served by Battiste[22] for six nonplanar phenyl groups in hexaphenyltropenylium ion.

(22) M. A. Battiste and T. J. Barton, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 13, 1966.

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Cleavage of Sulfonamides with Sodium Naphthalene[1]

Sir:

We wish to report that regeneration of amines from many types of sulfonamides can be achieved in excellent yield by treatment with sodium naphthalene anion radical in 1,2-dimethoxyethane solution. The procedure consists simply of mixing either the solid sulfonamide or its solution (in dimethoxyethane) with 3–6 equiv of sodium naphthalene in dimethoxyethane under nitrogen or argon and stirring the resulting solution for ~1 hr at room temperature. Addition of a small amount of water quenches the reaction, and the amine may be isolated by usual procedures. Some typical results are presented in Table I.

The technique is quite similar to that reported earlier for cleavage of toluenesulfonates,[2] but the sulfonamide cleavage appears to proceed slightly better in dimethoxyethane than in tetrahydrofuran solution.[3] Dimethoxyethane does react slowly with sodium naphthalene[4] but the process is slow enough at room temperature that it does not interfere with the cleavage reaction.

From Table I it can be seen that benzene- and *p*-toluenesulfonamides of most simple amines are cleaved in yields of over 90%, but methanesulfonyl derivatives exhibit variable behavior. In particular, it appears that methanesulfonamides of primary or aliphatic amines are inert to the cleavage conditions. Toluenesulfonamides of some simple dipeptides have been cleaved in good yield by this technique (see Table I), and the method may be of use in peptide synthesis. The well-known ease of N-alkylation of sulfonamides of primary amines[5] also makes possible a relatively simple synthesis of a wide variety of pure secondary amines.

Table I. Cleavage of Sulfonamides with Sodium Naphthalene[a]

Sulfonamide (mp, °C)	Yield of amine, %[b,c]	Sulfonamide (mp, °C)	Yield of amine, %[b,c]	Sulfonamide (mp, °C)	Yield of amine, %[b,c]
N-*p*-Tolylbenzene-	99 (86)[d]	N-*p*-Tolyl-*p*-chlorobenzene	89	N-Octylmethane- (56.3–56.6°)[e]	<2[i]
N-Methyl-N-phenylbenzene-	100	N-Methyl-N-phenyl-*p*-chlorobenzene- (95–95.4°)[e]	67	N-*p*-Tolylmethane-	9
N-Octylbenzene- (52.5–53.5°)[e]	97 (65)	N-*p*-Tolyl-*p*-bromobenzene-	89	N-Methanesulfonyl-piperidine (48.5–50°)[e]	0[i]
N-*p*-Tolyl-*p*-toluene- Sodium salt (>300°)[f]	87 (93)[d] 88	N-*p*-Tolyl-*p*-acetamidobenzene-	80	N-Methyl-N-phenylmethane-	92
N-*p*-Anisyl-*p*-toluene-	98 (94)[d]	N-*p*-Tolyl-*p*-methoxybenzene- (109.5–110°)[e]	95 (83)	N,N-Diphenylmethane- (116.5–117°)[e]	94
N-Phenyl-*p*-toluene-	(97)	N-Methyl-N-phenyl-*p*-methoxybenzene- (109–110.3)[e]	92	N-*p*-Toluenesulfonylglycylglycine	87[i]
N-Hexyl-*p*-toluene- (59–60°)[e]	(96)[d]	N-*p*-Tolyl-β-naphthalene-	89 (93)[d]	N-*p*-Toluenesulfonyl-DL-alanyl-DL-leucine[k,l]	95[i]
N-Octyl-*p*-toluene-	98 (95)	N-Methyl-N-phenyl-β-naphthalene- (102–102.6°)[e]	91	N-*p*-Toluenesulfonyl-DL-leucyl-DL-alanine[k,m]	93[i]
N-(2-Heptyl)-*p*-toluene- (oil)[g]	(91)	N-Octyl-α-toluene- (100–101°)[e]	84	N-*p*-Toluenesulfonyl-DL-alanyl-DL-valine (188–190°)[k]	89[i]
N-(1-Phenylethyl)-*p*-toluene- (82–83°)[e]	(98)	N-α-Toluenesulfonylpiperidine (137.5–138°)[e]	62	N-*p*-Toluenesulfonyl-DL-alanyl-DL-phenylalanine (167–168°)[k]	96[i]
N-(*m*-Chlorophenyl)-*p*-toluene-	(94)[h]				
N-Methyl-N-phenyl-*p*-toluene-	96 (68)[d]				
N-*p*-Toluenesulfonylpiperidine	82				

