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1,1-BIS(BENZENESULFONYL)ETHYLENE: A SYNTHETIC EQUIVALENT OF ETHYLENE 1,2-DIPOLE

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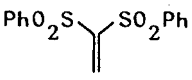
Summary: 1,1-Bis(benzenesulfonyl)ethylene (1) acts as a synthetic equivalent of ethylene 1,2-dipole as it gives with olefins products derived from a postulated dipolar reaction mechanism that can be readily desulfonylated into the formal ethylene adducts.

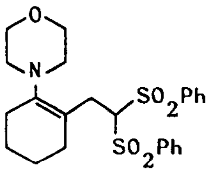
In order to bypass the intrinsic reluctance of ethylene to enter into concerted cycloaddition reactions, a number of ethylene synthetic equivalents has recently been proposed. Among them, sulfur containing olefins look to be the most effective, both because of the strong activation imparted by the sulfur functionalities and because of their ready removal or substitution from the adducts.[1]

Herewith we describe the use of 1,1-bis(benzenesulfonyl)ethylene[2] (1) as a synthetic equivalent of ethylene 1,2-dipole since it very readily gives adducts with olefins that can be reconduced to an electrophilic addition of the β-vinylic carbon of 1, followed by proton transfer or cyclization of the derived zwitterion. The resulting products can be readily desulfonylated to the formal ethylene adducts.

For example 1 reacts instantaneously at 0°C with N-morpholinocyclohexene to afford quantitative yields of adduct 2 that was isolated and characterized as ketone 3 after acidic work up.[3] The same ketone has been independently synthesized in the reaction of 1 with cyclohexanone as described in the next paper. Indeed the reaction with this substrate is known to occur also with the less activate benzene vinyl sulfone but under more forced conditions.[4]



(1)



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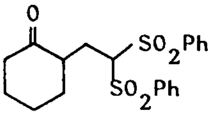

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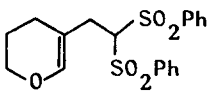
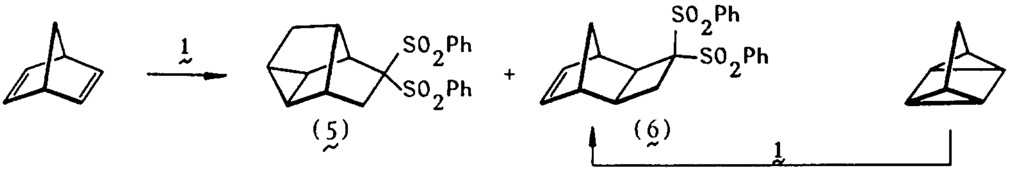
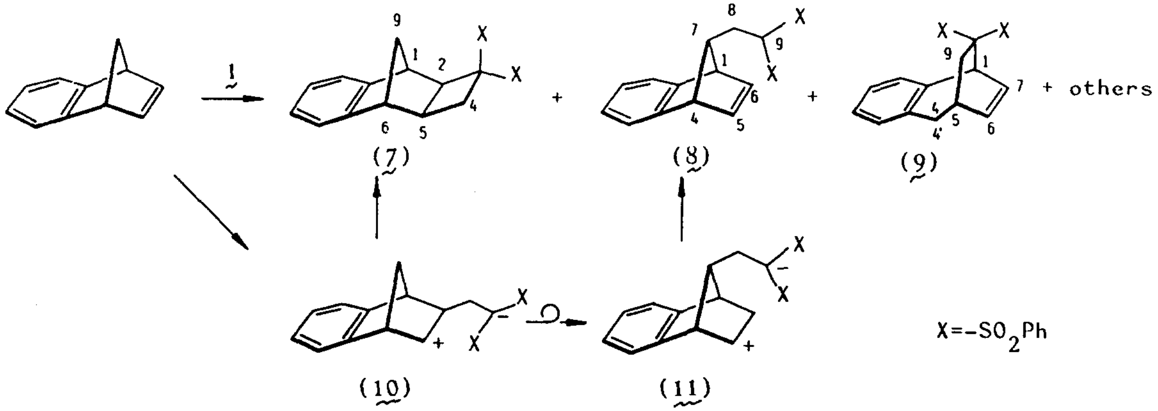


