NN-Diacyl Arylsulphenamides as an Unambiguous and Convenient Source of Arylsulphenium Ions

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Summary Singlet *p*-nitrophenylsulphenium ions can be generated conveniently from the readily available *NN*-diacetyl-*p*-nitrophenylsulphenamide and trifluoroacetic acid, as confirmed by kinetic studies; it adds stereospecifically to olefins and substitutes into anisole quantitatively.

WE have recently extended our work on arylnitrenes[1] to aryloxenium ions,[2] and to arylsulphenium ions.[3] The latter species have been the subject of much interest[4] for, in addition to being isoelectronic with carbenes, nitrenes, and oxenium ions, phenylsulphenium ion itself has been reported to complex with molecular nitrogen.[5] Most of the evidence for sulphenium ion formation is based on analogy, *i.e.* the types of products formed compared with those obtained in carbenium ion chemistry. The kinetic data available[4a] are not clear cut and suffer from the additional complication that a nitro-group is present *ortho* to the potential sulphenium ion, so that one can imagine the possibility of neighbouring group participation by the *o*-NO_2 group in the elimination process resulting in the formation of an S–O bond.[4a] If this were the case a free sulphenium ion would not be formed.

The possible formation of *p*-nitrophenylsulphenium tetrafluoroborate from *p*-nitrophenylthiopyridinium tetrafluoroborate, and its reaction with anisole, have been reported.[3] We now describe a convenient unambiguous generation of the free *p*-nitrophenylsulphenium ion (**1**) and some of its reactions.

Preliminary results[2a] indicated that *NN*-diacetyl-*p*-nitrophenoxyamine served as a source of *p*-nitrophenoxenium ion when it was heated in the presence of 1 equiv. of trifluoroacetic acid. *NN*-Diacetyl-*p*-nitrophenylsulphenamide (**2**)‡ was readily obtained (92%; m.p. 87 °C) from diacetamide, *p*-nitrobenzenesulphenyl chloride, and triethylamine in CCl_4. Treatment of (**2**) in CH_2Cl_2 with anisole and 2·6 equiv. of dry CF_3CO_2H at room temperature gave 4-methoxyphenyl 4′-nitrophenyl sulphide (**3**)[6] (96%) and diacetamide (99%). If the reaction was carried out at 190—200 °C (**3**) was again formed (100%) but so was some *p*-methoxyacetophenone (21%), presumably owing to the formation of an acetylium ion from diacetamide and acid at elevated

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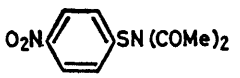
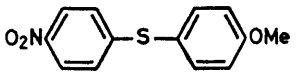
‡ All new compounds gave satisfactory microanalytical and spectral data.

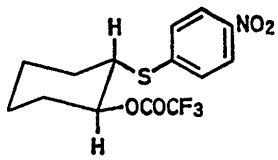
temperature. On the other hand, (**2**) did not react with benzene in the presence of CF_3CO_2H at room temperature Only bis-*p*-nitrophenyl disulphide was formed.



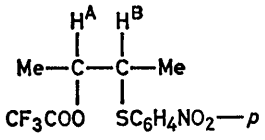
(**2**)



(**3**)



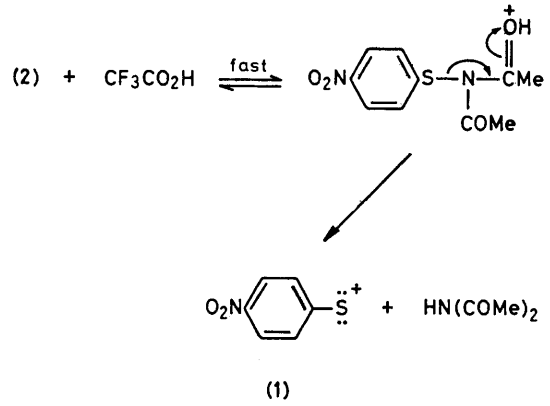
(**4**)



(**5**) *threo*

(**6**) *erythro*

Reaction of (**2**) with cyclohexene in the presence of CF_3CO_2H gave (**4**) (99%), m.p. 56—57 °C, and diacetamide (100%). The *trans* geometry in (**4**) was clearly indicated by the coupling constants for the diaxial protons at C-1 and C-2: δ 5·0 (sextet, $J_{1,2}$ 13 Hz, 2-H), 3·5 (sextet, $J_{1,2}$ 13 Hz, 1-H). The addition is highly stereoselective and proceeds with retention in the geometry of the groups in the starting olefin. Thus, (**2**) and *trans*-but-2-ene with CF_3CO_2H in CCl_4 gave *threo*-2-trifluoroacetoxy-3-(*p*-nitrophenylthio)butane (**5**) (J_{AB} 3·9 Hz), b.p. 155 °C/0·1 mmHg (74% isolated yield), completely free of any *erythro*-isomer as indicated by h.p.l.c. on a 4 mm × 30 cm μporasil column using methylene dichloride–iso-octene (20:80 v/v) as a solvent and a flow rate of 2 ml/min. Similarly, (**2**) and *cis*-but-2-ene gave *erythro*-isomer (**6**) (J_{AB} 4·6 Hz), m.p. 50—51 °C, (73% isolated yield), free of *threo*-isomer. In both cases, diacetamide was isolated quantitatively. H.p.l.c. analysis of the crude reaction mixture from *trans*-but-2-ene showed the presence of only the *threo*-isomer (**5**). With *cis*-but-2-ene, (**6**) (96·6%) and (**5**) (3·4%) were detected and characterised. The corresponding *threo*- and *erythro*-alcohols (from the trifluoroacetates and Et_3N) had J_{AB} 3·2 and 5·6 Hz, respectively, which are in the relative order of magnitudes expected.[7]



(**1**)

Definitive evidence for the intermediacy of (**1**) in these reactions came from kinetic studies. The decomposition of (**1**) in CCl_4 containing anisole or cyclohexene in the presence of CF_3CO_2H was studied at 20—70 °C. In all cases, the reactions were first order in (**1**) and were independent of the concentration of anisole or of cyclohexene.§[8] Thus, protonated (**2**) undergoes remarkably smooth heterolysis under very mild conditions to generate diacetamide and singlet *p*-nitrophenylsulphenium ion (**1**). Addition to olefins probably involves formation of an intermediate episulphonium salt[4d] which then undergoes rearside attack by the available counterion, $CF_3CO_2^-$ in this case, to give (**4**), (**5**), or (**6**). It remains to be determined whether attack on aromatic nuclei involves initial formation of an episulphonium salt (*cf.* aryl-[9] and sulphonyl-nitrene reactions[10]) or the direct formation of a σ-complex.

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§ With both substrates the following rate constants were found: $k_{20} = 0{\cdot}25 \times 10^{-5}$ s^{-1}, $k_{40} = 2 \times 10^{-5}$ s^{-1}, $k_{60} = 14 \times 10^{-5}$ s^{-1} and $k_{70} = 17 \times 10^{-5}$ s^{-1}. The activation parameters in both cases were: $E_a = 82{\cdot}84$ kJ mol^{-1} and $\Delta S^{\ddagger} = -78{\cdot}24$ J K^{-1} mol^{-1} (ref. 8).

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