[a] Unless otherwise specified, reactions were carried out by treating sulfonamide with 3–6 equiv of sodium naphthalene in dimethoxyethane at 25° under N_2 or Ar and stirring the mixture for about 1 hr before quenching with water. [b] Determined by gas chromatographic measurement of the amine or corresponding acyl derivative unless otherwise specified. Reproducibility was at least ±5%. [c] Figures in parentheses refer to yields using tetrahydrofuran solvent. [d] Isolated and weighed. [e] New compound; carbon–hydrogen analyses agree with calculated values. [f] Titration required 99.3% of theoretical amount of standard HCl solution. [g] Identity of material based on recovery of 2-heptylamine from cleavage reaction. [h] Product was aniline. [i] Unreacted sulfonamide recovered from reaction mixture. [j] Reactions run for 0.5–1 hr using 20 equiv of sodium naphthalene. Analysis was by ninhydrin colorimetry; identity of product was checked by thin-layer chromatography. [k] Identity of material based on recovery of corresponding dipeptide from cleavage reaction. [l] Ethyl ester: mp 95–98°. [m] Ethyl ester: mp 108–110°.

The only comparable cleavage techniques are those using alkali metal–liquid ammonia (or amine) com-

(1) Supported in part by the National Science Foundation (Grant GP-5658) and by the Public Health Service (Research Grant No. 1-RO1-AM11419-01 from the National Institute of Arthritis and Metabolic Diseases).

(2) W. D. Closson, S. Bank, and P. Wriede, *J. Am. Chem. Soc.*, **88**, 1581 (1966).

(3) An additional advantage of DME is the greater ease of formation of the anion radical in this solvent. For example, one can carry out the reaction by placing enough sodium, naphthalene, and DME in an erlenmeyer flask to yield a solution 0.5–1.0 *M* in anion radical, capping it with a rubber septum, and stirring it magnetically (glass-covered bar) for 1–1.5 hr. By this time the anion radical will have formed and have scavenged the O_2 from the interior of the flask, and a solution of the sulfonamide may then be injected by syringe through the septum. Quantitative yields of N-methylaniline from its toluenesulfonamide have been obtained in this fashion, and the technique should work equally well for toluenesulfonate ester cleavage.[2] The sodium–naphthalene dispersion (mole/mole, crushed solid), available from the Matheson Co., yields the anion radical even more rapidly on solution in DME, but the homogeneity of this material leaves a bit to be desired.

(4) N. D. Scott, J. F. Walker, and V. L. Hansley, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

(5) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, Chapter 7 and references listed therein; P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 1, W. A. Benjamin, Inc., New York, N. Y., 1965, p 73.

binations,[6] and the sodium naphthalene procedure is clearly more convenient for most cases. As in the case of alkali metal–ammonia cleavages, easily reduced functional groups, *e.g.*, halogen and cyano, do not survive, but the limitations this imposes on this new procedure have not yet been established.

The only organic products other than the amine formed in the cleavage reaction appear to be the corresponding sulfinate salt and desulfonated hydrocarbon, *e.g.*, toluene from toluenesulfonamides. No thiol product has been observed in any of the reactions, and both benzenethiol and *p*-toluenethiol were shown to be stable to the reaction conditions. Toluenesulfinate ion (from the sodium salt dihydrate) is slowly converted to toluene by excess sodium naphthalene in dimethoxyethane,[7] but this process does not seem to be fast enough to account for all the toluene produced in a typical cleavage reaction. More likely, there are two distinct cleavage processes involved, one yielding toluene directly and one producing sulfinate anion, similar to those postulated by Kovacs and Ghatak for sodium–liquid ammonia cleavage of tosylamides[8] but with the pathway for reduction of sulfinate to thiol being unavailable in the anion radical reaction.

One further interesting point is the lack of proton abstraction from the highly acidic sulfonamides of primary amines. Quenching in air (which does not affect dihydronaphthalenes already present) of the reaction mixture from *p*-toluidinetosylamide and sodium naphthalene yields no dihydronaphthalene, implying that only electron transfer from naphthalene occurs during the reaction. The sodium salt of this sulfonamide, which could also be produced by reaction of the amide anion with unreacted tosylamide, *is* cleaved in respectable yield (see Table I).

(6) V. du Vigneaud and O. K. Behrens, *J. Biol. Chem.*, 117 27 (1937); A. J. Birch and H. Smith, *Quart. Rev.* London), 12 17 (1958).

