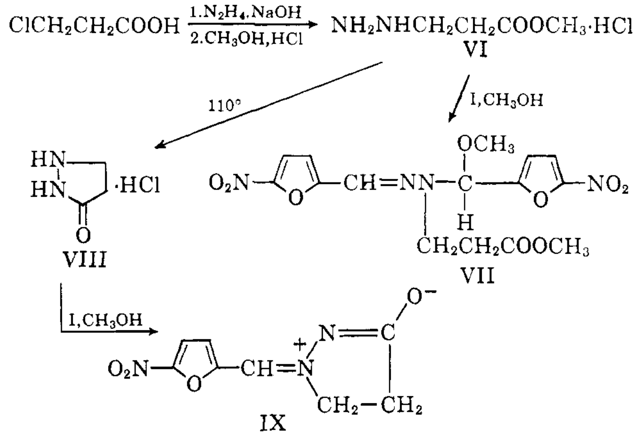

Experimental[8]

General Procedure for α-Alkoxyalkylhydrazones. Method A.—To a stirred solution of 0.2–0.3 mole of the aldehyde in 150 ml. of the appropriate alcohol was added slowly 0.1 mole of the hydrazine in 50 ml. of the alcohol. One milliliter of concentrated hydrochloric acid was added and the mixture was stirred at room temperature or on the steam bath until precipitation of the yellow product was judged complete. The crystals were collected, washed with the alcohol, and dried at room temperature. Recrystallization was carried out in the alcohol except with XII (benzene) and IV (benzene and methanol).

Method B. The aldehyde hydrazone was added to 1.5 equivalets of the appropriate aldehyde in an excess of the desired alcohol which contained several drops of concentrated hydrochloric acid. The mixture was warmed at 50° until complete solution occurred, then Darco was added and the mixture was filtered. The crystalline product which precipitated was purified as in Method A.

Methyl 3-Hydrazinopropionate Hydrochloride, VI.—To 164 g. (4.1 moles) of sodium hydroxide dissolved in 824 g. (14 moles) of 85% hydrazine hydrate was added slowly with stirring 220 g. (2.03 moles) of 3-chloropropionic acid in 180 ml. of water. The temperature was kept between 90 and 95° by the rate of addition. Introduction of the acid was completed in 1.5 hr. and the mixture was stirred with heating for 1 hr. longer. Water and excess hydrazine were then removed at reduced pressure and a semisolid residue remained. To this was added 1.5 l. of methanol; the solution was saturated with anhydrous hydrogen chloride, heated on the steam bath for 30 min., then filtered to remove the sodium chloride. The methanolic filtrate gave colorless crystals after cooling and scratching. These were collected and washed with amounts of cold methanol and ether. After drying in a desiccator over sodium hydroxide, the weight was 235 g. (75%). The substance melted slowly over a broad range up to 90° and was extremely hygroscopic. Attempts at recrystallization from methanol and reprecipitation from methanol by ether either failed or gave 3-pyrazolidinone hydrochloride.

3-Pyrazolidinone Hydrochloride, VIII.—The crude methyl 3-hydrazinopropionate hydrochloride, 62 g. (0.40 mole), was heated overnight in an open dish placed in an oven at 110°. The yield was 42 g. (85%), m.p. 230–208°. Recrystallization from methanol raised the m.p. to 209–210° (sealed capillary, uncorrected). This compound was reported by Rondestvedt and Chang[5] to melt at 199–200°. The present sample gave an infrared spectrum essentially identical to theirs.

Anal. Calcd. for $C_3H_7ClN\ O$: C, 29.40; H, 5.75; Cl, 29.01; N, 22.85. Found: C, 29.43; H, 5.71; Cl, 29.15; N, 22.83.

