afforded a minute quantity of an oil with the characteristic odor of phenylhydrazine. Evaporation of the dried methylene chloride solution afforded a crude solid which on one recrystallization from ethanol gave 1.1 g (26%) of 1-benzoyl-2-phenylhydrazine, mp and mmp 168–169° (lit.[18] mp 168°).

Registry No.—1,1,1-Trimethylhydrazinium benzoate, 15038-93-4; 1,1,1-trimethylhydrazinium *p*-nitrobenzoate, 14908-51-1; 1,1,1-trimethylhydrazinium *p*-anisate, 15038-94-5; 1,1,1-trimethyl-2-(2-methoxybenzoyl)hydrazinium iodide, 14908-52-2; 1,3-dicyclohexyl-1-(4-nitrobenzoyl)urea, 14908-53-3.

Acknowledgment.—This work was supported by a National Science Foundation Undergraduate Research Participation Grant and a grant-in-aid from the Research Foundation of the State University of New York. We also wish to acknowledge the kindness of Mr. Kenneth Fleischer and his staff of the Sterling-Winthrop Research Institute for the microanalyses.

[18] E. Fischer, *Ann.*, **190**, 126 (1878).

2-Azoxybenzoic Acids as Benzyne Percursors

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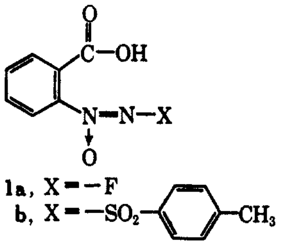
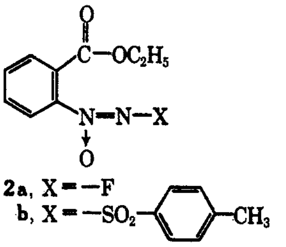
Received August 18, 1967

Various *ortho*-substituted benzoic acids have served as benzyne precursors.[1–3] As part of our study of fluoroazoxy[4] and related azoxy compounds,[5] it was of interest to see if the 2-substituted benzoic acids **1a** and **1b**, or their salts, would also generate benzyne when heated.

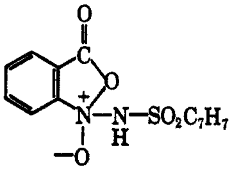


1a, X = —F
b, X = —SO$_2$—C$_6$H$_4$—CH$_3$



2a, X = —F
b, X = —SO$_2$—C$_6$H$_4$—CH$_3$

To prepare **1a** and **1b**, ethyl 2-nitrosobenzoate was converted to esters **2a** and **2b** by interaction with tetrafluorohydrazine[4] and chloramine-T,[6] respectively. The esters were converted into the acids by alkaline saponification. Only the infrared spectrum of **1b** requires additional comment. Although the infrared spectrum of **1a** (see Experimental Section) was that expected for a carboxylic acid dimer, that of **1b**, run in a Nujol mull, showed a bonded —OH at 3.13 μ and a sharp carbonyl band at 5.82 μ. Since **1b** is esterified by diazomethane or alcohols (acid catalyzed) to give **2b** and related esters, it appears that intramolecular hydrogen bonding, rather than a cyclic structure such as **3** or **4**, accounts for the unexpected infrared properties.[7]



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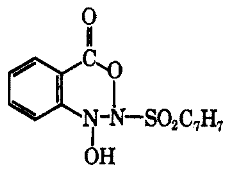
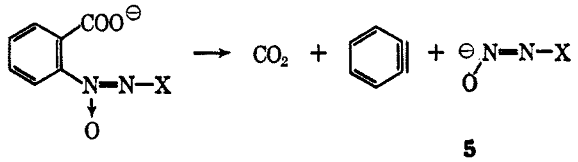


4

Only a small amount of N_2O was produced when **1a**, **1b**, or their salts were pyrolyzed in *o*-dichlorobenzene or in the dimethyl ether of triethyleneglycol (triglyme). Nitrogen and CO_2 were the major gaseous products. And, evidence for the intermediacy of benzyne was found in the thermal decomposition of salts of **1a** and of acid **1b**.[8]

Triptycene (2%) was isolated when a mixture of anthracene and the sodium salt of **1a** was refluxed in *o*-dichlorobenzene. However, triptycene (25%) was obtained from acid **1b** and anthracene in triglyme after 3 hr at 190°. Another effective trap for the benzyne produced from **1b** was 2,3,4,5-tetraphenylcyclopentadienone;[3] 1,2,3,4-tetraphenylnaphthalene (24%) was isolated in this experiment.

