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DIENOPHILIC REACTIVITY OF TRANS-1,2-BIS(PHENYLSULPHONYL)ETHYLENE: A VALID ALTERNATIVE TO MALEIC ANHYDRIDE

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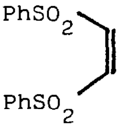
Trans-1,2-bis(phenylsulphonyl)ethylene (7) is a valid alternative to maleic anhydride since it possesses comparable dienophilic reactivity and its adducts can be desulphonylated by reductive processes while those of maleic anhydride need oxydative conditions.

Recently we have reported that cis-1,2-bis(phenylsulphonyl)ethylene (1) is a powerfull dienophile and a valuable acetylene equivalent in cycloaddition reactions[1]. 1 represents already an interesting substitute to maleic anhydride or related carbonyl derivative for the synthesis of mono and polycyclic olefins as they can be easily obtained by the Diels-Alder reaction of 1 with appropriate dienes and reductive elimination of the phenylsulphonyl groups, whereas maleic anhydride requires strong oxydative conditions to perform such transformation[2].



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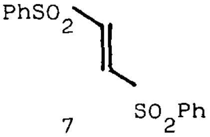


7

However we had to notice that the reactivity of 1 is lower than that of maleic anhydride as it does not cycloadd to less conventional dienes like furane (2), cycloheptadiene (3), cyclooctatetraene (4), indene (5) and ß-naphtol (6) preventing a convenient access to a family of quite interesting polycyclic dienes by this route. We have observed that the reactivity limits of 1 were, at least in part, related to its thermal instability which did not allow to adopt more forcing conditions (higher temperatures, longer reaction times, etc.) that the lower reactivity of these dienes would have required[3]. We therefore focused our attention on the trans isomers of 1, i.e. trans-1,2-bis(phenylsulphonyl)ethylene (7) which is thermally more stable even though much less soluble in usual solvents. It turned out that 7 is not only more stable but also more reactive than 1[4]. Indeed it reacted with everyone of the typical "unreactive" dienes and indeed with everyone we tested.

Quite surprisingly 7 reacts with furane (2) in methylene chloride at room temperature to give in a few days almost quantitative yields of 8. This contrasts with earlier work[5] which reported the failure of this reaction. However, different solvents were then used and the almost complete insolubility of 8 in methylene chloride may be the driving force of the reaction under our experimental conditions.

The other reactions studied, summarized in the table, required more drastic conditions (see the table for details and yields).

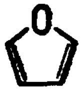
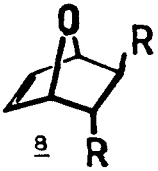
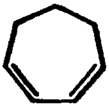
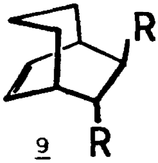
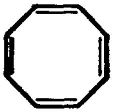
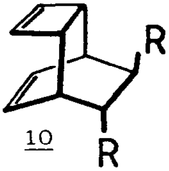
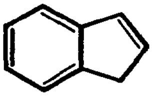
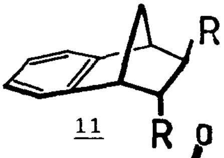
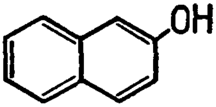
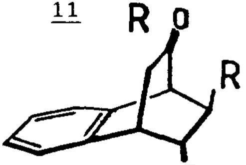
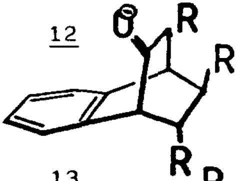
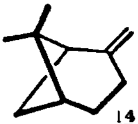
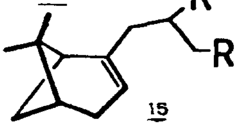
When the reactions are carried out in toluene or orto-dichlorobenzene as solvents, the end of the reaction can be easily monitored by simple cooling. In fact the dienophile 7 is practically insoluble in these solvents at room temperature and the completion of the reaction is indicated by the absence of any insoluble material in the cold clear yellow solution. The mole ratio between substrate and dienophile is also reported in the table. This ratio is particularly important in the case of cyclooctatetraene (4) reaction where, when a too high concentration is used, products derived by cycloaddition of 7 to dimeric structure of 4 are also formed.

The work up of the reaction usually involves evaporation of the solvent at reduced pressure and silica gel column chromatography (ca. 10/1 weight ratio silica to substrate) eluting with a gradient methylene chloride-ethyl ether up to 5% of the latter. The resulting oil is recrystallized by the appropriate solvent (see table).