1-(5-Nitro-2-furfurylidene)-3-hydroxy-2-pyrazolinium Hydroxide, Inner Salt, IX.—To 600 mg. (4.92 mmoles) of 3-pyrazolidinone hydrochloride in 5 ml. of water was added 696 mg. (4.94 mmoles) of 5-nitro-2-furaldehyde in 5 ml. of methanol. An orange precipitate rapidly formed. After standing for 30 min. at room temperature the solid was collected and washed with 5 ml. of each of methanol and ether. After drying at 110°, the yield was 930 mg. (91%). An analytical sample was prepared by recrystallization from nitromethane. The compound did not melt below 300°.

Anal. Calcd. for $C_8H_7N_3O_4$: C, 45.93; H, 3.38; N, 20.09. Found: C, 45.68; H, 3.37; N, 19.76.

5-Nitro-2-furaldehyde Methylhydrazone,[9] II.—To 141 g. (1.00 mole) of 5-nitro-2-furaldehyde in 1 l. of absolute ethanol was added dropwise with stirring 50 g. (1.08 moles) of methylhydrazine. The mixture became dark red and the temperature rose to 35°. Soon a thick red solid mass separated. The precipitate was collected, washed with ethanol, and dried at 60°. The yield was 111 g. (66%), m.p. 142–144. Recrystallization from isopropyl alcohol raised the m.p. to 143–143.5°.

Anal. Calcd. for $C_6H_7N_3O_3$: C, 42.60; H, 4.17; N, 24.85. Found: C, 42.55; H, 4.04; N, 24.6.

Preparation of III from the Crude Distillate Resulting from the Thermal Decomposition of 1-Hydrazino-2-propanol.—Substitution of the crude distillate[2] (b.p. 125–145°) for methylhydrazine resulted in a 34% yield of III based on the hydrazino alcohol.

Acknowledgment.—We wish to thank Dr. Pauline Chang[5] for sending us a copy of the infrared spectrum of 3-pyrazolidinone hydrochloride, and Benjamin Stevenson and Michael Heigle of these laboratories for technical assistance.

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[8] All m.p.'s except where noted were taken on a Fisher–Johns block and are corrected. The elemental analyses and molecular weight determination were carried out under the direction of Mr. Gordon Ginther and Dr. Victor Ells of these laboratories, and Schwarzkopf Analytical Laboratory, Woodside, N. Y.

(9) This compound was first prepared by R. Raffauf of this laboratory.

Preparation of Aryldiazoalkanes by the Bamford–Stevens Reaction

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In their first paper on the decomposition of toluene-*p*-sulphonylhydrazones by alkali,[2] Bamford and Stevens noted that this reaction constituted a moderately successful method for the preparation of aryldiazo compounds. For example, benzaldehyde toluene-*p*-sulfonylhydrazone afforded a 60% yield of phenyldiazomethane upon treatment with ethanolic sodium ethoxide at 50° for five to eight hours. The reaction was somewhat less useful for the preparation of 1-phenyldiazoethane,

$$C_6H_5CHNNHTs \xrightarrow[CH_3CH_2OH]{NaOCH_2CH_3} C_6H_5CHN_2\ (60\%)$$

yielding 27% of the diazo compound in seven hours at 65–70°. Possibly because of this lack of general applicability and the long reaction times necessary, the method has not taken a significant place among the methods available for the preparation of aryldiazoalkanes.[3]

In view of the ready availability of toluene-*p*-sulfonylhydrazones, it seemed desirable to us to examine the effect of some experimental variables on the synthetic utility of the Bamford–Stevens reaction. It was considered that there might be a convenient set of conditions which would give aryldiazomethanes in reasonable yields. In particular, the effect of some different bases and solvents on the decomposition of

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(1) Sloan Foundation Fellow, 1962.

(2) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

(3) J. Meinwald, P. G. Gassman, and E. G. Miller, *J. Am. Chem. Soc.*, **81**, 4751 (1959); P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958); C. D. Gutsche and E. F. Jason, *J. Am. Chem. Soc.*, **78**, 1184 (1956).

some toluene-*p*-sulfonylhydrazones and *o*-nitrobenzenesulfonylhydrazones was investigated.