The nature of the decomposition process giving rise to nitrogen and benzyne remains obscure. Azoxy toluenesulfonates, structures similar to **1**, undergo thermal decomposition by an apparent radical mechanism and give nitrogen and aryl radicals.[9] An ionic pathway that produces CO_2, benzyne, and a nitrogen precursor such as diimide **5** is also conceivable.



5

Experimental Section

Preparation of N-(2-Carboethoxyphenyl)-N′-fluorodiimide N-Oxide (2a).—Ethyl 2-nitrosobenzoate (3 g) in 30 ml of chlorobenzene was exposed to an atmosphere of tetrafluorohydrazine[10] at 0–20°. When the uptake of tetrafluorohydrazine was complete, the solution was degassed thoroughly. The solution was chromatographed on silica gel in the usual manner.[4] The ester **2a** was isolated as a yellow oil. The F^{19} nmr spectrum had a single peak at φ −51.1.

Anal. Calcd for $C_9H_9N_2O_3F$: C, 50.93; H, 4.27; N, 13.21; F, 8.96. Found: C, 50.88; H, 4.35; N, 12.63; F, 8.41.

Preparation of N-(2-Carboxyphenyl)-N′-fluorodiimide N-Oxide (1a).—Compound **2a** (5 g), 100 ml of methanol, 10 ml of water, and 33 ml of 1.4 *N* sodium methoxide in methanol was refluxed for 1 hr. The mixture was poured into water, acidified, and extracted with methylene chloride. Evaporation of the methylene chloride left a solid residue, which was recrystallized from chloroform. Thus **1a** (3.2 g), mp 144–145°, was obtained. The F^{19} nmr spectrum had a single peak at φ −53.9.

Anal. Calcd for $C_7H_5N_2O_3F$: C, 45.66; H, 2.74; N, 15.22; F, 10.32. Found: C, 45.46; H, 2.90; N, 14.72; F, 10.66.

The infrared spectrum (Nujol mull) of **1a** indicated that it existed in the usual dimeric form. The bonded O–H stretch was 3.7–4.0 μ, and the carbonyl absorption was 5.95 μ.

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[1] Reviewed by G. Wittig, *Angew. Chem. Intern., Ed. Engl.*, **4**, 731 (1965).

[2] E. McNelis, *J. Org. Chem.*, **28**, 3188 (1963).

[3] F. M. Beringer and S. J. Huang, *ibid.*, **29**, 445 (1964).

[4] T. E. Stevens and J. P. Freeman, *ibid.*, **29**, 2279 (1964).

[5] T. E. Stevens, *ibid.*, **29**, 311 (1964).

[6] W. V. Farrar and J. M. Gulland, *J. Chem. Soc.*, 368 (1944).

[7] The infrared spectrum of deuterated **1b** was examined in an attempt to determine the functional group (azoxy or sulfonyl) involved in hydrogen bonding. No noticeable change in the azoxy absorption at 6.7–6.9 μ (masked by Nujol) or in the symmetric S=O stretch at 8.65 μ was observed, but the asymmetric S=O stretch at 7.45 μ in **1b** was a doublet, 7.45 and 7.55 μ, in the deuterated sample.

[8] The cesium salt of **1b** decomposed readily at about 180° and the acid **1b** required a temperature of about 200°. Since decomposition of the acid appeared clean, the benzyne trapping experiments were conducted with it.

[9] E. A. Dorko and T. E. Stevens, *Chem. Commun.*, 871 (1966).

[10] Currently available from K & K Laboratories, Inc.

The cesium salt of **1a** was prepared using aqueous cesium carbonate. The infrared spectrum of the salt had no OH bands; carboxylate bands at 6.2 and 7.3 μ were present.

Anal. Calcd for $C_7H_4N_2O_3FCs$: C, 26.60; H, 1.28; N, 8.87. Found: C, 26.77; H, 1.46; N, 9.56.

N-(2-Carboethoxyphenyl)-N′-*p*-toluenesulfonyldiimide N-oxide (2b) was prepared from ethyl 2-nitrosobenzoate and chloramine-T according to the procedure of Farrar and Gulland.[6] It was recrystallized from chloroform–hexane, mp 90–92°.

