1,1,1-Trifluoro-2-diazopropane

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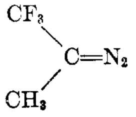
In contrast to the stability of the diaryldiazomethanes, such as diphenyldiazomethane and 9-diazofluorene, the dialkyldiazomethanes decompose readily, often at room temperature. In particular, the pronounced instability of 2-diazopropane (dimethyldiazomethane) has long been known.[1-3] It quickly decomposes, even in solution, at room temperature. Recently, the synthesis and reactions of 1,1,1,-3,3,3-hexafluoro-2-diazopropane (perfluorodimethyldiazomethane) have shown it to be the most stable dialkyldiazomethane.[4,5] For example, it is not sensitive to organic acids, and, in one of its reactions, yields an insertion product in which nitrogen has been retained after 8 hr at 150°.[4] This stability has been attributed to the inductive effect of the two strongly electron-withdrawing trifluoromethyl groups.[5]

We wish to report the synthesis of several new 1,1,1-trifluoropropane compounds substituted in the 2-position, among them 1,1,1-trifluoro-2-diazopropane (I). In its stability, color, and reactivity, we find this new diazo compound to be intermediate between 2-diazopropane and the perfluoro analog. As examples, solutions of 1,1,1-trifluoro-2-diazopropane, unlike solutions of 2-diazopropane, are quite stable at room temperature, but, unlike solutions of the perfluoro analog, react immediately with acids. The neat 1,1,1-trifluoro-2-diazopropane is a volatile, orange liquid, compared with the red 2-diazopropane[1] and the pale yellow perfluoro analog.[4] Caution should be exercised in handling neat 1,1,1-trifluoro-2-diazopropane; it should be kept below 0° at all times. When a small portion of it was allowed to warm to room temperature, it detonated.



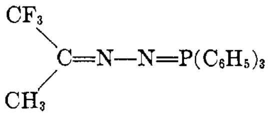
$(CF_3)(CH_3)C{=}N_2$

I

Three methods of generating 1,1,1-trifluoro-2-diazopropane in solution have been investigated: the oxidation of 1,1,1-trifluoropropanone hydrazone, the reaction of 1,1,1-trifluoropropanone oxime[6,7] with chloramine, and the diazotization of 1-methyl-2,2,2-trifluoroethylamine.[7]

The previously unreported hydrazone of 1,1,1-trifluoropropanone is prepared at room temperature, using an aqueous solution of hydrazine dihydrochloride and sodium acetate. The hydrazone is oxidized to 1,1,1-trifluoro-2-diazopropane in organic solvents using silver oxide. Contrary to previous reports,[6,7] the 1,1,1-trifluoropropanone oxime can be prepared at atmospheric pressure and room temperature, using an aqueous solution of hydroxylamine hydrochloride and sodium acetate. The oxime reacts with an aqueous solution of chloramine in the presence of a supernatant organic solvent to produce a solution of 1,1,1-trifluoro-2-diazopropane. Lithium aluminum hydride reduction (*hazardous*) or catalytic hydrogenation of 1,1,1-trifluoropropanone oxime produces 1-methyl-2,2,2-trifluoroethylamine. Its hydrogen chloride salt is easily diazotized with an aqueous solution of sodium nitrite in the presence of a supernatant organic solvent to yield the diazo compound in solution.

Several reactions of the yellow to yellowish orange solutions of 1,1,1-trifluoro-2-diazopropane have been investigated. It reacts readily with triphenylphosphine to produce the phosphazine (II). Reaction of a solution of 1,1,1-trifluoro-2-diazopropane with benzoic acid gives the previously reported 1-methyl-2,2,2-trifluoroethyl benzoate.[8] *p*-Toluenesulfonic acid and a solution of the 1,1,1-trifluoro-2-diazopropane give 1-methyl-2,2,2-trifluoroethyl *p*-toluenesulfonate, identical in all respects with the ester as prepared from 1,1,1-trifluoro-2-propanol and *p*-toluenesulfonyl chloride.



$(CF_3)(CH_3)C{=}N{-}N{=}P(C_6H_5)_3$

II

Experimental Section

Melting points and boiling points are uncorrected; all infrared spectra were taken on a Beckman IR-5 spectrophotometer.

The elemental analyses were carried out by the Schwartzkopf Microanalytical Laboratory, Woodside, N. Y.

1,1,1-Trifluoropropanone Hydrazone.—To a solution of 210 g (2.0 moles) of hydrazine dihydrochloride and 612 g (4.5 moles) of sodium acetate trihydrate in 3 l. of water at 0° was added, with stirring, 112 g (1.0 mole) of 1,1,1-trifluoropropanone. The reaction mixture was allowed to warm to room temperature, stirred at room temperature for 7 days, and then extracted with ether. The combined ether extracts were washed with water, saturated $NaHCO_3$ solution, and water again, dried over anhydrous Na_2SO_4, and distilled to yield 75.5 g (60%) of the hydrazone, bp 51.0–51.5° (20 mm), $n^{25}D$ 1.3803.

