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FASCINATING PROBLEMS IN ORGANIC REACTION MECHANISMS V[1] : PYROLYSIS OF BROMONITROBORNANE

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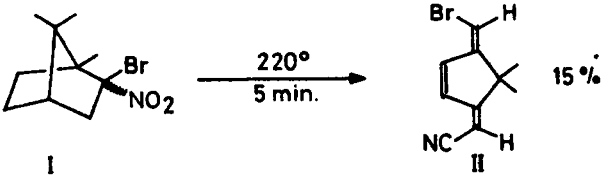
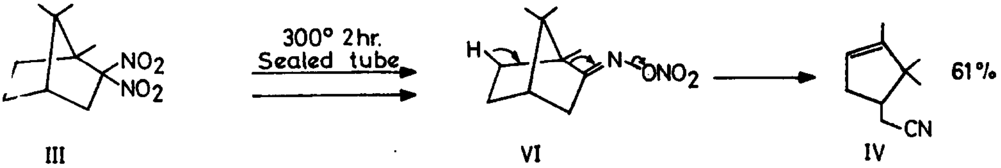
This communication presents the fascinating transformation depicted below :

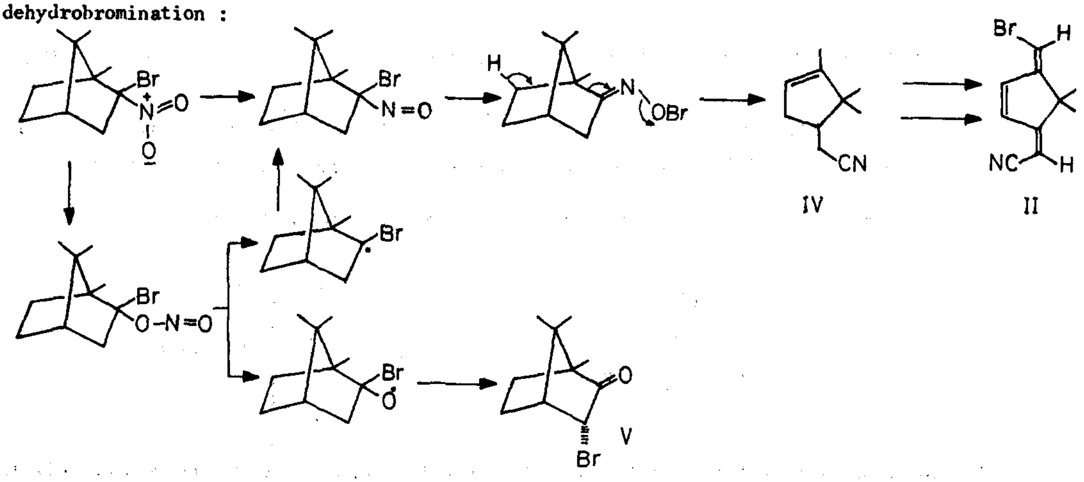


The structural assignment for II is based on analytical[2], ir, nmr, ms and uv data as well as chemical studies on samples collected by preparative vpc[3]. The development of the gross structure of the pyrolysis product to II, particularly the placing of the functional groups, was beset with apparently impossible difficulties. Eventually it became possible to understand the novel and deep seated I → II change on the basis of the identification of one of the minor products (∿ 2%) in the pyrolysis of I as 3-endo-bromo-2-bornanone (V) and the discovery of yet another interesting transformation (III → IV). The formation of V[4], rationalized in terms of fragmentation of I to camphor (1)[5] followed by bromination, showed the availability of brominating species and the III → IV change led to the identification of the probable substrate involved in the formation of II. The 2,2-dinitrobornane, mp 107°, reported in the literature[6] is largely (> 80%) camphornitrimine containing the desired III as the minor product. Chromatographic separation could be cleanly effected to give pure III, mp 214°[2,7]. The high yield (61%) of the nitrile IV[8] in the III → IV change precludes mechanisms based on simultaneous formation of another terpenoid fragment. This change can be rationalized in terms of the further fragmentation of intermediate VI, which, in turn, could arise either by a sequence of free radical reactions leading with 2-nitrobornyl radical or via nitrosonitrobornane formed by oxygen loss from III[9].

