Tetrahedron Letters, Vol.22, No.24, pp 2301 - 2302, 1981
Printed in Great Britain

0040-4039/81/242301-02$02.00/0

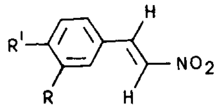
AN UNUSUAL ONE STEP SYNTHESIS OF ACETYLENES

Pradeep G.Karmarkar, Alka A. Thakar and Murzban S.Wadia*
Department of Chemistry, University of Poona, Pune 411 007, India

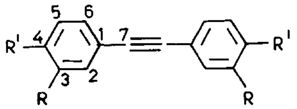
Substituted nitrostyrenes on reaction with H_2O_2/NEt_3 give 1,2 diaryl acetylenes in ∽ 30 % yield.

Nitro olefins have been converted[1] to epoxy nitro compounds by reaction with $H_2O_2/\bar{O}H$. However it has been reported[1] that this reaction fails in the case of β-nitrostyrene as the epoxide derived from it contains an acidic hydrogen. In order to circumvent this problem we attempted epoxidation with H_2O_2/NEt_3. Under these conditions we observed an unusual one step synthesis of symmetrical acetylene **2**, starting with compound **1**.

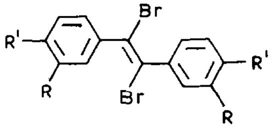
Reaction of **1** with H_2O_2/NEt_3 furnished a crystalline nitrogen free solid, $C_{16}H_{14}O_2$ (M^+ 238), m.p. 142°, yield 30 %. Its I.R. (no bands at 3300 or 2100 or 1700 or 1530 cm^{-1}) and PMR spectra indicated the presence of two methoxy groups, (3.8 δ,s) and eight aromatic protons present as two mutually coupled doublets at (6.87 and 7.45 δ J= 9Hz). These conclusions were supported by the cmr spectrum which showed only six signals suggesting that a condensation of two moles of **1** with loss of $C_2H_4O_4N_2$ had occured to yield a symmetrical molecule. This data along with the cmr chemical shift of 85.8 ppm suggested the presence of an acetylene (The acetylenic carbons of diphenyl acetylene appear at 89.9 ppm)[2]. The cmr assignments [C-1 (111.6, s); C-2 and C-6 (111.41, d); C-3 and C-5 (132.8, d); C-4(159.5, s); C-7 (85.8, s); OCH_3 (55.18, q)] and off resonance multiplicities then led unequivocally to structure **2** for this compound.



1 R'=OMe, R=H,
4 R=R'=OMe
5 R',R=-O-CH_2-O



2 R'=OMe, R=H
6 R=R'=OMe
8 R',R=-O-CH_2-O-



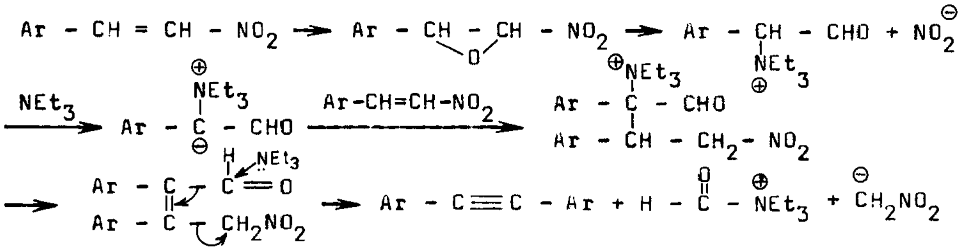
3 R'=OMe, R=H
7 R=R'=OMe
9 R',R=-O-CH_2-O-

Structure **2** is also supported by the observation that reaction with Br_2/AcOH gives a product, m.p. 197°. The observation that PMR spectrum shows practically no change 3.8 (6H, s); 6.87 (4H, d J=9Hz); 7.41 (4H, d J=9 Hz) clearly suggests that this product, $C_{16}H_{16}O_2Br_2$, is indeed an addition product 3. Significantly m.p. of 2 and 3 are in close agreement with the m.p. (142° and 197° respectively) reported in literature[3] for these compounds.

These structures were confirmed by a reported[4] unambiguous synthesis. The synthetic acetylene and its dibromide were identical in every respect (m.p., m.mp, T.L.C., I.R.) with the samples obtained above.

The general nature of this reaction could be demonstrated by carrying out the reaction on compounds 4 and 5. Reaction of 4 with H_2O_2/NEt_3 afforded a compound $C_{18}H_{18}O_4$, M^+ 298, m.p. 156° (yield 31.5 %). Its spectral properties and that of the derived bromocompound (Br_2/Et_2O) are consistent with structure 6 and 7 respectively[5]. The literature m.p. of these compounds (155-6° and 208° respectively)[6] are also in agreement with these structures.

A similar reaction of 5 furnished a compound m.p. 195° (yield 29 %). Its spectral properties and that of derived dibromide (Br_2/HOAc) m.p.228° are in agreement with structure 8 and 9. Both these compounds are hitherto unknown. The mechanism given below represents one of the possible methods for the formation of these compounds.



The scope and mechanism of the reaction are under investigation.

1. H. Newman and R.B. Angier, Tetrahedron, 26, 825 (1970).
2. G.C. Levy and G.L. Nelson, Carbon-13, Nuclear Magnetic Resonance for organic chemists, Wiley Interscience, New York, p. 72 (1972).
3. H. Wiechell, Ann. 279, 338 (1894).
4. L.F. Fieser, J.Chem.Education, 31, 291 (1954) and references cited therein.
5. All compounds reported in this communication gave expected elemental analysis and spectral data.
6. P. Fritsch, Ann. 329, 45 (1903).

We are grateful to Professor N.S.Narasimhan for encouragement. One of us (AAT) is indebted to U.G.C. for a fellowship.

(Received in UK 7 April 1981)