Anal. Calcd for $C_3H_5F_3N_2$: C, 28.57; H, 4.00; N, 22.22. Found: C, 28.54; H, 4.11; N, 22.34.

1,1,1-Trifluoropropanone Oxime.—To a solution of 278 g (4.0 moles) of hydroxylamine hydrochloride and 653 g (4.8 moles) of sodium acetate trihydrate in 3 l. of water at 0° was added, with stirring, 224 g (2.0 moles) of 1,1,1-trifluoropropanone. The reaction mixture was allowed to warm to room temperature, stirred at room temperature for 3 days, and finally refluxed for 18 hr. The reaction mixture was worked up as in the hydrazone preparation above to yield 217 g (85%) of the oxime, bp 101–104° (lit.[6] bp 102.5–103°).

It was not found necessary to run the preparation in a sealed tube, as was done in the two previous reports[6,7] of this oxime.

1-Methyl-2,2,2-trifluoroethylamine.—The oxime (76 g, 0.60 mole) was hydrogenated using the conditions of Dickey, *et al.*,[7] with the exception that Adams catalyst was used in place of Raney nickel. The amine was obtained as its hydrochloride, 24.0 g (27%), mp 254–256° (sealed tube).

Diazotization of 1-Methyl-2,2,2-trifluoroethylamine.—To a solution of 14.9 g (0.10 mole) of 1-methyl-2,2,2-trifluoroethylamine hydrochloride and 6.9 g (0.10 mole) of sodium nitrite in

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(1) H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).

(2) D. E. Applequist and H. Babad, *J. Org. Chem.*, **27**, 288 (1962).

(3) J. R. Dyer, R. B. Randall, and H. M. Deutsch, *ibid.*, **29**, 3423 (1964).

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(5) E. P. Mochalina and B. L. Dyatkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 926 (1965).

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(7) J. B. Dickey, *et al.*, *Ind. Eng. Chem.*, **48**, 209 (1956).

(8) E. J. Bourne, *et al.*, *J. Chem. Soc.*, 3268 (1958).

100 ml of water was added a supernatant layer of 50 ml of ether. The two-phase system was vigorously stirred at 0° for 15 min. The yellow organic layer was separated, and 50 ml of fresh ether was added to the aqueous layer. The extractions were continued in this manner until the ether layer remained colorless. The combined ether extracts were washed successively with 5% Na_2CO_3 solution and water, and then dried over anhydrous Na_2SO_4.

Triphenylphosphine Adduct of 1,1,1-Trifluoro-2-diazopropane (II).—To a solution of 1,1,1-trifluoro-2-diazopropane in ether, prepared by diazotization of 14.9 g (0.10 mole) of the amine hydrochloride, was added 2.6 g (0.01 mole) of triphenylphosphine. There was a loss of all yellow color within 30 min, with no gas evolution. Removal of all volatiles under aspirator vacuum yielded 3.8 g (10%, based on amine hydrochloride) of the crude phosphazine. Separation of the phosphazine from a small amount of unreacted triphenylphosphine proved difficult, but repeated recrystallization of the tan solid from hexane yielded the white phosphazine, fairly pure, mp 127–128.5°.

Anal. Calcd for $C_{21}H_{18}F_3N_2P$: C, 65.29; H, 4.70; F, 14.76. Found: C, 66.24; H, 5.02; F, 14.08.

1-Methyl-2,2,2-trifluoroethyl Benzoate.—To a solution of 1,1,1-trifluoro-2-diazopropane in ether, prepared by diazotization of 14.9 g (0.10 mole) of the amine hydrochloride, were added 12.2 g (0.10 mole) of benzoic acid and 1.4 g (0.01 mole) of boron trifluoride etherate in ether, with stirring. There was an immediate evolution of a colorless gas, and loss of all yellow color within 1 min. The reaction mixture was washed successively with saturated $NaHCO_3$ solution and water, dried over anhydrous Na_2SO_4, and distilled to yield 1.7 g (8%, based on amine hydrochloride) of the ester, bp 78° (8 mm), $n^{25}D$ 1.4452 [lit.[8] bp 88° (20 mm), $n^{17}D$ 1.4476], identical in infrared spectrum with the ester as prepared from 1,1,1-trifluoro-2-propanol and benzoyl chloride.

Oxidation of 1,1,1-Trifluoropropanone Hydrazone.—To a solution of 12.6 g (0.10 mole) of 1,1,1-trifluoropropanone hydrazone in 200 ml of anhydrous ether were added 23.2 g (0.10 mole) of silver oxide and 10 ml of a saturated solution of KOH in absolute ethanol. The reaction mixture was stirred vigorously for 1 hr at room temperature and filtered to yield a deep yellowish orange solution of the diazo compound.

This oxidation was also carried out in pentane; the filtrate was distilled into a chilled receiver until the condensate was colorless, to yield a yellow distillate containing only the diazo compound in pentane, as shown by comparison of its infrared spectrum with that of the solution prepared from the neat diazo compound in pentane.

