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(DIMETHYLAMINO)-PHENYL-(2-PHENYLVINYL)-OXOSULFONIUM FLUOROBORATE. A MODEL REAGENT FOR ETHYLENE TRANSFER TO DIBASIC NUCLEOPHILES[1]

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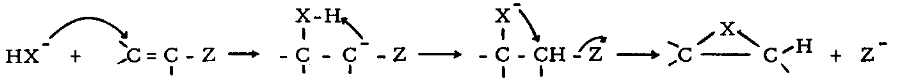
Reactive Michael receptors in which the electronegative activator (Z) is also an excellent leaving group should be capable of ethylene transfer to dibasic nucleophiles (HX^-) (eq. 1). In such reactions the intermediate, after



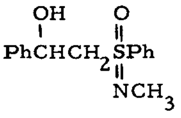
(1)

proton transfer, would be identical with that produced by the addition of an ylide or anion to $>C=X$ (eq. 2). Relatively few examples of reactions of

$$>C=X \; + \; {}^{-}\underset{|}{C}H-Z \longrightarrow -\underset{|}{\overset{X^-}{\overset{|}{C}}}-\underset{|}{C}H-Z \qquad (2)$$

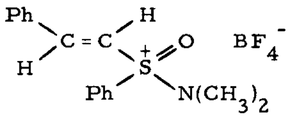
the type described in eq. 1 are known. Somewhat related is the addition of primary amines to α-bromobenzalacetophenone to yield N-substituted 2-benzoyl-3-phenylaziridines.[2] The most direct examples are found in the work of Gosselck and coworkers[3] who have produced polysubstituted cyclopropanes by the addition of active methylene compounds to substituted vinyldimethylsulfonium salts.

Reaction of lithium N-methylbenzenesulfonimidoylmethide with benzaldehyde gave 1,[4] which was readily dehydrated (TsOH, toluene) and N-methylated (trimethyloxonium fluoroborate) to give trans-dimethylaminophenyl-(2-phenylvinyl)-oxosulfonium fluoroborate (2), mp 130-131.5°, nmr ($CDCl_3$) δ 3.09 (s, 6), 7.3-8.4 (m, 12). The ease of preparation and handling of 2, coupled with its versatility in high yield reactions of the type described in eq. 1 prompts this preliminary discussion of our results.



$\overset{\text{OH}}{\text{PhCH}}\text{CH}_2\overset{\text{O}}{\underset{\text{NCH}_3}{\text{S}}}\text{Ph}$

1



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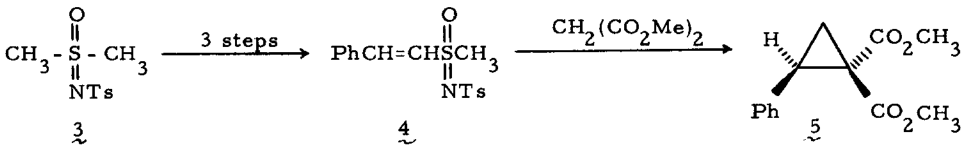
The variety of dibasic nucleophiles to which ethylene transfer from salt 2 has been achieved includes primary amines, enamines, and active methylene compounds. In large part, the reactions summarized in Table I are straightforward, but particular note should be made of the production of the dihydrofuran (reaction 5) and the structural variation of the products from enamines (reactions 3 and 4).

The general method is applicable to assymetric synthesis. Optically active (-)-(*S*)-2, $[\alpha]_D$ -5.7° (c 1.05, acetone), mp 113-115°, was obtained from optically pure (-)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine. Reaction of (-)-(*S*)-2 with methyl cyanoacetate in methanol containing 1 equiv. of sodium methoxide gave exclusively the (*E*)-isomer (81%), (+)-(1*S*, 2*R*)-methyl 1-cyano-2 phenylcyclopropanecarboxylate, $[\alpha]_{546}$ 64° (c 0.62, ethyl acetate) of 25.5% optical purity.[4]



3

4

5

In a related chemistry reagent, 4, mp 150-152.5°, nmr ($CDCl_3$) δ 2.38 (s, 3), 3.42 (s, 3), 7.05 and 7.7 (AB quartet, 2 J = 16 Hz), 7.2-8.0 (m, 8), has been produced in three steps from the commercially available[5] *N*-*p*-toluenesulfonyl dimethylsulfoximine (3); the benzoyl derivative prepared by condensation of the sodium salt[6] of 3 with methyl benzoate or benzonitrile was reduced ($NaBH_4$) and dehydrated. Preliminary work indicates the 4 is less reactive than 2, but it has the potential advantages of simpler preparation and by-product insolubility. Reaction of 4 with dimethyl malonate in ethanol-sodium ethoxide gave 77% of dimethyl 2-phenylcyclopropanedicarboxylate (5).

Acknowledgement

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TABLE I

Reactions of Dimethylaminophenyl-(2-phenylvinyl)oxosulfonium Fluoroborate (**2**)

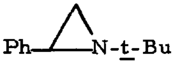
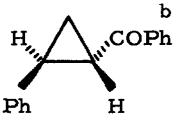
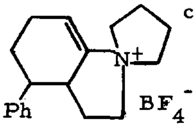
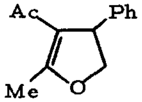
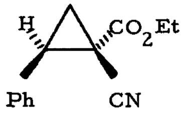
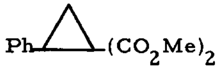
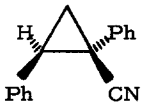
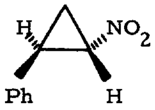
Reaction	Dibasic Nucleophile	Conditions, 25°	Product[a]	Yield, %
1	tert-Butylamine	xs, THF		86
2	Methylamine	xs, THF		34[d]
3	α-Dimethylaminostyrene	1 equiv, THF	 [b]	72
4	1-Pyrrolidinocyclohexene	1 equiv, THF	 [c]	91
5	Acetylacetone	NaOMe (1 equiv.), MeOH		85
6	Ethyl cyanoacetate	NaOEt (1 equiv.), EtOH		95
7	Methyl cyanoacetate	NaOMe (1 equiv.), MeOH		80

Table I continued

8	Dimethyl malonate	NaOMe (1 equiv.), MeOH		91
9	Phenylacetonitrile	n-BuLi (1 equiv.), THF		60
10	Nitromethane	NaOMe (1 equiv.), MeOH		44

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[a] All products were identified by comparison with literature data and/or authentic samples (except reaction 4). [b] After hydrolysis with methanolic HCl. [c] Product resistant to hydrolysis by methanol HCl and aqueous NaOH. [d] Plus 34% of N-methylbenzylidenimine.

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