Anal. Calcd for $C_{16}H_{16}N_2O_5S$: C, 55.16; H, 4.63; N, 8.04. Found: C, 55.04; H, 4.75; N, 8.00.

The uv spectrum (ethanol) had λ_{max} 224 and 277 mμ (ϵ_{max} 18,800 and 9700).

Preparation of N-(2-Carboxyphenyl)-N′-*p*-toluenesulfonyldiimide N-Oxide (1b).—A 3.48-g sample of **2b** in a mixture of 5 ml of water and 55 ml of methanol containing 14 mmoles of sodium methoxide was stirred overnight. The mixture was poured into water and acidified, and the solid removed by filtration. Two recrystallizations of the solid (chloroform–ethyl acetate) gave 1.8 g of **1b**, mp 195–196° dec.

Anal. Calcd for $C_{14}H_{12}N_2O_5S$: C, 52.49; H, 3.78; N, 8.75. Found: C, 52.65; H, 4.14; N, 8.69.

The infrared spectrum of **1b** (Nujol mull) had an –OH peak at 3.13 μ and a sharp carbonyl peak at 5.82 μ.

The uv spectrum (ethanol) had λ_{max} 224 and 262 mμ (ϵ_{max} 17,100 and 8100). In 0.1 *N* sodium hydroxide in ethanol, λ_{max} 228 mμ (ϵ 13,700) and $\lambda_{shoulder}$ 272 mμ (ϵ 7300) were observed.

The cesium salt of **1b** had no –OH absorption in its infrared spectrum. Bands due to the carboxylate group were at 6.2 and 7.35 μ.

Esterification of 1b. A. With Acidic Methanol.—A mixture of 15 ml of 1,2-dichloroethane, 0.80 g of **1b**, 1 ml of methanol, and two drops of concentrated sulfuric acid was refluxed for 6 hr. The mixture was cooled and washed with H_2O and 10% aqueous sodium bicarbonate. The residue obtained upon evaporation of the organic layer was recrystallized from ethanol. Thus, N-(2-carbomethoxyphenyl)-N′-*p*-toluenesulfonyldiimide N-oxide, mp 125–127°, was obtained.

Anal. Calcd for $C_{15}H_{14}N_2O_5S$: C, 53.9; H, 4.22; N, 8.38. Found: C, 53.8; H, 4.43; N, 8.21.

The uv spectrum (ethanol) had λ_{max} 225 and 277 mμ (ϵ_{max} 18,600 and 9300).

B. With Acidic Ethanol.—When ethanol was substituted for methanol in the procedure A, and the mixture was refluxed for 24 hr, **2b**, mp and mmp 90–92°, was produced.

C. With Diazomethane.—To 0.5 g of **1b** in 50 ml of tetrahydrofuran (THF) at 0° was added an excess of ethereal diazomethane. When gas evolution ceased, the THF was removed at reduced pressure. The residue, recrystallized from ethanol, had mp 123–125° and an infrared spectrum identical with the methyl ester produced by procedure A.

Pyrolysis of the Cesium Salt of 1a.—A 0.32-g (1 mmole) sample of the cesium salt of **1a** was heated at 180–190° in 15 ml of triglyme. After 2 hr, the closed tube was vented into a calibrated volume. A total of 29 cc of gas, 79% N_2 and 23% CO_2 by mass spectrum was collected. An additional 16 cc of CO_2 was collected by quickly pumping the gases from the solution into a −196° trap.

When 0.63 g of the cesium salt was heated in 10 ml of *o*-dichlorobenzene for 2 hr at 170°, 70 cc of gas was obtained. This was 9% N_2O, 37% CO_2, and 54% N_2, as determined by mass spectrum.

Pyrolysis of 1b and its Cesium Salt.—When 0.45 g of the cesium salt of **1b** in 15 ml of dichlorobenzene was heated (180°) for 2 hr, 22 cc of gas, 73% N_2 and 27% CO_2, was collected. Degassing into a −196° trap collected another 10 cc of gas (99% CO_2 and 1% NO by mass spectrum).

From 0.32 g of **1b** (1 mmole) in 15 ml of triglyme (200°, 1 hr), 20 cc of gas, 75% N_2 and 25% CO_2, was collected.