1-Methyl-2,2,2-trifluoroethyl *p*-Toluenesulfonate. A. From 1,1,1-Trifluoro-2-diazopropane and *p*-Toluenesulfonic Acid.—To a solution of 1,1,1-trifluoro-2-diazopropane in ether, prepared by oxidation of 12.6 g (0.10 mole) of the hydrazone, was added 19.0 g (0.10 mole) of *p*-toluenesulfonic acid monohydrate in anhydrous ether, with stirring. There was an immediate evolution of a colorless gas and loss of all color within 2 min. The reaction mixture was washed successively with saturated $NaHCO_3$ solution and water, dried over anhydrous Na_2SO_4, and distilled to yield 4.8 g (18%, based on the hydrazone) of the ester, identical in boiling point, index of refraction, and infrared spectrum with the ester as prepared from 1,1,1-trifluoro-2-propanol and *p*-toluenesulfonyl chloride.

B. From 1,1,1-Trifluoro-2-propanol and *p*-Toluenesulfonyl Chloride.—To a solution of 43.4 g (0.38 mole) of 1,1,1-trifluoro-2-propanol and 74.3 g (0.39 mole) of *p*-toluenesulfonyl chloride in 350 ml of acetone at 50° was added, with stirring, a solution of 16.0 g (0.40 mole) of sodium hydroxide in 50 ml of water. The reaction mixture was stirred at room temperature for 10 days.

The mixture was concentrated to approximately 250 ml on the steam bath, poured into 100 ml of water, and extracted with petroleum ether (bp 30–60°). The combined petroleum ether extracts were washed successively with concentrated aqueous NH_3 and water, dried over anhydrous $MgSO_4$, and distilled to yield 44.8 g (43%) of the ester, bp 123–124° (2.8 mm), $n^{25}D$ 1.4619.

Anal. Calcd for $C_{10}H_{11}F_3O_3S$: F, 21.25. Found: F, 21.34.

Isolation of 1,1,1-Trifluoro-2-diazopropane.—A solution of 1,1,1-trifluoro-2-diazopropane in di-*n*-butyl ether was prepared by oxidation of 1.26 g (0.01 mole) of the hydrazone. Using the technique described by Gilman and Jones,[9] the diazo compound was isolated as a volatile, orange liquid. An approximate boiling point determination was made by allowing a small amount of the neat diazo compound to warm up from −80° at a constant pressure of 67 mm. The compound boiled at −10° (67 mm). Infrared spectra of the compound were taken in several solvents and showed strong absorptions at 4.78 μ for the diazo function and at 8.5 and 9.0 μ for the trifluoromethyl group.

When a small amount (approximately 0.2 g) of the neat diazo compound was allowed to warm to room temperature at atmospheric pressure, its temperature continued to rise above room temperature, and it detonated at 32° with a loud report.

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[9] H. Gilman and R. G. Jones, *J. Am. Chem. Soc.*, **65**, 1458 (1943).

1,4-Di-*t*-butylcyclohexene

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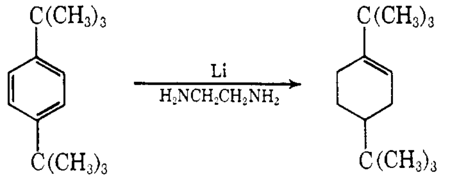
Garbisch has reported preparation in low yield of 1,4-di-*t*-butylcyclohexene (II), a compound of interest for use in studies of steric effects upon addition reactions to the carbon–carbon double bond.[1] Assured that a better procedure for the synthesis of II would find immediate use, we wish to report the direct preparation of II from *p*-di-*t*-butylbenzene (I),[2] by reduction with lithium in ethylenediamine.[3]



I II

The procedure was adapted from an experiment of Reggel, *et al.*, which gave 97% of octalin by reduction of tetralin with lithium in ethylenediamine.[4] *t*-Butylbenzene, under similar conditions, was reported to give 1-*t*-butylcyclohexene and 3-*t*-butylcyclohexene in the ratio 7:3.[5]

p-Di-*t*-butylbenzene (I) can be reduced readily by catalytic hydrogenation to give a mixture of *cis*- and *trans*-1,4-di-*t*-butylcyclohexane[6] (*cis* III and *trans* III), but no previous direct reduction of I to give products intermediate between I and III has come to our attention. One attempted partial reduction has been noted. Whereas *p*-xylene is reduced to 2,5-dihydro-*p*-xylene in 96% yield with lithium–ammonia–ethanol, under the same conditions, *p*-di-*t*-butylbenzene (I) gives negligible reaction.[7]

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(2) L. F. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1964, p. 184.

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(4) L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957), Table I, expt 5.

(5) R. A. Benkeser, R. K. Agnihotri, and M. L. Burrous, *Tetrahedron Letters*, **No. 16**, 1 (1960).

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