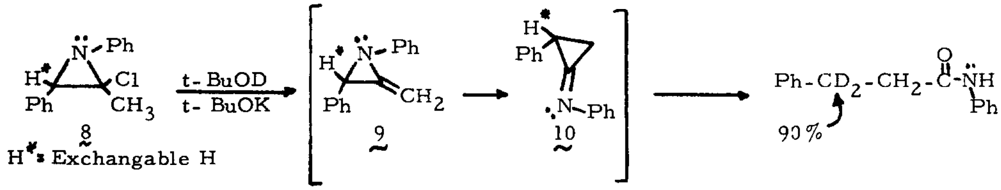


Some indication of the stability of 3 was noted from the fact that after three days at -10° in HMPA, the anion gave 66% of 7 upon $D_2O$ quenching. Further, quenching of 3 (formed in DME) after five days at -78° again gave only 7 [7].

The combined electron withdrawing power of two chlorines, the ring nitrogen, and the p-nitrophenyl group serves to make the ring proton of 6 acidic. Also, the p-nitrophenyl substituent stabilizes the conjugate base 3 by providing for electron release into the aryl ring.

These results are compatable with those of Deyrup on the analogous system 8 [2b]. In 8, the presence of the methyl group affords an alternate mode of reaction not available to 6 (Scheme II). The deuterium studies on 3 also give a plausible rational for the deuteration results obtained from 8, in which the aziridine ring proton was found to be 90% exchanged. The present work indicates that 8 and 9, as well as 10 might be the exchanging species.

Scheme II



A close analogy for proton removal in 6 is found in the reaction of oxaziridine 11 with strong base to afford 12 [8]. This reaction is shown in Scheme III.

Scheme III

11 12

Ar= *p*-nitrophenyl

Treatment of 3 at -78° in DME with excess silver perchlorate resulted in the formation of silver chloride and a paramagnetic green solution. Preliminary work indicates that the paramagnetic species is not the triplet predicted for 4, but rather a different species, possibly resulting from a living polymer derived from 4. We are attempting at this time to define the structure of this polymer in order to obtain evidence for the intermediacy of 4. Finally, since no effective method exists for alkylating aziridine rings via aziridinyl C-anions, the nucleophilic reactions of 3 and its analogs are being studied to this end.

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