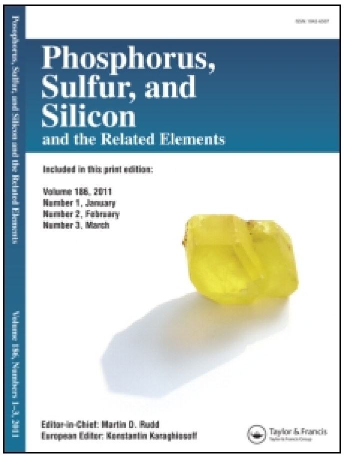


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

GENERAL APPLICABILITY OF Z-1,2-DIPHENYLSULFONYLETHYLENE AS ACETYLENE SYNTHON IN CYCLOADDITION REACTIONS: A TWO STEP SYNTHESIS OF TETRACYCLO[4.3.0.0^{2,4}.0^{3,7}]NON-8-ENE AND TRICYCLO[4.2.1.0^{2,5}]NONA-3,7-DIENE

Ottorino De Lucchi[a]; Giorgio Modena[a]
[a] Centra Studi Meccanismi di Reazioni Organiche del C.N.R. Istituto di Chimica Organica dell 'Universita', Padova, Italy

To cite this Article De Lucchi, Ottorino and Modena, Giorgio(1983) 'GENERAL APPLICABILITY OF Z-1,2-DIPHENYLSULFONYLETHYLENE AS ACETYLENE SYNTHON IN CYCLOADDITION REACTIONS: A TWO STEP SYNTHESIS OF TETRACYCLO[4.3.0.0^{2,4}.0^{3,7}]NON-8-ENE AND TRICYCLO[4.2.1.0^{2,5}]NONA-3,7-DIENE', Phosphorus, Sulfur, and Silicon and the Related Elements, 14: 2, 229 — 231

To link to this Article: DOI: 10.1080/03086648308075945

URL: http://dx.doi.org/10.1080/03086648308075945

Phosphorus and Sulfur, 1983, Vol. 14, pp. 229–231
0308-664X/83/1402-0229/$18.50/0

GENERAL APPLICABILITY OF Z-1,2-DIPHENYLSULFONYLETHYLENE AS ACETYLENE SYNTHON IN CYCLOADDITION REACTIONS: A TWO STEP SYNTHESIS OF TETRACYCLO[4.3.0.0^{2,4}.0^{3,7}]NON-8-ENE AND TRICYCLO[4.2.1.0^{2,5}]NONA-3,7-DIENE.

OTTORINO DE LUCCHI and GIORGIO MODENA

Centro Studi Meccanismi di Reazioni Organiche del C.N.R. Istituto di Chimica Organica dell'Universita', Via Marzolo 1, 35131 Padova, Italy

(*Received September 6, 1982*)

Z-1,2-diphenylsulfonylethylene is shown to be a dienophile of general use since not only it cycloadds to conjugated 1,3-dienes but also to homo-conjugated double bonds and strained σ-bonds as those of norbornadiene and quadricyclane. The adducts can be reduced with sodium amalgam in methanol to the corresponding polycyclic olefins thus providing a new, efficient entry to the title hydrocarbons otherwise obtainable only through more complex routes.

Among the several acetylene synthons that have been studied[1] to overcome the inertness of acetylene in cycloaddition reactions most of them are limited in reactivity and in modes of cycloaddition. Recently we reported that Z-1,2-diphenylsulfonylethylene (**1**) is a superior reagent as it is very reactive and easily reducible to the required double bond.[2] Nonetheless the reported examples dealt with the most classical [4 + 2]-cycloaddition and hence, they lead only to 1,4-cyclohexadienes through Diels–Alder reaction with conjugated 1,3-dienes. Herewith we report that Z-1,2-diphenylsulfonylethylene (**1**) is also reactive with the non-conjugated double bonds of norbornadiene and with the strained σ-bonds of quadricyclane and that the adducts can be converted to the respective olefin by reductive elimination, thus **1** has to be considered of general applicability as acetylene synthon in cycloaddition reactions.