In the case of ß-naphtol (6) the reaction gives better results when carried out without any solvent and affords the two isomeric products 12 and 13. Although they have been easily separated by column chromatography under the reported conditions they presents complex NMR spectra at 60 MHz so that a precise determination of the stereochemistry of the two adducts is still missing. A more in depth investigation has been undertaken including an X-ray structure determination.

Trans-1,2-bis(phenylsulphonyl)ethylene (7) may also give ene-reactions

Table: Conditions, Yields and Physical Contants of the Adducts of trans-1,2-bis(phenylsulphonyl)ethylene (7).

Diene	Adduct[a] $R=SO_2Ph$	Mole Ratio Substrate/ Dienophile	Reaction Conditions	Yield %	mp °C (Recryst. Solvent)
 2	 8	2	CH_2Cl_2 room temp. 2 days	95	216-226 (CH_2Cl_2)
 3	 9	1.3	Toluene[d] reflux 12 hrs	87	141-142 (CH_2Cl_2/ EtOET)[b]
 4	 10	1.0	o-DCB[c,d] reflux 4 hrs	85	155-156 (EtOEt)
 5	 11	1.5	o-DCB[c] reflux 24 hrs	20	87-88 (EtOEt)
 6	 12	2.5	neat 160-180°C 14 hrs	80 (ca. 1:1)	91-92[e] (EtOH)
	 13				239[e] (CH_2Cl_2/ EtOEt)[b]
 14	 15	1.5	Toluene[d] reflux 12 hrs	90	125-126 (EtOEt)

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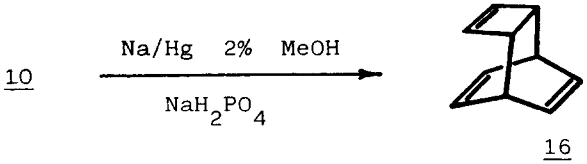
a) All new compounds present satisfactory elemental analysis and their IR and NMR spectra are in accordance with the proposed structures. b) Dissolved in the minimum amount of CH_2Cl_2 and added of ether. c) o-dichlorobenzene. d) Reactions runned into screw capped vials. e) The stereochemistry of these adducts is unknown.

with appropriate substrates as shown in the case of ß-pinene (14). α-Pinene, as in the case with maleic anhydride, did not react with 7 even under more drastic conditions.

The Diels-Alder adducts of 7 undergo reductive elimination under conditions similar to those already described for the cis isomers, opening new possibilities to the synthesis of interesting polycyclic olefins. As an example the Nenitzescu hydrocarbon 16[6], which is also the precursor of barralene[7], may be obtained in 75% yields by treatment of 10 with 2% sodium amalgam in methanol' buffered with sodium-dihydrogenphosphate.



This route to tricyclo $[4.2.2.0^{2.5}]$deca-3,7,9-triene (16) appears quite competitive in yields but expecially in semplicity to the ones so far reported, as 16 is obtained in greater than 50% overall yields in only a two step reaction.

We are continuously investigating the properties of sulphonylethylenes and further transformations of its adducts in view of the variety of synthetic processes which sulphones can be subjected to.

REFERENCIES AND NOTES

1. O. De Lucchi and G. Modena, J. Chem. Soc., Chem. Commun., 1982, 914; O. De Lucchi and G. Modena, Phosphorus and Sulfur, in press.
2. F. Merger in Houben-Weyl: "Methoden der Organischen Chemie", Thieme, Stuttgart, 1972, Vol. 5/1b, pp 345-351.
3. Partial decomposition as well as cis-trans isomerization of 1 was observed with the result to obtain intractable reaction mixtures.
4. J. Sauer, H. Wiest, and A. Mielert, Chem. Ber., 1964, 97, 3183.
5. H. R. Snyder and D. P. Hallada, J. Am. Chem. Soc., 1952, 74, 5595; W. E. Truce and R. J. McManimie, Ibid., 1953, 75, 1672.
6. M. Avram, E. Sliam, and C.D. Nenitzescu, Liebigs Ann. Chem., 1960, 636, 184.
7. W. G. Dauben, G. T. Rivers, R. J. Twieg, and W. T. Zimmerman, J. Org. Chem., 1976, 41, 887.

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