(7) This is contrary to the observed inertness of this salt in THF solutions,[2] but this difference in behavior may simply be due to differing solubilities of the salt in the different ether solvents. It is not very soluble in either.

(8) J. Kovacs and U. R. Ghatak, *J. Org. Chem.*, 31, 119 (1966).

(9) On leave from the Department of Chemistry, Brooklyn College, 1965–1966.

(10) National Science Foundation Undergraduate Research Participant, 1966.

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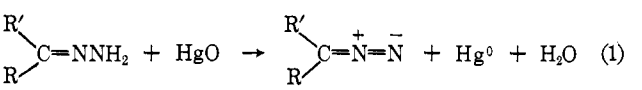
Diazoalkanes from Hydrazone Anions. A Novel Oxidation Reaction

Sir:

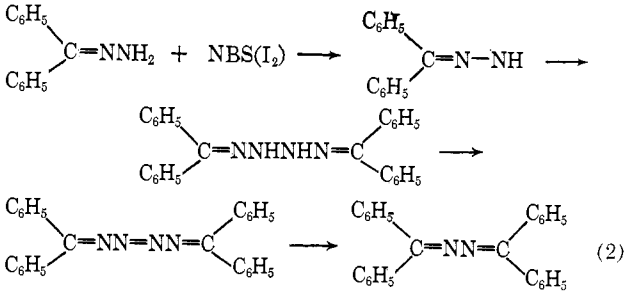
The oxidation of hydrazones with metal oxides such as those of mercury, silver, and manganese has long been a very useful method for the preparation of diazoalkanes.[1]

(1) P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. II, W. A. Benjamin, Inc., New York, N. Y., 1966, pp 258–259; C. G. Overberger, J.-P. Anselme, and J. G. Lombardino, "Organic Compounds with Nitrogen–Nitrogen Bonds," The Ronald Press Co., New York, N. Y., 1966, p 49.



(1)

Although not well understood, the mechanism is probably not radical in nature since, under conditions in which radicals are involved, the corresponding azines are obtained directly *without* the intervention of diazoalkanes. For example, the oxidation of benzophenone hydrazone with N-bromosuccinimide[2] or iodine[3] gives benzophenone azine, possibly *via* the following sequence of reactions.



(2)

During the course of our investigations of the chemistry of anions of nitrogen derivatives, we have discovered a remarkable oxidation. To a solution of benzophenone hydrazone in tetrahydrofuran at room temperature was added through a rubber septum an equimolar solution of methyllithium in tetrahydrofuran. The evolution of methane began immediately and a yellow solution of benzophenone hydrazone anion was obtained. Upon being stirred, the solution began to assume a reddish coloration and within 60 min became deep wine-red in color. The solution was shaken with water and the organic phase separated and dried. Upon evaporation of the solvent, a red oil was obtained. It was identified as diphenyldiazomethane by comparison of its infrared spectrum with that of an authentic sample and by its conversion to benzhydryl 3,5-dinitrobenzoate.

If the solution of the anion was stirred under *nitrogen*, the characteristic red color failed to appear even after 2 hr. However, when oxygen was bubbled through the yellow solution, and immediate and rapid change to red was observed, and the formation of diphenyldiazomethane was essentially completed in 15 min. The aqueous phase gave a positive test for peroxide. In a quantitative run, the yield of diphenyldiazomethane was 37%, calculated from the weight of the 3,5-dinitrobenzoate ester. Titration of the acidified aqueous phase with permanganate indicated a 30% yield of peroxide. Benzophenone hydrazone was recovered in 44% yield. The corresponding diazoalkanes were obtained from the anions of fluorenone, acetophenone, and benzil hydrazones.[3a]

The oxidation of the hydrazone anions may be viewed as proceeding *via* the formation of peroxy anions followed by a prototropic shift and the elimination of

(2) M. Z. Barakat, M. F. A. El-Wahab, and M. M. El-Sadr, *J. Am. Chem. Soc.*, 77, 1670 (1955).

(3) D. H. Barton, R. E. O'Brien, and S. Sternhell, *J. Chem. Soc.*, 470 (1962).

(3a) NOTE ADDED in PROOF. H. Staudinger and A. Gaule (*Ber.*, **49**, 1951 (1916)) reported the preparation of diazofluorene by the action of oxygen on fluorenone hydrazone in the presence of base. However, other hydrazones subjected to the same conditions failed to give the corresponding diazoalkanes except in the case of benzil monohydrazone where the orange color of the diazo compound was observed.