Reaction of Anthracene and Sodium Salt of 1a.—To 4 mmoles of the sodium salt of N-(2-carboxyphenyl)-N′-fluorodiimide N-oxide, prepared from 0.75 g of the free acid, was added 1.2 g of anthracene and 25 ml of dichlorobenzene. The mixture was refluxed 4 hr. Excess dichlorobenzene was removed at 1 mm; excess anthracene was removed with maleic anhydride as usual.[3] The solid residue obtained after this treatment was chromatographed on silica gel. Elution was carried out with pentane containing increasing (2, 3, 5, 10%) methylene chloride. Anthracene (63 mg) and triptycene (18 mg) were recovered from the column. The triptycene had mp 251–253° (lit.[3] mp 254°) and infrared and nmr spectra identical with those reported.[3]

When 0.62 g of the cesium salt of **1a**, 0.72 g of anthracene, and 25 ml of triglyme were heated 3 hr at 180–190°, and the reaction worked up as described above, only 5 mg (1%) of triptycene was isolated.

Reaction of Anthracene and 1b.—A mixture of 0.64 g of **1b** (2 mmoles), 0.72 g of anthracene, and 25 ml of triglyme was heated (190–200°) for 3 hr. The mixture was cooled, poured into water, and extracted with hexane. The residue from the hexane was freed of anthracene as usual.[3] Chromatography of the final residue on silica gel gave 0.129 g of triptycene, mp 251–253°.

Reaction of 1b and 1,2,3,4-Tetraphenylcyclopentadienone.—Four mmoles, 1.28 g, of **1b**, 1.92 g (5 mmoles) of tetraphenylcyclopentadienone and 25 ml of triglyme was heated at 200° for 3 hr. The mixture was cooled and chromatographed on silica gel. Elution was carried out with pentane–methylene chloride (20:1, 5:1, 2:1). The first fraction eluted was 1,2,3,4-tetraphenylnaphthalene 0.426 g, mp 205–207° (lit.[3] mp 204°). The nmr spectrum corresponded to that reported.[3]

Registry No.—**1a,** 15037-76-0; **1a** cesium salt, 15037-77-1; **1b,** 15037-78-2; **1b** cesium salt, 15037-79-3; **2a,** 15037-80-6; **2b,** 15037-81-7; N-(2-carbomethoxyphenyl)-N′-*p*-toluenesulfonyldiimide N-oxide, 15037-82-8; triptycene, 477-75-8; 1,2,3,4-tetraphenylnaphthalene 751-38-2; benzyne, 462-80-6.

Acknowledgment.—This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract No. DA-01-021 AMC-11536(Z).

Synthesis of Isoquinolines. VII.
4-Hydroxy-1,2,3,4-tetrahydroisoquinolines[1]

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Received April 4, 1967

In our original paper describing a new synthesis of 1,2,3,4-tetrahydroisoquinolines[3] (1 → 2 → 5), we postulated that the reaction proceeded through a 1,2-dihydroisoquinoline such as **3** (Scheme I). This postulate was based upon the facts that the products of acid treatment of **2** gave dimers characteristic of 1,2-dihydroisoquinolines and that reaction of **2** with benzaldehyde in acid yielded 4-benzylisoquinolines,[4] again a reaction best described through a 1,2-dihydroisoquinoline intermediate.

It now appears that such is not the case under the conditions used. When derivatives of **2** were dissolved in 6 *N* hydrochloric acid and the acid was evaporated under vacuum, 4-hydroxy-1,2,3,4-tetrahydroisoquinoline hydrochlorides (**4**) were obtained in good yield. On hydrogenolysis with hydrogen and palladium-on-

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(1) (a) Paper VI: J. M. Bobbitt, D. N. Roy, A. Marchand, and C. W. Allen, *J. Org. Chem.*, **32**, 2225 (1967). (b) This work was supported by Grant CA-3905 from the National Cancer Institute of the National Institutes of Health, Public Health Service, and by Contract DA-49-193-MD-2948 from the U. S. Army Medical Research and Development Command, Publication 151.

(2) Abstracted in part from the M.S. Thesis of J. C. S., The University of Connecticut, Storrs, Conn., 1966.

(3) J. M. Bobbitt, J. M. Kiely, K. L. Khanna, and R. Ebermann, *J. Org. Chem.*, **30**, 2247 (1965).

(4) J. M. Bobbitt, D. P. Winter, and J. M. Kiely, *ibid.*, **30**, 2459 (1965).