

REACTIVITY OF PHENYL(TOLYLSULFONYL)ACETYLENE TOWARDS DIENES AND
HOMO-DIENES: CYCLOADDITIONS VERSUS FRAGMENTATION-ADDITION REACTIONS

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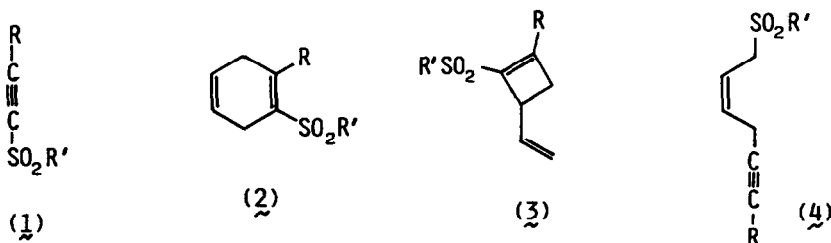
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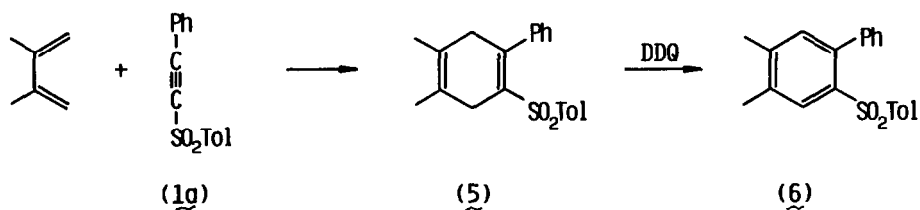
Summary: Depending upon the diene, phenyl(tolylsulfonyl)acetylene (1a) affords the (4+2), the (2+2)-cycloadducts or products derived by 1,4-addition of the two fragments formed from homolytic cleavage of the carbon-sulfur bond.

Acetylenic sulfones (1) represent an interesting class of dienophiles in view of the various reaction modes which can be predicted on the basis of their unusual ways of addition to unsaturated substrates.¹⁻⁴ For example, (4+2)-cycloaddition¹ could afford adduct 2, (2+2)-cycloaddition² would result in adducts 3, fragmentation-addition⁴ would possibly give the 1,4-addition product 4.

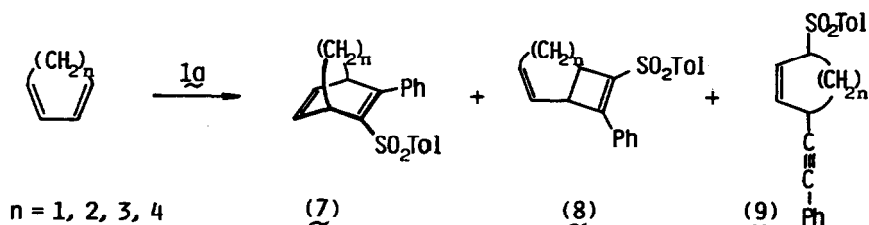


Following our interest in the cycloaddition behavior and in the synthetic potentiality of unsaturated sulfonyl derivatives⁵ we have examined the reactivity of phenyl(tolylsulfonyl)acetylene (1a: R=Ph, R'=Tol)⁶ with conjugated and homo-conjugated dienes and herewith we report that it may cover all the three aforementioned reaction modes depending upon the substrate.

Reaction of 1a with the acyclic diene, 2,3-dimethyl-1,3-butadiene in refluxing toluene afforded cycloadduct 5 (mp 128-130 °C from CH₂Cl₂/Et₂O) and small, variable quantities of 6 (mp 149-150 °C from MeOH) in 90 % combined yield.⁷ Biphenyl 6 may be accounted for air oxidation of the primary cycloadduct under the reaction conditions. Alternatively it could be obtained quantitatively by treatment of 5 with dichlorodicyanoquinone (DDQ) in refluxing chloroform.