On heating in an oil-bath a toluene solution of norbornadiene and **1** at 130–140°C for 24 h a white solid is obtained whose NMR parameters are consisting with 8,9-diphenylsulfonyltetracyclo[4.3.0.0^{2,4}.0^{2,7}]nonane (**2**).†

Treatment of **2** with 2% sodium amalgam in methanol buffered with sodium dihydrogen phosphate at room temperature gives the corresponding known olefin **3** in 58% yields.‡

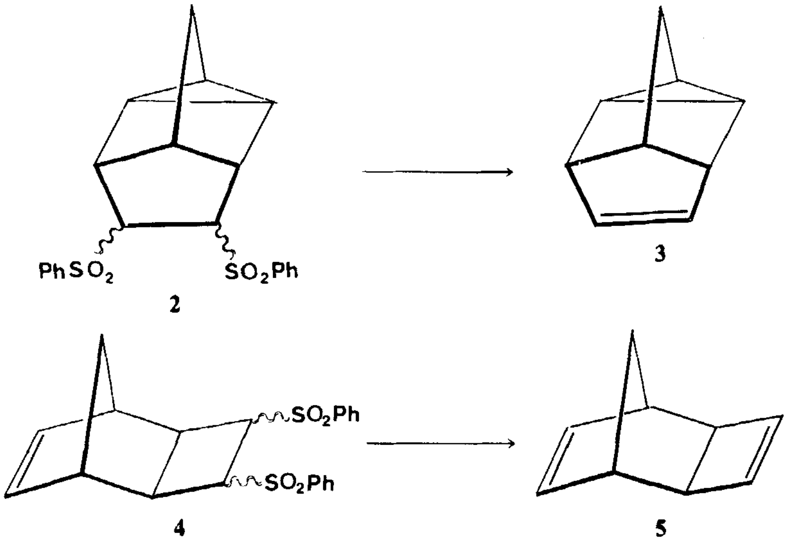
The adduct **4**, of quadricyclane and **1** is obtained under much milder conditions by dissolving the two reagents in chloroform and on stirring one week at room temperature. White crystals separate in practically quantitative yield.

Similarly as for **3** the diene **5** was obtained in 59% yield by reaction of **4** with 2% sodium amalgam buffered with sodium dihydrogen phosphate.

---

† X-rays are in progress to define the stereochemistry of the adducts.

‡ Yields have not been optimized.



It has to be emphasized that the present methodology for the preparation of **3** and **5** is by far more convenient than those reported in the literature.[3] Especially **5** can now be prepared avoiding manipulation of sensitive organometallic reagents and the separation of the mixture of products obtained by the described synthesis.[3a] Furthermore, the present procedure is also suitable to be scaled up to large quantities.

The combined high reactivity of **1** and the ease of the elimination step make Z-1,2-diphenylsulfonylethylene (**1**) one of the most general dienophiles and a reagent of choice for introducing an acetylene molecule in a cycloaddition reaction.

We are continuously investigating the properties of **1** in other cycloadditions and the possibility of further manipulations of its adducts in view of the large synthetic usefulness of sulfones in organic synthesis.

EXPERIMENTAL

Melting points are uncorrected. NMR spectra were taken on a Varian EM-360 or on a Bruker WP-60 both operating at 60 MHz. IR spectra were recorded on a Perkin Elmer 580 spectrometer. Microanalysis were performed in-house by Prof. E. Celon staff. Known compounds used in this research were either purchased from standard chemical suppliers or prepared according to literature procedures and purified to match the reported physical and spectral data.

8,9-Diphenylsulfonyltetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (2): A 10-ml screw-capped, heavy-walled, Pyrex test tube was charged with freshly distilled norbornadiene (0.2 g, 2.2 mmol) and Z-1,2-dipheylsulfonylethylene (0.5 g, 1,6 mmol) in 2 ml of toluene. The test tube was tightly closed and immersed into an oil-bath preheated at 130°C. The reaction was kept stirring at this temperature for 24 h during which a white precipitate deposited. After cooling, ether (5 ml) was added and the solid filtered with suction and washed with more ether to afford 0.6 g (92% yield) of a white powder. An analytical sample was obtained by recrystallization from CH_2Cl_2 (mp 334–336°C with partial decomposition ^{1}HNMR (CD_2Cl_2, TMS) δ (ppm): 8.1–7.3 (10H,C_6H_5,m); 4.0(2H,$H_{8,9}$,m); 2.8(1H,m); 2.4(2H,m); 1.6–0.9(5H,m). IR (KBr); 3070, 2960, 2940, 2870, 1480, 1450, 1340, 1315, 1285, 1150, 1090, 810, 760, 690, 605, 540 cm^{-1}.