(4)

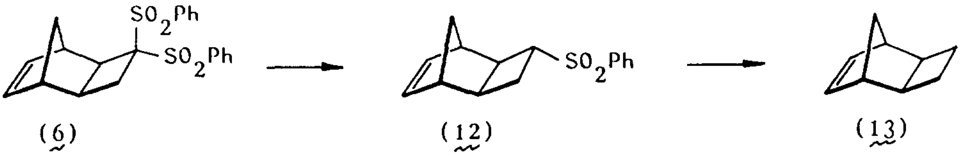
The high reactivity exhibited with enamines, prompted us to test **1** in the reaction with other olefins. For example, it reacts readily in refluxing acetonitrile with 2,3-dihydropyrane to afford adduct **4**, in virtually quantitative yield.[5] While we were unable to observe any (2+2)-cycloaddition product in this and in the former reaction, a (2+2) adduct was instead observed in the reaction of **1** with the less activated olefin norbornadiene. In fact, aside the "normal" Diels-Alder product **5** derived by an homo (4+2)-cycloaddition, the tricyclic bissulfone **6** derived from a formal (2+2)-cycloaddition was obtained in *ca.* 10% yield.[6,7] The two products have been separated by silica gel flash chromatography (> 230 mesh, *ca.* 20:1 weight ratio adsorbant to substrate, dichloromethane as eluant) and characterized from their C,H analysis and ^{1}H-NMR spectral data. The structure of the (2+2)-cycloadduct has also been chemically secured by comparison of the spectral and physical data with those obtained by the adduct of **1** to quadricyclane.[6]



If the mechanism of formation of this latter adduct involves a dipolar reaction mechanism, one would expect also formation of products derived by Wagner-Meervein rearrangement of the norbornenyl skeleton. In this specific example, rearranged products might have been superseded by the overwhelming predominance of the homo (4+2)-cycloadduct **5**. For this reason we submitted **1** to the reaction with benzonorbornadiene, that having part of the diene function comprehended into a benzene ring, is prevented to give concerted cycloaddition. On heating a mixture of **1** and benzonorbornadiene at 140°C overnight the set of products shown in the scheme is obtained together with variable yields of 1,1,3,3-tetra-(benzenesulfonyl)propane likely derived from partial decomposition of **1**. While **9**[8] probably derives by partial isomerization of norbornadiene to benzotropylidene[9] in the reaction conditions, **7** and **8**[10] can only derive by the zwitterionic intermediate **10**, before and after Wagner-Meervein rearrangement. Proton migration in intermediate **11** looks to be favoured with respect to ring closure as observed with the previously discussed nitrogen or oxygen activated olefins.



The viability of the present method as a way of introduction of ethylene with a dipolar mechanism is demonstrated with the partial and total reduction of adduct **6** to sulfone **12**[11] and to hydrocarbon **13**[12] (70% yield from **6**). The structure of **12**, that was the only observed stereoisomer, has been established



on the basis of nuclear Overhauser effect experiments. The formation of only one stereoisomer is analogous to the partial reduction of related gem-dihalides.[13] Sulfone **12**[14] can be further manipulated to the corresponding ketone,[15] or alkylated[1,16] to a variety of homologues, thus simulating the addition of ketone or of a therminal olefin.

The mechanism of action of 1,1-bis(benzenesulfonyl)ethylene is still uncertain. We think that the approach of the reagents is controlled by frontier orbital interactions, and is followed by a rapid degeneration to a zwitterionic intermediate that then collapses to products. Partially related examples may be encountered in the chemistry of triazolinediones[17] and in the Lewis acid catalized cycloaddition of propiolates to olefins.[18]

The reactivity of **1** as ethylene 1,2-dipole synthetic equivalent is related to the recently reported use of 1,1-bis(benzenesulfonyl)cyclopropane as propylene 1,3-dipole synthon by Trost et al.[19] that similarly utilizes benzenesulfonyl groups as activating functionalities both for the reactivity and for the versatility of manipulations of the derived products.

