TABLE I

4-R-1,2,4-TRIAZOLINE-3,5-DIONES

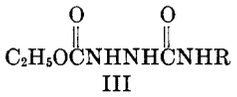
Structure of R	Yield, %[b]	Mp, °C[c]	Anal, %[a] Carbon Calcd	Carbon Found	Hydrogen Calcd	Hydrogen Found	Visible absorption λ_{max}, mμ	Visible absorption ε
C_6H_5	86	Dec	...	...	...	...	545[d]	135
CH_3	81	98.0–98.5	31.87	31.95	2.67	2.61	538[d]	152
n-C_4H_9	71	44.0–44.5	46.45	46.60	5.85	5.79	544[e]	211
C_6H_{11}	86	95–96[f]	53.03	53.03	6.12	6.13	545[e]	205
p-$NO_2C_6H_4$	20	128–129[f]	43.65	43.48	1.83	1.76	540[d]	150
p-$CH_3OC_6H_4$	60	130–131[f]	52.69	52.71	3.44	3.37	546[d]	151

[a] Analyses were performed by Mr. J. Nemeth and associates of the University of Illinois. [b] Purified material. [c] Uncorrected. [d] In methylene chloride. [e] In cyclohexane. [f] There is some prior decomposition (Kofler block).

The requisite 4-substituted urazoles were prepared by base-promoted cyclization[10] of the appropriate 4-substituted-1-ethoxycarbonyl semicarbazides (III). These semicarbazides result from the addition of aryl or alkyl isocyanates to ethoxycarbonylhydrazine.[11] Tables II and III give data relevant to previously unreported semicarbazides and urazoles which were prepared in the course of this work. The physical properties of our samples of 4-phenyl, 4-methyl, 4-n-butyl, and 4-cyclohexyl urazoles agree with reported values.[2,11–13]

TABLE II

4-SUBSTITUTED-1-ETHOXYCARBONYL SEMICARBAZIDES



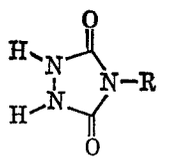
III

Structure of R	Yield, %	Mp, °C[b]	Anal, %[a] Carbon Calcd	Carbon Found	Hydrogen Calcd	Hydrogen Found
CH_3	100	141.0–141.5	37.26	37.55	6.88	6.89
p-$NO_2C_6H_4$	92	218.0–218.5	44.78	44.50	4.51	4.46
p-$CH_3OC_6H_4$	98	170.5–171.5	52.17	51.99	5.97	5.91

[a] See footnote a in Table I. [b] Uncorrected.

TABLE III

4-SUBSTITUTED URAZOLES



Structure of R	Yield, %	Mp, °C[b]	Anal, %[a] Carbon Calcd	Carbon Found	Hydrogen Calcd	Hydrogen Found
p-$NO_2C_6H_4$	82	271.0–271.5	43.25	43.25	2.72	2.75
p-$CH_3OC_6H_4$	55	219.5–220.5	52.17	52.04	4.38	4.30

[a] See footnote a in Table I. [b] Uncorrected.

To our knowledge, this is the first instance of oxidation of diacylhydrazines to the corresponding azo compounds by nitrogen tetroxide.[14] The mechanism of this oxidation is being investigated.

Experimental Section

Owing to the similarity of the nitrogen tetroxide oxidation procedures by which the various 1,2,4-triazoline-3,5-diones were prepared, the experimental details of only one of these oxidations are presented, these being exemplary of the others.

Preparation of 4-Cyclohexyl-1,2,4-triazoline-3,5-dione.—Gaseous nitrogen tetroxide[15] was passed through a narrow tube into a cold (0°) slurry of 1.00 g of 4-cyclohexylurazole (5.46 mmoles) and 10 g of anhydrous sodium sulfate in 50 ml of methylene chloride until all the urazole had dissolved. The solution was maintained at 0° during the reaction. The sodium sulfate was removed by filtration and the clear, red filtrate was evaporated to dryness at reduced pressure. The red, crystalline residue was twice sublimed (0.01 torr, 40°) in the dark to yield 0.784 g (86.5%) of analytically pure 4-cyclohexyl-1,2,4-triazoline-3,5-dione of indicated (Table I) melting point and composition.

(10) G. Zinner and W. Deucker, *Arch. Pharm.*, **294**, 370 (1961).

(11) F. Arndt, L. Loewe, and A. Tarlan-Akön, *Rev. Fac. Sci. Forest Univ. Istanbul*, **13A**, 127 (1948); *Chem. Abstr.*, **42**, 8190 (1948).

(12) T. Tsuji, *Pharm. Bull.* (Tokyo), **2**, 403 (1954).

(13) G. Zinner and B. Böhlke, *Arch. Pharm.*, **299**, 43 (1966).

(14) Monoacylhydrazines have been shown [G. B. Bachman and W. Michalowicz, *J. Org. Chem.*, **23**, 1800 (1958)] to yield acylazides upon treatment with nitrogen tetroxide.