Analysis: Calculated for $C_{21}H_{20}O_4S_2$: C, 62.97; H, 5.03. Found: C, 63.02; H, 5.14.

3,4-Diphenylsulfonyltricyclo[4.2.1.0^{2,5}]non-7-ene (4): Into a 25-ml round-bottomed flask were placed 1.0 g (3.2 mmol) of Z-1,2-diphenylsulfonylethylene (**1**) and 0.4 g (4.3 mmol) of quadricyclane in ca. 8 ml of chloroform. The solution was kept stirring at room temperature while monitoring the disappearence of the dienophile by thin layers chromatography (silica gel, CH_2Cl_2 as eluant, UV detection). When no more **1** was present (approximately one week) ether was added to complete precipitation and the white product filtered off: 1.2 g (93% yield). Recrystallization from $CHCl_3$ yielded the analytically pure sample. Mp 260–263°C with partial decomposition. ^1H NMR (CD_2Cl_2, TMS) δ (ppm); 8.1–7.4 (10H,C_6H_5,m); 5.9(2H, $H_{7,8}$,m); 3.5(2H,$H_{3,4}$,m); 2.6 (2H,m); 2.3(2H,m); 1.1(2H,m). IR (KBr): 2980, 2960, 2940, 1480, 1450, 1330, 1310, 1300, 1160, 1140, 1090, 718, 690, 615, 580 cm^{-1}.

Analysis: Calculated for $C_{21}H_{20}O_0S_2$: C, 62.97; H, 5.03. Found: C, 63.15; H, 4.84.

Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene (3): *1 g (2.5 mmol) of 8,9-diphenylsulfonyltetracyclo[4.3.0.0^{2,4}0^{3,7}]nonane* **(2)** was placed into a 100-ml three-necked, round-bottomed flask equipped with an efficient mechanical stirrer and mixed with ca. 6 g of $NaH_2PO_4 \cdot 2H_2O$ and ca. 50 ml of dry CH_3OH. The mixture was purged, while stirring, with nitrogen and 2% sodium amalgam [obtained from ca. 0.4 g of Na (17 mmol) and ca. 30 g of clean mercury] was added in portions. The reaction was kept stirring overnight at room temperature, then poured into brine and extracted (3 × 20 ml) with 30–50 petrolether. The extracts were washed with brine (3 × 30 ml), water and dried over anhydrous Na_2SO_4. Rotoevaporation of the *solvent at 0°C afforded an oil (0.17 g, 58% yield) the spectral data of which are essentially indentical to* those reported for **3**.[3]

Tricyclo[4.2.1.0^{2,5}]nona-3,7-diene (5): **5** was prepared in the same way as described for tetracyclo [4.3.0.0^{2,4}.0^{3,7}]non-8-ene **(3)**. Starting from the same quantities of reagents 0.175 g (59% yield) of a colorless oil was obtained. The spectral data are in accordance with those reported in the literature.[3a]

REFERENCES

1. L. A. Paquette, R. E. Moerck, B. Harirchian and P. D. Magnus, *J. Am. Chem. Soc.*, **100**, 1597 (1978); A. P. Davies and G. H. Whitham, *J. Chem. Soc., Chem. Commun.*, **1980**, 639; L. A. Paquette and R. V. Williams, *Tetrahedron Lett.*, **23**, 4643 (1981), and references cited in these papers.
2. O. De Lucchi and G. Modena, *J. Chem. Soc., Chem. Commun.*, **1982**, 914.
3. (a) L. G. Cannell, *Tetrahedron Lett.*, **1966**, 5967. (b) R. A. Snow, C. R. Degenhardt and L. A. Paquette, *Tetrahedron Lett.*, **1976**, 4447, (c) G. A. Russell, G. W. Holland, K. -Y. Chang, R. G. Keske, J. Mattox, C. S. C. Chung, K. Stanley, K. Schmitt, R. Blankespoor and Y. Kosugi, *J. Am. Chem. Soc.*, **96**, 7237 (1974), (d) P. K. Freeman and D. M. Balls, *J. Org. Chem.*, **32**, 2354, (1967), (e) T. J. Katz, J. C. Carnahan, Jr. and R. Boecke, *Ibid.*, **32**, 1301 (1967).