REFERENCES AND NOTES

1. For example benzene vinyl sulfone (Carr, R.V.C.; Paquette, L.A. J. Am. Chem. Soc. 1980, 102, 853) and (Z)- and (E)-bis(benzenesulfonyl)ethylene (De Lucchi O.; Pasquato, L. Gazz. Chim. It. in press) have been shown to be reactive ethylene equivalents for ground state (4+2)-cycloadditions and vinyl sulfides are known as ethylene substitutes for (2+2)-photocycloadditions (Vanderhoek, J.Y. J. Org. Chem. 1969, 34, 4184).
2. Stetter, H.; Steinbeck, K. Liebigs Ann. Chem. 1974, 1315.
3. 3: 80% yield; mp 144.5-145.5°C (EtOH); 'H-NMR ($CDCl_3$): 1.17-1.40 (1H,m) 1.52-2.18 (5H, m) 2.33 (2H,m) 1.96 (partially hidden) and 2.53 (2H, diastereotopic CH_2, AB system split in d, J_{AB} 15.3) 3.09 (1H,m) 4.99 (1H,dd,J 9.2 and 3.7) 7.49-7.76, 7.86-8.00 (10H,C_6H_5, m).
4. Fatutta, S.; Risaliti, A. J. Chem. Soc. P. I 1974, 2387.
5. 4: 85% yield, mp 174.5-175.5°C (EtOH); 'H-NMR ($CDCl_3$): 1.70 (4H,m) 2.81 (2H,d,J 6.1) 3.71 (2H,m) 4.52 (1H,t,J 6.1) 6.04 (1H,s) 7.53-7.76, 7.92-7.99 (10H, C_6H_5, m).
6. "Normal" Diels-Alder reactions of **1** are published separately (Gazz. Chim. It., in press).
7. Analytical and spectral data of compound 6 are published in ref. 6.
8. 9: 5% yield; mp 154-155°C (EtOH); 'H-NMR ($CDCl_3$): 1.43, 2.25 (2H, H_9, AB pattern, J_{AB} 9.5) 2.28 (1H,$H_{4'}$,dd,$J_{4,4'}$ 13.7,$J_{4',9}$ 3.0) 2.80 (1H,H_4,dd,$J_{4,5}$ 3.7) 3.07 (1H,H_5,bs) 3.44 (1H,H_1,m) 6.16 (1H, H_7, dd,$J_{6,7}$ 5.5; $J_{1,7}$ 3.0) 6.31 (1H,H_6,dd,$J_{5,6}$ 3.4) 7.48-7.74, 7.95-8.04 (10H,C_6H_5, m)-
9. Cristol, S.J.; Caple, R. J. Org. Chem. 1966, 31, 585.
10. 7: 50% yield; mp 154-155°C (EtOH); 'H-NMR ($CDCl_3$): 1.81 (1H,H_7,dm,$J_{7,7'}$ 10.4) 2.33 (1H,H_5,qm,J_q 7.0) 2.83-2.95 (3H,m) 3.32 (1H,bs) 3.83 (1H,bs) 7.04-7.18 (4H,C_6H_4,m) 7.44-7.76, 7.84-7.91, 7.97-8.04 (10H, C_6H_5, m). 8: 10% yield; oil; 'H-NMR ($CDCl_3$): 2.36 (2H, H ,dd, $J_{7,8}$ 7.0, $J_{8,9}$ 5.0) 2.94 (1H,H_7,t) 3.58 (2H,$H_{1,4}$,m) 4.27 (1H,H_9,t) 6.38 (2H,$H_{5,6}$,m) 6891 and 7.15 (4H,C_6H_4, AA'BB' pattern) 7.51-7.98 (10H,C_6H_5, m).
11. 12: 70% yield, oil; 'H-NMR (C_6D_6): 1.10 (2H,H_9,m) 1.21 (1H,H_4,m) 1.90 (1H,H_5,m) 2.26 (1H,H_6,m) 2.30 (1H,H_1,m) 2.55 (1H,H_2,m) 2.60 (1H,H_4,m) 2.93 (1H,H_3,m) 5.62 (1H,H_8,dd, $J_{7,8}$ 5.8, $J_{1,8}$ 3.0) 5.72 (1H,H_7,dd,$J_{6,7}$ 3.0) 6.94-7.04, 7.80-7.89 (5H,C_6H_5, m).
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