(15) Commercial material obtained from the Matheson Co.

Perfluoroalkanesulfonate Esters. The Reaction of 2,2,2-Trifluoroethyl Trifluoromethanesulfonate with *p*-Dimethylaminophenylmagnesium Bromide

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Trifluoroethylation of diethylamine with 2,2,2-trifluoroethyl trifluoromethanesulfonate (I) has been described recently.[1] In the present work, ester I was further investigated as an alkylating agent of *p*-dimethylaminophenylmagnesium bromide (II), a typically reactive Grignard reagent under recent study in these laboratories.[2]

It is known that alkyl esters of arylsulfonic acids react with Grignard reagents in two ways. The "normal" reaction,[3] first reported by Ferns and Lapworth,[4] involves the alkylation of the Grignard reagent. It is most commonly employed for preparative purposes. In addition, sulfonic esters are capable of undergoing sulfone formation with Grignard reagents. This tendency appears to be intensified in the reaction of aryl Grignard reagents with alkyl esters of alkanesulfonic acids and aryl esters of aryl sulfonic acids.[3] By analogy, one of the products expected from a reaction of Grignard reagent II with compound I was 1-(*p*-dimethylaminophenyl)-2,2,2-trifluoroethane (III). How-

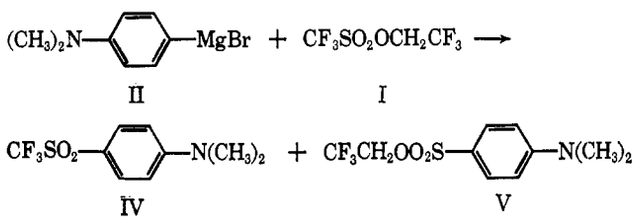
(1) R. L. Hansen, *J. Org. Chem.*, **30**, 4322 (1965).

(2) A. Mendel, *J. Organometal. Chem.*, **6**, 97 (1966).

(3) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp 1278–1285.

(4) J. Ferns and A. Lapworth, *J. Chem. Soc.*, **101**, 273 (1912).

ever, in this investigation, the reaction of compound I with the Grignard reagent II afforded, instead of compound III, two acid-insoluble products, *p*-dimethylaminophenyl trifluoromethyl sulfone (IV) and 2,2,2-trifluoroethyl *p*-dimethylaminobenzenesulfonate (V). These two compounds, obtained in low yield, were characterized by elementary and spectroscopic analyses (see the Experimental Section).



Although no evidence (*via* infrared) for compound III was noted, an acid-soluble, nonfluorine-containing (*via* infrared), purple material was isolated. Attempts to purify this material by chromatography failed. It was not further characterized. Analogous reaction of *p*-dimethylaminophenyllithium with compound I afforded a large amount of acid-soluble, purple semisolid which was not characterized. An acid-insoluble product was not obtained.

Experimental Section[5]

Reaction of *p*-Dimethylaminophenylmagnesium Bromide with 2,2,2-Trifluoroethyl Trifluoromethanesulfonate.—The experiment was conducted in a purified nitrogen atmosphere. The Grignard reagent, prepared from 2.04 g (0.084 g-atom) of "activated" magnesium[2] and 16.8 g (0.084 mole) of purified *p*-bromodimethylaniline[2] in 150 ml of purified tetrahydrofuran[2] was added dropwise over 30 min at room temperature to 23.2 g (0.1 mole) of pure ester I[1] in 100 ml of anhydrous ether. Thereafter the product was heated under reflux for 1 hr and poured into water. The mixture was acidified and extracted with ether. The separated ether extract was dried (anhydrous magnesium sulfate) and filtered. Upon evaporation of the filtrate, there was obtained 4.64 g of off-white solid melting at 100–105°. Qualitative elementary analyses for nitrogen, sulfur, and fluorine were positive for this solid. Infrared analysis of this sample indicated possible *para* substitution (12.25 μ), sulfone and/or sulfonate ester (*ca.* 7.4 μ, *ca.* 8.85 μ), and carbon–fluorine bonds (*ca.* 8.5 μ). On the basis of a broad melting range and proton and fluorine magnetic resonance studies, the sample was thought to be a mixture with identification of a trifluoroethyl group (τ 5.25), a trifluoromethyl group (ϕ^* 79.6), and the methyl groups on the nitrogen atom (τ 7.14). The aromatic region was complicated owing to the nature of the solvent mixture. [Basification of the aqueous extract afforded 8.4 g of nonfluorine-containing (*via* infrared), purple solid of a dye nature, which was not further investigated.]

