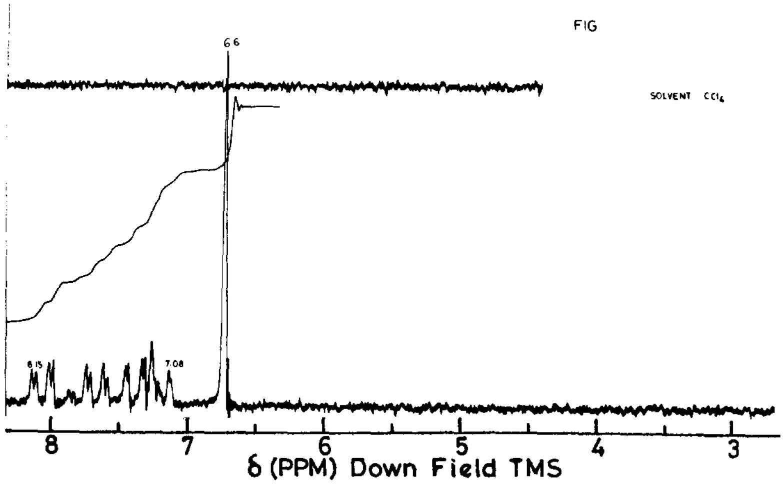
Tetrahedron Letters No. 3, pp 283 - 284.
0040-4039/79/0115-0283$02.00/0

A SPIRO ADDUCT OF VINYLENE CARBONATE WITH BENZENEIUM 2-CARBOXYLATE

by Jampani Madhusudana Rao* and S.Mallikarjuna
Regional Research Laboratory, Hyderabad-500 009, India

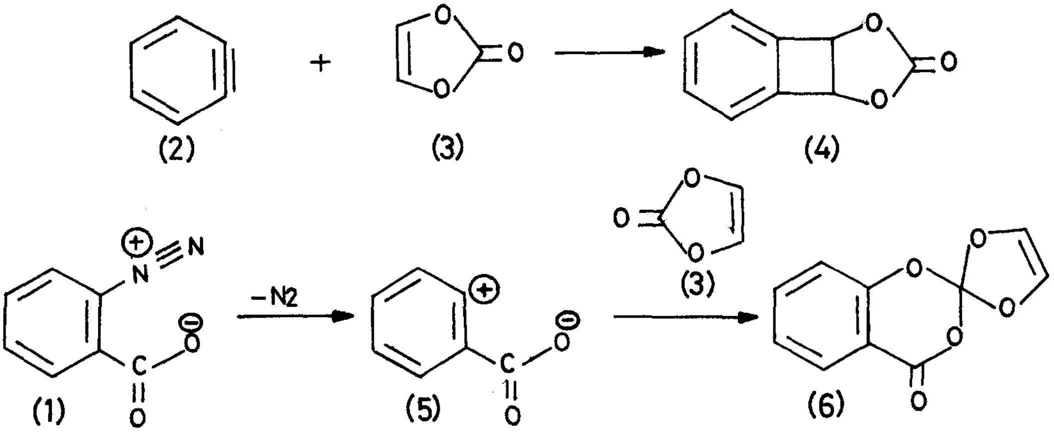
In an attempt to find a synthetic route to benzocyclobutene-1,2-dione we attempted the reaction of benzyne with vinylene carbonate[1] (3). Decomposition of benzene diazonium 2-carboxylate (1) to give benzyne[2] in THF or 1,2-dichloroethane in presence of vinylene carbonate (3) failed to give either the expected adduct (4) or any other characterisable compound. Reaction carried out in pure excess vinylene carbonate at 35-45°C for 60 minutes gave a product mixture showing seven spots on T.L.C. (silica gel-G, Merck, eluent benzene). Of these a light yellow liquid has been isolated after passing over silica gel column (NCL-Poona, eluent: benzene) as the first fraction in about 2.3 percent yield. The compound is highly unstable to heat and light and has been tentatively assigned the structure spiro[1,3-benzodioxan-2,2'-[1,3]-dioxole]-4-one (6) based on Mass, I.R. and P.M.R. spectral data discussed below.

A 1:1 adduct of benzyne with vinylene carbonate should give M^+ at m/e 162 whereas the mass spectrum of the compound isolated shows M^+ at m/e 206, i.e. 44 mass units higher. The appearance of an intense band at 1770 cm^{-1} in the I.R. spectrum points to the presence of a carbonyl group different from the type in vinylene or ethylene carbonate which appear above 1800 cm^{-1}. The 60 MHz-PMR spectrum (see figure below) recorded in CCl_4 showed only two groups of signals, a singlet at δ 6.6 and 4 multiplets, some of them



FIG

overlapping, in the aromatic region between δ 7.05–8.15, integrating for protons in the ratio 1:2 respectively. The position and splitting pattern of the multiplets are typical of ortho substituted benzene as in esters of o-anisic acid^3 and methyl salicylate^4. This leads to the assignment of the singlet appearing at δ 6.6 to two olefenic protons on a symmetrically disubstituted double bond.



(2) (3) (4)

(1) (5) (3) (6)

The absence of the carbonate function and presence of a symmetrically substituted double bond combined with other spectral data demonstrate that reaction occurred at the carbonyl function of (3). The reacting species is not benzyne but benzeneium 2-carboxylate (5) formed by loss of nitrogen from (1). Then a 4 + 2 cycloaddition between the betaine (5) and the carbonyl group of vinylene carbonate (3) will lead to spiro[1,3-benzodioxan-2,2'-[1,3]dioxole]-4-one (6). That (1) decomposes to benzeneium 2-carboxylate can be inferred from the isolation of stable platinum complexes reported^{5,6}. A final confirmation of the structure (6) as well as isolation and identification of other products is under investigation.

Acknowledgement:- We wish to thank Dr.G.S.Sidhu, Director, Regional Research Laboratory for providing facilities to carry out this work. One of us (S.M.) owes his thanks to the University of Hyderabad for the award of fellowship.

REFERENCES

1) Melvin S.Newman and Roger W. Addor, J.Am.Chem.Soc. 75, 1263 (1953).
2) Francis M.Logullo, Arnold. H.Seitz and L.Friedman, in Organic Synthesis Coll. Vol. V, Page 54. John Wiley and Sons, (1973).
3) C.Heathcock. Can.J.Chem. 40, 1865 (1962).
4) R.Freeman, N.S.Bhacca and C.A.Reilly, J.Chem. Phys. 38, 293 (1963).
5) C.D. Cook and G.S.Janhal, J.Am.Chem.Soc., 90, 1464 (1968).
6) T.L.Gilchrist, F.J.Graveling and C.W.Rees, J.Chem.Soc. (C), 977 (1971).

(Received in UK 14 November 1978)