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1,1-BIS(BENZENESULFONYL)ETHYLENE: A USEFUL SYNTHON FOR NEUTRAL HOMOLOGATION OF KETONES

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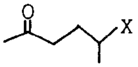
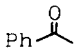
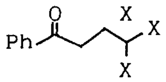
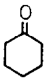
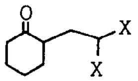
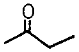
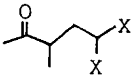
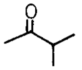
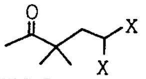
Summary: 1,1-Bis(benzenesulfonyl)ethylene (1) is a versatile building block in organic synthesis since it reacts under neutral conditions with enolizable ketones to afford adducts that can be subjected to a variety of synthetic transformations.

The reactivity of 1,1-bis(benzenesulfonyl)ethylene (1) toward olefins reported in the previous communication, prompted us to test it with other functional groups. Herewith we report that 1,1-bis(benzenesulfonyl)ethylene reacts, under neutral conditions, with enolizable ketones, to give adducts that can be transformed into a variety of useful molecules.[1]

On refluxing 1 in acetone for 2 h and evaporating the resulting clear solution, adduct 2 is obtained in virtually quantitative yield as colorless oil. The corresponding adducts have also been obtained when other enolizable ketones, as acetophenone and cyclohexanone, are used as substrates. Table 1 reports on the reaction conditions, yields and physical constants of these and the other obtained adducts. For those cases in which small quantities of substrate are on hand, and generally with precious ketones, the reaction can be performed in refluxing acetonitrile using equimolar amounts of reagents. It bears mentioning that if a 2:1 ratio reagent/ketone is used, possibility of polyadducts has to be considered.

With asymmetrical ketones both possible adducts are formed, although the one derived from the addition to the more stable enolic form strongly predominates. For example 2-butanone gives the adduct to the more substituted carbon in 80% while the other is formed only in traces. Even with the more sterically hindered isopentan-3-one the adduct to the disubstituted carbon is obtained regio-

Table: Reaction Conditions, Yields and Physical Constants of the Adducts of 1,1-Bis(Benzenesulfonyl)Ethylene **1** to Ketones ($X = SO_2Ph$).

Substrate	Product	Reaction Conditions	Solvent	Time h	Yield	mp (°C) (recryst. solv.) or bp (°C) Kugelrohr
		reflux	neat	4	90	oil (250, 0.002 torr)
		110°C	acetonitrile	8	80	132-134 (EtOH)
		110°C	acetonitrile	4	75	144.5-145.5(EtOH)
		reflux	neat	4	75	84-85 (MeOH)
		reflux	neat	6	80	117 (MeOH)

selectively (see Table). The 2-phenyl substituted 1,1-bis(benzenesulfonyl)-ethylene did not react under the present experimental conditions neither with acetone nor with cyclohexanone.[2]

The mechanism responsible for the addition is still uncertain, but it is likely that the reaction involves electrophilic attack of the ß-carbon of **1** to the enolic carbon, followed by proton transfer. The ^{13}C-NMR spectrum of **1** shows the two carbon resonances at δ 145 and 130 respectively for C_1 and C_2. Although a positive charge at the C_2 carbon is not evident, the driving force for the reaction might be the generation of a doubly sulfonyl stabilized anion.

The present method of homologation of ketones which does not require basic conditions, presents as main future with respect to the existing procedures that the regiochemistry of alkylation is the opposite of that preferred in the alkylation of enolates[3] and enamines.[4] We are currently investigating the application of this methodology and the transformation of the adducts into useful molecules.[1]

REFERENCES AND NOTES

1. For the transformation of 1,1-bis(benzenesulfonyl)derivatives see for example: Trost, B.M.; Shimizu, M. J. Am. Chem. Soc. **1983**, 105, 6757.
2. Preliminary experiments show that **1** reacts also under neutral conditions with alcohols, thiols, amines as well as with other nucleophiles and that it can serve as a convenient protective reagent of these functional groups.
3. House, H.O. Rec. Chem. Prog. **1968**, 28, 99.
4. Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrel, R. J. Am. Chem. Soc. **1963**, 85, 207; Alt, G.H. in "Enamines"; Cook, A.G. Ed.; M. Dekker, New York 1969.

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