

NUCLEOPHILIC SUBSTITUTION REACTIONS OF I-BROMO-I-ALKOXYMETHYLALLENES

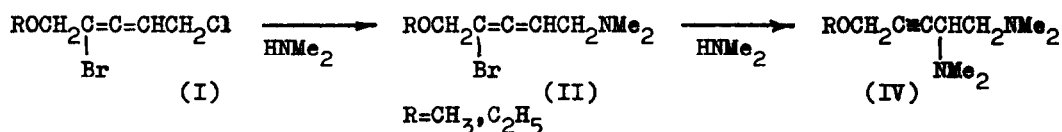
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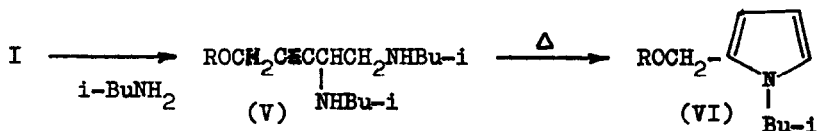
As part of our interest which is directed towards the synthetic utility of bromoallene systems ^I, the reaction of certain new alkoxyethyl-substituted bromoallene derivatives (I-III) ^{2,3} with a variety of amines was investigated.

We have found that (I) or (II) react with excess dimethylamine at 40° for 12-15 hr. This reaction involves the displacement of bromine by the nucleophile with concomitant allene-acetylenic rearrangement resulting in acetylenic diamino derivatives (IV) with 35-45% yields.



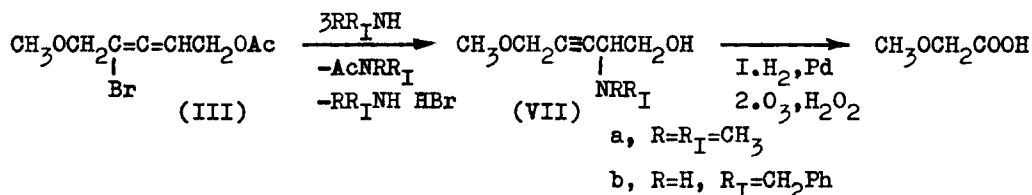
The structure of the obtained diamines (IV) follows from the analytical and spectral data. Their ir-spectra reveal weak characteristic acetylenic bands at 2210 cm⁻¹. The nmr spectrum of compound (IV, R=CH₃) shows a well resolved pattern at δ 2.37 (2H, d, J=7Hz, CH₂N), 3.36 (1H, m., ≡CCHN), 4.0 (2H, d, J=2Hz, ≡CCH₂O) indicative of CH₂C≡CCHCH₂-grouping in a deshielded environment, thus ruling out the alternative structure.

The reaction also succeeds when (I) and primary amine are heated in a sealed tube in CH₃CN at 120° for 10-12 hr, yielding pyrrole (VI) in 30-40% yield. The formation of (VI) may be explained by initial displacement of bromine followed by intramolecular cyclization ⁴ of intermediate (V) as shown below.



The analogous reaction of acetate (III) with dimethylamine or benzylamine

gives rise to the acetylenic aminoalcohols (VII a,b). Compound (VIIa) exhibits nmr spectrum (JEOL-100 in CCl_4) with δ 4.1 (s, 2H, $\equiv\text{CCH}_2\text{O}$) and 3.46 (s, 3H, attributed to the $\equiv\text{CCH}(\text{N})\text{CH}_2\text{O}$ group) which do not allow to establish unambiguously its structure. Conclusive evidence of the structure (VII) was obtained by partial hydrogenation over Lindlar catalyst (1 equiv. H_2 uptake) and subsequent ozonolysis which afforded a 62% yield of the methoxyacetic acid.



The generally accepted mechanism of nucleophilic substitution in allenic halides involves the formation of a stabilized propargyl zwitterion-allenecarbenium intermediate.⁵ Such intermediate is not conceivable in our case. The present study affords no evidence concerning the detailed mechanism of this conversion but gives some indications that the reaction probably follows an $\text{S}_{\text{N}}1$ -like course⁶.

References and Notes

1. M.V.Mavrov, E.S.Voskanyan and V.F.Kucherov, Izv.Acad.Nauk U.S.S.R., Ser.Khim., 884 (1968), Tetrahedron, **25**, 3277 (1969).
2. I was prepared by reaction of appropriate alkoxyethylchlorides with vinylbromoacetylene at ambient temperature in ether in the presence of ZnCl_2 ; details will be reported elsewhere.
3. All allenic compounds exhibit analytical properties, ir and nmr spectral data consistent with their assigned structures.
4. It is worthwhile noting that the formation of the pyrroles had been also observed for other acetylenic diamines, see E.S.Voskanyan, M.V.Mavrov and V.F.Kucherov, Izv.Acad.Nauk U.S.S.R., Ser.Khim., 1836 (1968); M.L.Poutsma and P.A.Ibarbia, J.Org.Chem., **36**, 2572 (1971) and acetylenic hydroxyamines, see R.Fuks and H.G.Viehe, in "The Chemistry of Acetylenes", pp.532-536, Marcel Dekker, New-York (1969).
5. G.F.Hennion and D.E.Maloney, J.Am.Chem.Soc., **73**, 4735 (1951); V.J.Shiner and J.S.Humphrey, J.Am.Chem.Soc., **89**, 622 (1967) and references cited therein.
6. A number of various aryl-substituted haloallenes have been shown to undergo essentially uncomplicated $\text{S}_{\text{N}}1$ ionisation in solvolytic conditions, see M.D.Schiavelli, R.P.Gilbert, W.A.Boynton and C.J.Boswell, J.Am.Chem.Soc., **94**, 5061 (1972) and references cited therein.