Tetrahedron Letters No.6, pp. 337-340, 1965. Pergamon Press Ltd.
Printed in Great Britain.

CHEMISTRY OF α-DIAZOSULPHONES

The synthesis of α-diazo-β-carbonylsulphones

A.M.van Leusen, P.M.Smid and J.Strating
Department of Organic Chemistry of the University,
Bloemsingel 10, Groningen, The Netherlands

(Received 12 December 1964)

Aryl- and alkyl-sulphonyldiazomethanes (I) have been prepared by alkaline decomposition of substituted nitrosourethanes (1).

$$RSO_2CH_2N(NO)CO_2C_2H_5 \longrightarrow RSO_2CHN_2 \quad (I)$$

Bis-sulphonyldiazomethanes have been obtained by Klages and Bott (2) from bis-sulphonylmethanes with p-tosylazide and alkali (3). These authors report (without examples) that this method cannot be used for the synthesis of α-diazomonosulphones (I). We found this statement valid, even for the activated methylene in 2,4-dinitrobenzyl p-tolyl sulphone, using the procedures described below.

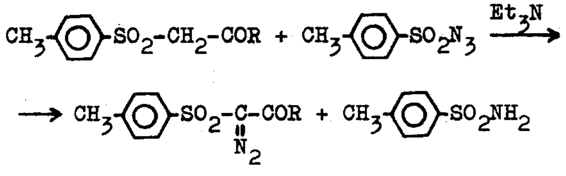
Recent work of Regitz (4) and Rosenberger and Yates (5) on the tosylazide-reaction with β-dicarbonylic compounds and benzylketones made a successful application of this reaction to β-carbonylsulphones very probable.

We have investigated this reaction with β-ketosulphones*)

---

*) Dr.M.Regitz kindly informed us very recently that he has investigated the same reaction and that a paper on a "α-Diazo-β-ketosulfon" is in the press (Chem.Ber.).

and with sulphonylacetic esters. Using the procedure of Klages and Bott (2), or preferably with triethylamine instead of sodium hydroxide (5), p-tolylsulphonylacetone was transformed into α-acetyl-α-(p-tolylsulphonyl)-diazomethane (II) (yield 70%).



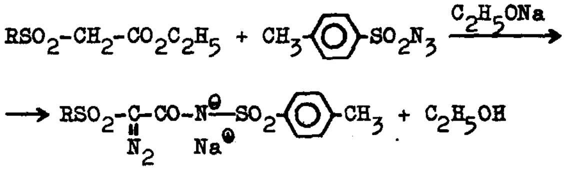
II R = CH_3-

III R = C_6H_5-

The structure of the yellow compound II (m.p. 109-110°, decomp.) follows: a) from the elemental analysis (C, H, N, S), b) from comparison of the NMR spectra of the starting material (methylene singlet at τ 5.85 in $CDCl_3$ with respect to TMS) and the product in which the methylene singlet is absent and c) from the diazo band in the IR spectrum at 2110 cm^{-1} and a carbonyl band at low frequency (1660 cm^{-1} in nujol).

In the same way α-benzoyl-α-(p-tolylsulphonyl)-diazomethane (III) was prepared in 60% yield; again a yellow compound (m.p.101-102°, decomp.) with a correct CHNS analysis, with no signal at τ 5.26 (in $CDCl_3$) as the starting material does and with a diazo band at 2100 cm^{-1} and a carbonyl absorption at 1650 cm^{-1} (nujol).

The reaction of the sulphonylacetic esters took a somewhat different course. With equimolecular quantities of ethyl p-tolylsulphonylacetate, sodium ethoxide (with triethylamine as a base no reaction occurred) and p-tosylazide in absolute ethanol-ether (1 : 1) (at 0°) a yellow precipitate was formed almost immediately (yield 70%) which was not the expected α-carboxyethyl-α-(p-tolylsulphonyl)-diazomethane but IV.



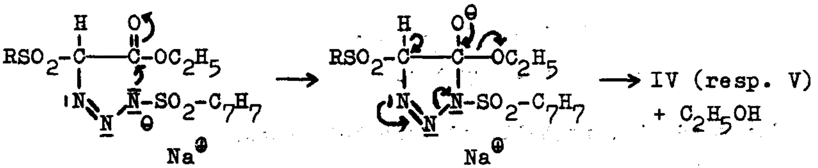
IV R = p-CH_3-C_6H_4-

V R = $(CH_3)_3C$-

Compound IV (crystallized from hot ethanol) decomposed at about 175°. The structure assigned to IV is in accordance with the following observations: a) a satisfactory elemental analysis (CHNNaS), b) the poor solubility in the common organic solvents, c) a diazo band at 2140 cm^{-1} and a carbonyl absorption at very low frequency (1595 cm^{-1} in nujol) and d) the NMR spectrum in D_2O (containing some water) revealed the presence of two different p-tolyl groups and apart from the H_2O peak no other signals were observed. As for the NMR spectrum two separate AB quartets for the phenyl protons in the region τ 2-3 and two methyl singlets at τ 7.81 and 7.72 could be discerned (the τ -values are measured with respect to TMS in CCl_4 run in a separate tube).

Similar results were obtained in the reaction of ethyl t-butylsulphonylacetate (6) giving 60% of V, a pale yellow compound (crystallized from ethanol-methanol mixture) decomposing at about 165°. Elemental analyses (CHNNaS) were correct again. The infrared spectrum revealed a diazo band at 2115 cm^{-1} and a carbonyl absorption (doublet) at 1585 and 1560 cm^{-1} (nujol). The NMR spectrum in D_2O (as above) now showed only one AB quartet for the phenyl protons(τ 2-3), one methyl singlet at τ 7.61 and a t-butyl singlet at τ 8.64.

A possible explanation of the formation of IV and V is indicated below, starting with the addition complex (VI) of the anion of sulphonylacetic ester and p-tosylazide:



(VI)

Alternatively p-toluenesulphonamide sodium, which is first split off from VI, attacks the ester group of the intermediately formed α-sulphonyldiazoacetate leading to the same products.

Similar results have been published recently by Regitz (4b) with ethyl p-nitrophenylacetate.

References.

(1) Part IV and V in this series: A.M.van Leusen and J.Strating, Rec.Trav.Chim., in the press (1965); preliminary communication, ibid. 81,966(1962). The present letter should be considered as part VI in this series.
(2) F.Klages and K.Bott, Chem.Ber. 97,735(1964).
(3) W.v.E.Doering and C.H.De Puy, J.Amer.Chem.Soc. 75, 5955(1953); T.Weil and M.Cais, J.Org.Chem. 28,2472 (1963).
(4) (a) M.Regitz, Chem.Ber. 97,2742(1964) and foregoing papers;
(b) M.Regitz, Tetrahedron Letters 1964,1403.
(5) M.Rosenberger and P.Yates, ibid. 1964,2285.
(6) Ref.(1), part IV.