Using benzaldehyde toluene-*p*-sulfonylhydrazone as the test case, it was found that a mixture of this compound with sodium methoxide as the base developed the characteristic orange color of phenyldiazomethane far more rapidly in pyridine solvent than in ethanol, ethylene glycol dimethyl ether, dimethylformamide, or dimethyl sulfoxide. When this observation was pursued further, it was found that phenyldiazomethane could be prepared quite conveniently in 65–70% yield by warming a 10% solution of the hydrazone in pyridine with one equivalent of commercial, dry powdered sodium methoxide for thirty minutes at 60°. Isolation of the diazo compound was readily effected by extraction into pentane from an aqueous mixture of the crude product. Pyridine could be effectively removed from the pentane extracts simply by washing with a few portions of cold water.

Substitution of commercial potassium *tert*-butylate for sodium methoxide resulted in extensive decomposition of the diazo compound. Substitution of dry, powdered lithium methoxide for sodium methoxide accelerated the reaction, permitting the preparation to be carried out at 50° in the same period of time. The yield of phenyldiazomethane was slightly lower, however, so that lithium methoxide was inferior to the more readily available sodium methoxide.

In an examination of the influence of certain further variables on the yield of phenyldiazomethane it was found that the amount of sodium methoxide used was critical. Use of either more or less than one equivalent resulted in decomposition of the diazo compound as evidenced by reduced yields and the appearance of broad absorption in the visible spectrum of the product which obscured the maximum at 485 mμ of phenyldiazomethane. Similar criteria established that water in concentrations greater than 1% had a detrimental effect on the reaction while small amounts of methanol (up to 5% concentration) had little effect. In fact, the methanol generated from the sodium methoxide used seemed to facilitate the reaction, since phenyldiazomethane was formed from the dried sodium salt of benzaldehyde toluene-*p*-sulfonylhydrazone in pyridine at only one third to one half the rate of its formation in the sodium methoxide reaction.

As in the earlier work,[2] there appeared to be an optimum time at a given temperature for the formation of phenyldiazomethane in maximum yield. This time was determined easily simply by working up aliquots of the reaction mixture, making up the resultant pentane solutions to volume, and determining their visible absorption spectra. The results of such a study are given in Table I for the toluene-*p*-sulfonylhydrazones of benzaldehyde, acetophenone, and propiophenone.

TABLE I

DECOMPOSITION OF TOLUENE-*p*-SULFONYLHYDRAZONES AT 75–80°

	Absorption at visible maximum					
	Time (min.)					
	10	20	40	60	80	100
Toluene-*p*-sulfonylhydrazone						
Benzaldehyde[a]	0.36	0.43	0.35		0.20	
Acetophenone[b]	.19	.20	.23		.16	
Propiophenone[c]		.22	.33	0.38	.37	0.36

[a] Visible maximum of phenyldiazomethane, 485 mμ. [b] Visible maximum of 1-phenyldiazoethane, 520 mμ. [c] Visible maximum of 1-phenyldiazopropane, 520 mμ.

Application of the method to the preparation of several aryldiazoalkanes gave the results shown in Table II. The yields and purity reported were determined by nitrogen evolution from weighed samples of material isolated by evaporation of a pentane extract of the crude products. This method of determination avoids the possible error introduced by contamination with basic impurities in the more usual benzoic acid titration. In fact, the Bamford and Stevens preparation, in our hands, afforded less than 50% yields of phenyldiazomethane as determined by nitrogen evolution.

TABLE II

PREPARATION OF ARYLDIAZOALKANES

	Temp., °C.	Time, min.	Yield of diazoalkane,[a] %	Purity of diazoalkane, %
Toluene-*p*-sulfonylhydrazone				
Benzaldehyde	55–60°	30	65–70	80
	75–80°	15	50–60	70
p-Methoxybenzaldehyde	55–60°	75	20[b]	60
	75–80°	15	33	53
Acetophenone	75–80°	40	32	58
m-Nitroacetophenone	75–80°	30	48	100[c]
Propiophenone	60–65°	60	55	90
	75–80°	40	42	60

[a] Yield of pure material. [b] *p*-Methoxyphenyldiazomethane decomposed rapidly at room temperature. [c] This high purity appears to be the result of the insolubility of the decomposition products in pentane.

