Tetrahedron Letters No. 19, pp 1565 - 1566, 1975. Pergamon Press. Printed in Great Britain.

ARYLDIAZOALKANES FROM *o*-NITROBENZENESULFENYLHYDRAZONES

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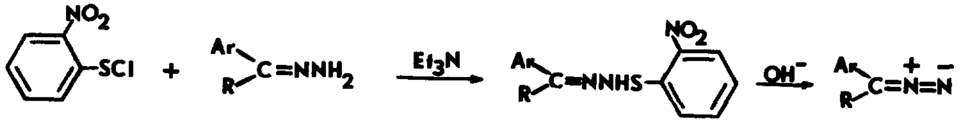
(Received in USA 27 February 1975; received in UK for publication 1 April 1975)

The value of the *sulfinate* ion as a leaving group in nitrogen chemistry has been amply demonstrated by a host of reactions such as the Bamford-Stevens,[1] McFadyen-Stevens,[2] Carpino[3] and diazo transfer[4] *inter alia*. Recently, we have shown that *sulfenate* ions can also be used for similar purposes.[5,6] Given the well-known stability of the mercaptide ion, it was natural to go down the sulfur oxidation scale and examine the mercaptide ion as a leaving group in base-catalyzed α-eliminations. The recent communication of Cacchi and Paolucci[7] which appeared while our work was in progress, prompts us to disclose our own results briefly.

The reaction of *o*-nitrobenzenesulfenyl chloride (*o*-NBSCl) with benzal- and benzophenone hydrazones (IIa and IIb) in the presence of triethylamine gave the corresponding *o*-nitrobenzenesulfenylhydrazones IIIa, mp. 128-128.5° and IIIb, mp. 147-147.5° as canary yellow compounds. These structures were supported by excellent combustion analyses and by the infrared spectra which exhibited bands at



a) Ar = Ph, R = H; b) Ar = R = Ph; c) Ar = R = 9-Fluorenyl

∿ 3200 cm^{-1} (NH), 1575 cm^{-1} (C=N), 1300 cm^{-1} (NO_2) and 850 cm^{-1} (N-S?) in addition to aromatic absorptions. IIIc was obtained as a fairly unstable orange-yellow amorphous solid, which could not be purified; however, an infrared spectrum of crude

IIIc showed all the bands listed above for IIIa and IIIb.

The structure of the o-nitrobenzenesulfenylhydrazones (III) was further confirmed by their reaction with base. Typically, treatment of a solution of III with an equimolar amount of a saturated solution of potassium hydroxide in methanol at room temperature, resulted in immediate darkening of the solution to bluish-black color. After having been washed with cold water and dried, the ethereal solution was evaporated in the cold to leave the diazoalkanes which exhibitied strong diazo bands at ∿ 2020 cm^{-1}.[8] IIIb was isolated in 75% yield as deep wine-red liquid whose infrared spectrum was identical to that of an authentic sample. IIIc was obtained in 72% yield as a reddish-orange solid, mp. 88-90°, lit.[9] mp. 94-95°. Its infrared spectrum was superimposable to that of an authentic sample. Since IIIa was rather unstable, its yield was determined by titration with benzoic acid (45%). Bis(o-nitrophenyl) disulfide, presumably arising from air oxidation of the mercaptide[10] was isolated in each case.

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†Taken from the B. A. Thesis of David E. Dana, University of Massachusetts at Boston, 1975.

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