filtered off and crystallized from hot water. It melted at 185.5–187° and was shown to be identical (mixed m. p.) with an authentic specimen of 5-bromo-2-furoic acid prepared according to the method of Whittaker.[14]

Summary

2-Furyltrimethylsilane and 2-thienyltrimethylsilane were synthesized from 2-furyllithium and 2-thienyllithium. The reaction of acetic anhydride with the above organosilicon compouunds, using iodine as the catalyst, gave 2-acetyl-5-trimethylsilylfuran and 2-acetyl-5-trimethylsilylthiophene, respectively.

LAFAYETTE, INDIANA RECEIVED DECEMBER 4, 1947

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[14] Whittaker, *Rec. trav. chim.*, **52**, 352 (1933).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Mechanism of the Nitration of Anisole

BY R. M. SCHRAMM AND F. H. WESTHEIMER

In the course of an investigation of the oxynitration of benzene,[1] the nitration of several phenols and of anisole was studied. The nitration of anisole leads to the formation of a mixture of nitroanisoles[2] and of nitrophenols[3] in proportions which depend upon experimental conditions. It is here shown that the nitration of anisole in dilute nitric acid solution is nitrite-catalyzed and that the nitrosoanisoles are probably intermediates in the reaction. These facts are of current interest because Bunton, Hughes, Ingold and Reed[4] have recently found that, under certain conditions, nitrosophenols are likewise intermediates in the nitration of phenols to nitrophenols.

More precisely, anisole has been found to react rapidly with 40 or 50% nitric acid containing a little nitrous acid, but fails during many hours to react with nitric acid containing urea.[5] When anisole is nitrated with 40% nitric acid (containing nitrous acid), the principal products are nitrophenols; when more concentrated (*e. g.* 60%) nitric acid is used, the principal products are nitroanisoles. The quantitative results of several experiments are reported in Table I.

TABLE I

THE REACTION OF ANISOLE WITH NITRIC ACID AND NITRITE

Conc. HNO_3, %	Conc. HNO_2, m./l.	Time of addition of anisole in minutes	Yield of nitroanisoles, % of theoretical	Yield of 2,4-dinitrophenol, % of theoretical
40	0.04	60	25	51
40	.18	60	18	63
50	.18	70	56	21
60	.18	60	71	Trace

p-Nitroanisole cannot be an intermediate in the nitrite-catalyzed nitration of anisole to nitrophenols because, if this substance is added to a nitrating mixture which reacts rapidly with anisole, it may be quantitatively recovered. On the other hand, experiments with *p*-nitrosoanisole show that it reacts readily with the same nitrating mixture.[6] The products obtained by the nitration of *p*-nitrosoanisole under a wide variety of conditions parallel those obtained from anisole under corresponding conditions (see Table II). Thus it appears that nitrosoanisole is an intermediate in the nitrite-catalyzed nitration of anisole.

TABLE II

THE REACTION OF *p*-NITROSOANISOLE WITH NITRIC ACID AND NITRITE

Conc. HNO_3, %	Conc. HNO_2, m./l.	Time of addition of anisole in minutes	Yield of nitroanisoles, % of theoretical	Yield of 2,4-dinitrophenol, % of theoretical
40	0.04	60	14	73
40	.18	60	11	76
50	.18	1	62	29
50	.18	10	54	36
50	.18	70	60	30
60	.18	60	91	5

Although the proportions of the two products (nitroanisoles and nitrophenols) obtained from *p*-nitrosoanisole are about the same as those obtained from anisole, there is no exact correspondence between the two nitrations. Several reasons for this discrepancy may be suggested. In the first place, anisole, when nitrated with nitric acid and nitrite, must yield a certain amount of *o*-nitrosoanisole[2] as an intermediate, and this isomer would not necessarily give further reaction products in the same proportions as does *p*-nitrosoanisole. In the second place, the actual nitrite concentrations are not exactly those given in the two tables, because, during the reaction, anisole and nitrosoanisole produced different amounts of oxides of nitrogen. Thirdly, the addition of gross quantities of *p*-nitrosoanisole to the reaction mixture rather than the formation of this compound

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[1] Westheimer, Segel and Schramm, THIS JOURNAL, **69**, 773 (1947).