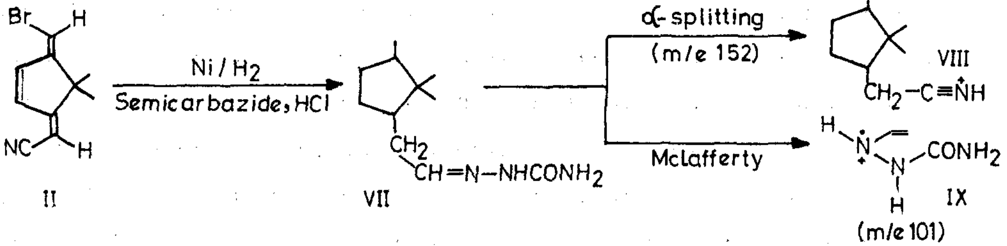


Extension of the type of fragmentation envisaged above to bromonitrobornane (I) led to the key nitrile IV, which was then readily linked to II by sequence involving bromination similar to the I → V change.

and dehydrobromination :



The IV → II link has been established by treatment of IV with NBS at 140°. The organic extracts exhibited ir and uv highly diagnostic of II[10]. Whilst the location of Br in II is inferred from nmr. that of CN has been additionally secured by the II → VII conversion. The structural assignment for the crystalline semicarbazone, mp 157°, is supported by ir, nmr, ms[11] and the typical ms fragmentation leading to ions VIII and IX[12] :



REFERENCES AND FOOTNOTES

1. Previous papers in this series: Tetrahedron Letters, 3299(1968);3747(1969);1225(1970);1855(1971).
2. Analysis in excellent accord with that calculated has been obtained for this compound.
3. II:ir:ν max (neat)(cm^{-1})2200(strong, conjugated CN),1600(C=C conjugated);uv:λ max(EtOH) 310 nm (ε=14770);ms:m/e 223 and 225; nmr:δ(CCl_4):7.0 (br,ringolefinic protons),6.05(s,small coupling, H-C-Br),4.95(s,small coupling,H-C-CN),1.2(s,methyls); vpc:silicone rubber, 5 ft, 145°;the middle cuts of single peak consisted preponderantly II admixed with the other 3 double bond isomers.Fraction enriched in each of the three minor isomers have been collected by careful monitoring and the nmr of these has helped in the stereochemical assignment for II. Similar results can be obtained by careful chromatography over $AgNO_3$ impregnated silica followed by evaporative distillation.
4. V:ir:ν max (neat)(cm^{-1}):1742(C=O);nmr:δ(CCl_4)4.53(q,3-exo-proton, J=5 and 1 Hz), 1.08, 0.94 (methyls); properties identical with authentic sample (A.W.Ingersoll and S.H.Babcock, J.Am.Chem.Soc.,55, 341 (1933)).
5. gem bromonitro systems connected with stabilizing functions undergo thermal change to ketones! (Willstatter and V. Hottenroth, Ber., 37, 1775 (1904)).
6. S.Mitchell and R. Gordon, J. Chem. Soc., 853 (1936).
7. III:ir:ν max (KBr)(cm^{-1}) 1560 (nitro,asym), 1365 (nitro,sym); nmr:δ($CDCl_3$)1.5(s,1-methyl), 1.03 (s,syn methyl), 0.92 (s, anti methyl).
8. IV:ir:ν max ($CHCl_3$)(cm^{-1})2260 (CN), 1618(C=C); nmr:δ(CCl_4) 5.3 (br,olefinic proton),1.61 (br, olefinic methyl), 1.1, 0.88 (methyls); nmr and tlc identical with authentic sample (F.Tiemann, Ber., 29 , 3006 (1896); W.H. Perkin and A.F. Titley, J. Chem. Soc., 119, 1089 (1921)).
9. We are grateful to the referee for suggesting the former pathway and for identifying VI as the most attractive intermediate.
10. the nmr was however complex.
11. VI:ir:ν max (KBr)(cm^{-1}) 3460, 3170 (NH_2), 1680(amide I), 1580(amide II); nmr: δ ($CDCl_3$) 9.92 (br,NH),7.15(br,vinyl proton),4.82(br,NH_2),0.9(methyls);assignments checked by exchange with D_2O; ms:m/e 211, 152, 101.
12. M.A. Baldwin, A.M.K.Konasiewicz, A.G. Loudon, A.Maccoll and D. Smith, J. Chem.Soc.,(B),34 (1968).