It can be seen from Table II that the modification of the Bamford–Stevens method provides a quick, simple synthesis to give fairly good yields of moderate to high purity aryldiazoalkanes. It should be noted that only in the cases of phenyldiazomethane and 1-phenyldiazopropane were the optimum time and temperature determined.

We confirm the earlier authors' observation that the less readily available *o*-nitrobenzenesulfonylhydrazone of benzaldehyde gave no better yields of phenyldiazomethane than the toluene-*p*-sulfonylhydrazone. The *o*-nitrobenzenesulfonylhydrazone of acetophenone gave a slightly better yield (38%) of diazocompound after 20 minutes at 75°. We were unsuccessful in attempts to prepare aliphatic diazoalkanes from the appropriate toluene-*p*-sulfonylhydrazones, including those from nortricyclenone and norcamphor. No decomposition was evident.

Experimental

Preparation of Toluene-*p*-sulfonylhydrazones.—The following general procedure was used. The carbonyl compound (1 equivalent) dissolved in the minimal volume of hot acetic acid (liquid carbonyl compounds were used directly) was mixed with one equivalent of a hot solution containing 4 g. of toluene-*p*-sulfonylhydrazine for every 5 ml. of acetic acid. The mixture was heated to the boiling point or until product crystallization began, then cooled to 5°. The crystalline product was filtered, washed with cold acetic acid, cold aqueous acetic acid, then water, and air dried in a warm place. The yields and melting points of the crude derivatives thus obtained are recorded in Table III.

Preparation of *o*-Nitrobenzenesulfonylhydrazones.—The general procedure was as follows. A mixture of the carbonyl com-

TABLE III

PREPARATION OF HYDRAZONES

Compound	M.p., °C.	Yield, %
Toluene-*p*-sulfonylhydrazones		
Benzaldehyde	155–158°	92
p-Methoxybenzaldehyde	112–114°	93
Acetophenone	147.5–150°	82
m-Nitroacetophenone	176.5–179°	93
Propiophenone	122–125°	96
Cyclohexanone	155–158°	67
Nortricyclenone	160–162°	74
Norcamphor	206.5–208°	89
o-Nitrobenzenesulfonylhydrazones		
Benzaldehyde	175–177°	65
Acetophenone	105–107°	60

pound (1 equivalent) and *o*-nitrobenzenesulfonylhydrazine[4] (1 equivalent) in cold acetic acid was digested on a hot plate for 5–10 min. The mixture was cooled to 5°, and the precipitated product was filtered, washed with cold acetic acid and water, and air dried. The yields and melting points of the *o*-nitrobenzenesulfonylhydrazones thus obtained are recorded in Table III.

Preparation of Diazoalkanes.—In general, a 10% solution of the hydrazone in fresh pyridine was mixed with the desired amount of the appropriate base. The mixture was then stirred in a water bath maintained at the desired temperature. Spectroscopic analysis was carried out by dilution of aliquots with ten times their volume of water, extraction of the diazoalkane into pentane, and dilution of the pentane extracts to volume with further pentane.

The following preparation of 1-phenyldiazopropane is illustrative of the procedure used on a preparative scale.

1-Phenyldiazopropane.—Propiophenone toluene-*p*-sulfonylhydrazone (1.0 g., 3.3 mmoles) and commercial sodium methoxide (180 mg., 3.3 mmoles) were mixed in fresh pyridine (10 ml.). The mixture was protected with a Drierite drying tube and heated with stirring for 1 hr. in a water bath held at 60–65°. The initial precipitate dissolved and a granular precipitate began to collect during this time, while the supernatant solution turned wine red. At the end of the heating period the mixture was poured into ice-water (50 ml.) and extracted with two 20-ml. portions of pentane. The combined pentane extracts were washed with four 25-ml. portions of cold water and once with saturated aqueous sodium chloride. The wine red organic solution was then dried over anhydrous sodium sulfate at 5°, filtered, and evaporated to dryness *in vacuo* at room temperature. The residual red oil (0.29 g.) liberated 1.8 mmoles of nitrogen (measured volumetrically and corrected to STP) when treated with acetic acid, corresponding to a yield of 55% and a purity of 90%.