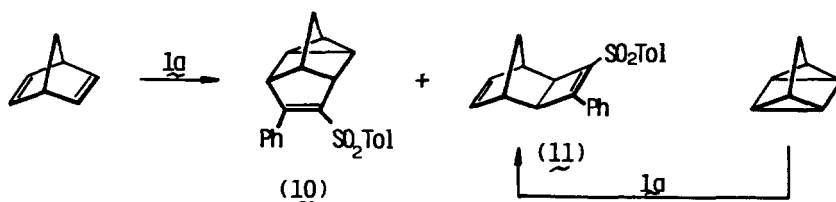


Cyclic dienes afforded with 1a different products depending on the ring size. Cyclopentadiene reacted in dichloromethane at room temperature and the expected Diels-Alder adduct 7 (n=1, mp 96.5-97.5 °C from MeOH) was formed quantitatively.⁷ 1,3-Cyclohexadiene heated neat with 1a at 120 °C for 4 h also gave the (4+2)-adduct 7 (n=2, 35 %, mp 134-136 °C from MeOH) but in lower yields, together with the (2+2)-cycloadduct 8 (n=2, 20 %, oil). The fragmentation-addition product 9 was formed beside 7 and 8 in the reaction of 1a with 1,3-cycloheptadiene (7, n=3, 25 %, oil; 8, n=3, 35 %, mp 131-2 °C from MeOH; 9, n=3, 15 %, oil) and was the only product observed in the reaction with 1,3-cyclooctadiene (9, n=4, 65 %, oil).⁷ The assignment of the structures was based upon IR, ¹H- and ¹³C-NMR spectra analyses. Unfortunately it could not be possible to determine the exact configuration of adducts 9 but it is supposed that the addition proceed preferentially with anti stereochemistry as it has been unequivocally shown in the addition of 1a to olefins.^{4,8} The relative position of the phenyl and tosyl group in the (2+2)-cycloadducts 8 relies on an X-ray structure determination of the adduct to cyclohexadiene.

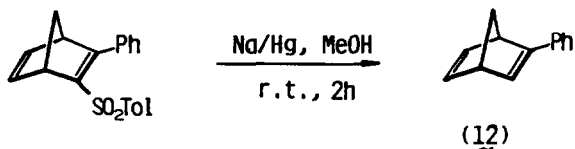


Although the observed regiochemistry is somewhat unexpected on the assumption of a dipolar character of the initial (2+2)-cycloaddition (which should preferentially set the negative charge next to the sulfur atom of the dienophile and the positive charge on the allylic carbon of the diene) there are precedents of similar results in related reactions.⁷

Norbornadiene afforded with 1a at 110 °C for 4 h the expected homo-(4+2)-cycloadduct 10 (mp 128-129 °C from CH₂Cl₂/Et₂O) and the (2+2)-cycloadduct 11 (mp 105-107 °C from MeOH) which were separated by silica gel column chromatography in 57 and 11 % yields respectively.⁷ Quadricyclane reacted slowly (ca. 15 days) with 1a in dichloromethane at room temperature to afford 60 % yield of the tricyclic compound 11 identical to the minor product obtained in the reaction with norbornadiene, confirming the structure assignment.



The adducts of 1a to dienes are of good synthetic potentiality as they can be subjected to the various and rich chemistry of unsaturated sulfones.¹⁰ For example, sodium amalgam reduction in buffered methanol of adduct 7 (n=1) gave hydrocarbon 12 in 95 % yield.¹¹ In this context 1a can be considered as a synthetic equivalent of phenyl acetylene in a cycloaddition reaction which is not possible with the direct use of the unactivated alkyne.¹²



Hydrocarbons of the type 12 can be obtained only in very low yield with alternative methods¹³ despite their potential utility because of the effect which can be produced in norbornadienes with appropriate aromatic substituents and which can be useful in solar energy storage.¹⁴ In this regard, the synthesis of other substituted norbornadienes and of other polycyclic unsaturated hydrocarbons is under investigation.

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- Correct elemental analysis and spectral data consistent with the given structures were obtained for all reported compounds. The yields of the adducts to cyclic 1,3-dienes may vary on changing the reaction conditions. Cycloadducts 7 do not convert into 8 under the employed reaction conditions, as shown by control experiments. The fragmentation-addition reactions are radical in character and susceptible to the presence of radical initiators (see ref. 2 and Russell, G.A.; Ngoviwatchai, P. Tetrahedron Lett. 1986, 27, 3479).
- The anti addition is supported by the comparison of the $^1\text{H-NMR}$ of 9 with that of the addition product of tolylsulfonyl cyanide to cyclooctadiene. We thank Prof. Fang for the spectral data.
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- In this respect the present method is an expansion of the use of tolylsulfonyl acetylene as equivalent of acetylene in cycloaddition reactions (Ref. 1a). For other examples see: De Lucchi, O.; Modena, G. Tetrahedron 1984, 40, 2585. Altenbach, H.-J.; Blech, B.; Marco, J.A.; Vogel, E. Angew. Chem., Int. Ed. Engl. 1982, 21, 778.
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