Isolation of *p*-Dimethylaminophenyl Trifluoromethyl Sulfone (IV).—The 4.64 g of off-white solid was dissolved in benzene and chromatographed on a column (85 × 30 mm) of 70 g of neutral alumina, activity II (Calbiochem alumina). Elution with 100-ml portions of 10% benzene–petroleum ether (fractions 1–4, see below) followed by elution with 100-ml portions of benzene (fractions 5–8, see below) comprised chromatogram I [fraction number, weight (mg), melting point where applicable, fraction description]: 1, 1637, white-yellow solid; 2, 326, 102–111°, white solid; 3, 33, 98–99°, white solid; 4, 30, 99–110°, white solid; 5, 623, 103–111°, white solid; 6, 386, 103–117°, white solid; 7, 73, 115–117°, white solid; 8, 10, yellow oil.

Fraction 1 of chromatogram I was dissolved in benzene and rechromatographed on a column (111 × 20 mm) of 40 g of neutral alumina, activity I (Calbiochem alumina). Elution with 50-ml portions of benzene (fractions 1–5, see below) followed by elution with 50-ml portions of anhydrous ether (fractions 6–8, see below) embraced chromatogram II [fraction number, weight (mg), melting point where applicable, fraction description]: 1, 420, semisolid; 2, 696, 144.5–146°, white solid; 3, 84, 138–142°, white solid; 4, 43, 97–103°, white solid; 5, 29, 110–112°, white solid; 6, 75, 115–117°, white solid; 7, 34, 117–118°, white solid; 8, 10, 115–116°, white solid.

Fraction 1 of chromatogram II was washed with acetone and filtered. Evaporation of the acetone filtrate left 181 mg of white solid, mp 140–144°, which was combined with fractions 2 and 3 of chromatogram II. Recrystallization (cyclohexane–Darco) of these combined fractions afforded 800 mg of compound IV, as white platelets, mp 144–145°.

Anal. Calcd for $C_9H_{10}F_3NO_2S$: C, 42.7; H, 4.0; F, 22.5; N, 5.5. Found: C, 42.5; H, 4.1; F, 22.2; N, 5.4.

Pmr studies of compound IV indicate a single peak at τ 7.14 which is consistent for the methyl groups on the nitrogen atom. F^{19} nmr studies show a single peak at ϕ^* 79.6 which is in agreement for a trifluoromethylsulfonyl group. Both spectra were taken on a 25-mg sample of compound IV dissolved in a mixture of 0.125 ml of $CFCl_3$ qnd 0.08 ml of pyridine.

Isolation of 2,2,2-Trifluoroethyl *p*-Dimethylaminobenzenesulfonate (V).—The following chromatographic fractions were combined (fractions 2–7, inclusive, of chromatogram I and fractions 4–8, inclusive, of chromatogram II) and recrystallized from cyclohexane (Darco) to yield 1.6 g of compound V as long, white needles, mp 117–118°.

Anal. Calcd for $C_{10}H_{12}F_3NO_3S$: C, 42.4; F, 20.1; N, 5.0; mol wt, 283. Found: C, 42.3; F, 19.6; N, 4.8; mol wt, 281.

Pmr studies of compound V show a single peak at τ 7.13 for the methyl groups on the nitrogen atom and a quadruplet centered at 5.25 (with a J value of 8.5 cps) which is in agreement for the trifluoroethoxy group.

F^{19} nmr studies of compound V show a triplet centered at ϕ^* 73.4 (with a J value of 8.5 cps) which is consistent for the trifluoroethoxy group. Both spectra were taken on a 60-mg sample of compound V dissolved in 500 mg of a 75% pyridine–25% $CFCl_3$ solvent mixture.

Acknowledgment.—The author thanks Dr. Robert L. Hansen for a sample of 2,2,2-trifluoroethyl trifluoromethanesulfonate and Dr. Charles E. Ring of the molecular spectroscopy group of the Minnesota Mining and Manufacturing Company for the spectral data.

(5) Melting points are corrected. They were taken with a Thomas–Hoover capillary melting point apparatus. Infrared spectra were taken with a Perkin-Elmer Model 21 spectrophotometer. Proton magnetic resonance spectra were taken with a Varian Model A-60 instrument. Values are reported in τ units using tetramethylsilane as internal reference. Fluorine magnetic resonance spectra were taken with a Varian Model V-43002 40-Mcps spectrophotometer. Values are reported in ϕ^* ($CFCl_3$ reference). Chromatographic alumina was purchased from California Corporation for Biochemical Research. Petroleum ether (bp 30–60°) was used. Analyses were performed by the microanalytical section of these laboratories. Molecular weights were determined by the thermistor method; see J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

Cleavage of Oximes with Bisulfite. A General Procedure

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Of the methods available for the cleavage of oximes to the parent oxo compounds, either direct acid hydrolysis or acid-catalyzed exchange with formaldehyde, pyruvic, or levulinic acids is commonly used.[1]

In connection with other synthetic work, we have found a simple, inexpensive, mild procedure for accomplishing this task. Moreover, the reaction is car-

(1) For example, see C. H. DePuy and B. W. Ponder, *J. Am. Chem. Soc.*, **81**, 4629 (1959); E. B. Hershberg, *J. Org. Chem.*, **13**, 542 (1948); M. P. Cava, R. L. Little, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2260 (1958).