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NOVEL TRANSFORMATIONS OF NITROCYCLOPROPANES WITH TRIISOPROPYLPHOSPHITE

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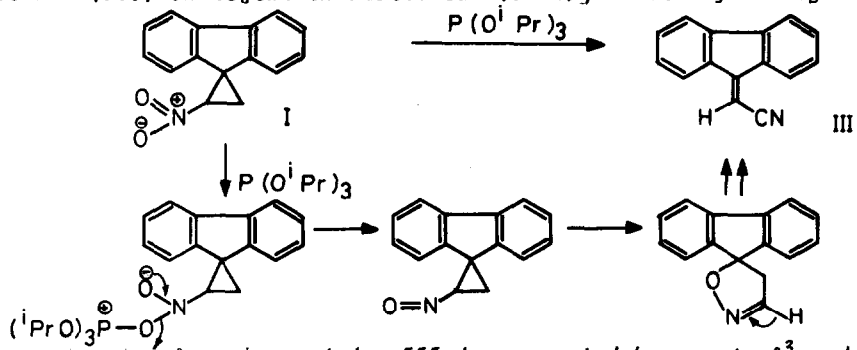
Nitrosocyclopropanes are the expected intermediates in the de-oxygenation with trialkylphosphites; further, the nitroso group can, in principle, either rupture the ring or be transformed to cyclopropyl nitrenes. In view of the current interest on the behaviour of electron excess systems created with trivalent phosphorous compounds and in view of virtual lack of information regarding nitrocyclopropanes, the novel pathways encountered with I and II are noteworthy.

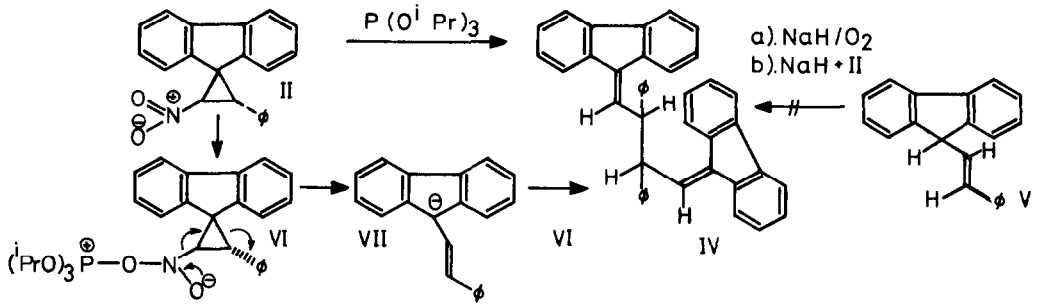
2-Nitrospiro (cyclopropane-1,9'-fluorene) (I)[1,2] was transformed to the nitrile III (38%) on reflux in distilled $P(O^iPr)_3$ under dry nitrogen:



The structural assignment for III is supported by spectral[3] and analytical data as well as by comparison with authentic sample prepared by H_2SO_4-AcOH dehydration of alcohol resulting from fluorenone and CH_3CN-NaH[4]. The de-oxygenation of I obviously stops at the nitroso stage and the I→III change can best be rationalized on basis of nitrosocyclopropane 3-H2-isoxazoline transformation.

2-Nitro-3-phenylspiro (cyclopropane-1,9'-fluorene) (II)[5] on the other hand gave as the sole isolable product, the dimeric hydrocarbon IV (mp-230-231°; 42%) on reflux in distilled $P(O^iPr)_3$ under dry nitrogen. To our knowledge this is the first example of complete removal of elements of nitro group with trivalent phosphorous. The assignment for IV is supported by analysis[2], NMR (A-60 and 250 MHz) and molecular weight. The NMR and mass spectrum of IV merit special mention[6]. The hydrocarbon IV readily gave the expected tetrahydro product[2,7] and on ozonolysis involving oxidative work-up gave fluorenone and meso-diphenyl succinic acid[8]. The monomer V[9], corresponding to IV, was shown to be not involved in the formation of the dimeric hydrocarbon under a variety of reaction conditions. The II→IV change is rationalized on basis of C-N rupture

of intermediate VI giving rise to the stabilised ion VII[10] which on further reaction with VI could lead to IV:



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REFERENCES AND FOOTNOTES

1. Prepared in quantitative yields by mixing benzene solutions of nitroethylene and 9-diazofluorene, mp 110-111°; IR (λ_{max}(KBr) 6.53(NO_2 asym); 7.4(NO_2 sym)μ); NMR (δCDCl$_3$ 7.4(m, aromatic), 4.94(q,α-proton), 2.97(q, syn proton), 2.3(q, anti proton). (H.Shechter and S. Ranganathan, Unpublished).

2. Analytical values in excellent accord with the calculated have been obtained for this compound.

3. III, IR (λ_{max}(KBr) 4.54(CN),6.25 (C=C)μ); NMR(δCDCl$_3$ 7.58 (m,aromatic), 6.08 (s,olefinic).

4. Several attempts to prepare the alcohol by procedure reported by W.Chodkiewicz, P.Cadiot and A.Will, Bull. Soc.Chim. France., 1586 (1958); Compt. Rend., 243, 280 (1956) failed.

5. Prepared according to A. Mustafa and A.H.E.Harhash, J.Am.Chem.Soc.,76,1383 (1954), NMR (δCDCl$_3$ 7.4 (m, aromatic), 6.2 (d,J=8 Hz; heavily shielded fluorenyl 8-proton), 5.42 (d,J=6 Hz; CHNO$_2$), 4.68 (d,J= 6 Hz,CHφ); IR (λ_{max}(KBr) 6.50 (NO_2 asym), 7.36 (NO_2 sym)μ); mass spectrum m/e 313(M^+).

6. The mass spectrum exhibited only peaks corresponding to the monomeric unit; however the molecular weight by osmometric method (540) was in good agreement with the dimer structure (534). The A-60 spectrum in CDCl$_3$ showed the benzilic protons as a doublet of triplets indicating their non-equivalence. The pattern was resolved to a doublet of quartets in a 250 MHz instrument (δCDCl$_3$ 5.12 (J=7 and 2 Hz), 4.98 (J=7 and 2 Hz) ppm).

7. mp 250-251°, mass spectrum m/e 538 (M^+).

8. Authentic meso diphenyl succinic acid was prepared according to J.A.McCree and R.A. Barnard, Org. Syn., 32, 63 (1952) and S. Wawzonek, J. Am. Chem.Soc., 62, 745 (1940).

9. R. Kuhn and D. Rewicki, Tetrahedron Letters, 3513 (1965).

10. Similar rupture in the case of I would give a less stabilized ion.