Acknowledgment.—The author wishes to thank the Petroleum Research Fund for support of this work under grant PRF 742A4.

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[4] A. T. Dann and W. Davies, *J. Chem. Soc.*, 1050 (1929).

The Preparation of Nitrosyl Perfluoroacylates from Perfluoro Acid Anhydrides and Dinitrogen Trioxide

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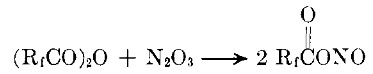
Recent publications have described the preparation of nitrosyl perfluoroacylates from the reaction of metal salts of perfluoro acids with nitrosyl chloride[1,2] and from the reaction of perfluoro acid anhydrides with nitrosyl chloride.[3]

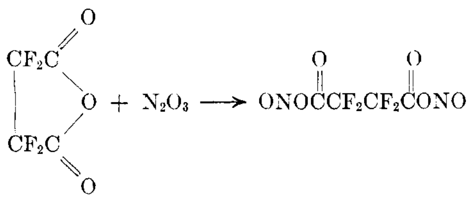
In the present investigation, it was found that nitrosyl perfluoroacylates can be prepared conveniently in high yields from the liquid phase reaction of perfluoro acid anhydrides with dinitrogen trioxide (equation 1).



$$(\mathrm{R_fCO})_2\mathrm{O} + \mathrm{N_2O_3} \longrightarrow 2\,\mathrm{R_f}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{ONO} \qquad (1)$$

The reaction is carried out by simply mixing equimolar quantities of the two reactants or by titrating one reactant with the other. Since dinitrogen trioxide is deep blue and nitrosyl perfluoroacylates are amber or yellow, the course of the reaction can be followed by the color of the reaction mixture. The reaction can be carried out at atmospheric pressure, using a Dry Ice-cooled reflux condenser to maintain dinitrogen trioxide in the liquid phase or in a sealed vessel under autogeneous pressure. For the case of trifluoroacetic anhydride and dinitrogen trioxide, reaction is complete in approximately twenty minutes at −5° and in 3.5 minutes at 25°.

When cyclic perfluoro acid anhydrides are used in the reaction, dinitrosyl perfluoroacylates are produced. For example, perfluorosuccinic anhydride and dinitrogen trioxide reacted at 0° to give dinitrosyl perfluorosuccinate (equation 2).



(2)

This compound is highly reactive and exhibits the normal reactions of nitrosyl perfluoroacylates with water, alcohols, metals, etc.[1] Pyrolysis at temperatures of 50° and higher[4] gives only perfluorosuccinic anhydride and dinitrogen trioxide in contrast to the nitrosyl perfluoroacylates derived from straight chain perfluoro acid anhydrides which yield perfluoronitrosoalkanes upon pyrolysis.[1,2]

Evidence indicates that the reaction is quite general. It proceeds most readily with acid anhydrides which are activated by electron-withdrawing groups. For example, reaction at room temperature has been observed with trichloroacetic anhydride but not with acetic anhydride. The reaction of dinitrogen trioxide with nonfluorinated acid anhydrides will be reported at a later date.

The reaction conditions and electronic requirements of the reaction indicate that the reaction mechanism is ionic, involving an initial attack of the negatively charged oxygen atom of the dinitrogen trioxide molecule

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[1] C. W. Taylor, T. J. Brice, and R. L. Wear, *J. Org. Chem.*, **27**, 1064 (1962).

[2] R. E. Banks, R. N. Haszeldine, and M. K. McCreath, *Proc. Chem. Soc.*, 64 (1961).

[3] J. D. Park, R. W. Rosser, and J. R. Lacher, *J. Org. Chem.*, **27**, 1462 (1962).

[4] The explosion hazards associated with super heating nitrosyl perfluoroacylates have been described by Taylor, Brice and Wear (ref. 1).