[2] Brunck, *Z. Chemie*, 205 (1867); see also Holleman, *Rec. trav. chim.*, **22**, 263 (1903); Martinsen, *Z. physik. Chem.*, **59**, 605 (1907); Griffiths, Walkey and Watson, *J. Chem. Soc.*, 631 (1934); Buttle and Hewitt, *ibid.*, **95**, 1755 (1909).

[3] J. J. Hoffman, Dissertation, University of Chicago, 1931. For similar results with other aromatic ethers see K. Meyer, *Ann.*, **398**, 661 (1913); Ryan and Drum, *Sci. Proc. Roy. Dubin Soc.*, **17**, 313 (1924); Reilley, *ibid.*, **19**, 461 (1930).

[4] Bunton, Hughes, Ingold and Reed, *Nature*, **158**, 514 (1946).

[5] This nitration is thus similar to that of phenol; see Martinsen, *Z. physik. Chem.*, **50**, 385 (1905).

[6] *Cf.* Bayer and Knorr, *Ber.*, **35**, 3034 (1902).

in situ (as in the reaction of anisole with nitric acid and nitrite) may have some effect on the course of the reaction. However, this effect is probably unimportant, since the period of addition of *p*-nitrosoanisole may be varied from one to seventy minutes without materially affecting the proportions of the reaction products.

Experimental

The Effect of Nitrite on the Reaction of Anisole with Nitric Acid.—(1) Anisole (20 g.) was added dropwise to 400 cc. of 40% nitric acid containing approximately 0.04 m./l. of nitrous acid. The addition required about half an hour; the reaction mixture was held at 30° and stirred for forty-eight hours. This long reaction time was necessary to convert all the mononitrophenols first formed into the more readily isolated dinitrophenol.[1] The mixture was then chilled in ice and filtered. The crude product obtained weighed 26.5 g. and melted at 100–108°. By recrystallization of this material from alcohol, 20 g. (59%) of pure dinitrophenol (m. p. 112–114°) was obtained. The identity of this compound was established by its melting point, the melting point of its mixture with an authentic sample of 2,4-dinitrophenol, and by the preparation of 6-bromo-2,4-dinitrophenol, m. p. 117–118°. In this experiment, the reaction mixture was not worked up for nitroanisoles; the product or products which arise from the methyl group of anisole have not been determined.

(2) In a second experiment, anisole (20 g.) was added dropwise over a period of one-half hour to 400 cc. of 40% nitric acid to which (one hour previously) 4 g. of urea had been added. After the mixture had been stirred for eighteen hours at about 30°, the reaction mixture was transferred to a separatory funnel and extracted with three successive 50 cc. portions of benzene. The benzene extract was washed with 60 cc. of water and dried over anhydrous sodium sulfate. Distillation from a small Claisen flask yielded 16.3 g. of anisole (81% of that used) boiling in the range 153–155°. There was no high-boiling residue.

(3) Seventy-five cc. of 50% nitric acid was allowed to stand with 1 g. of urea for three hours. Then anisole (about three g.) was added. The reaction mixture, after standing at room temperature for twelve hours was decidedly colored. The cause of the color was not determined; however, the extent of reaction was slight, since a three-drop sample of the mixture, when dissolved in a large excess sodium hydroxide solution, gave only a negligible yellow color. This test for nitrophenols is quite sensitive; and will easily reveal the presence of five parts per million of these compounds.

(4) One-hundred cc. of 50% nitric acid containing 0.1 m./l. of nitrous acid was mixed with three grams of anisole. The reaction mixture, after standing for two minutes at room temperature, was very dark. A three-drop sample of this reaction mixture, when dissolved in excess sodium hydroxide, gave a strong yellow color. The color was identified as that of nitrophenols, since (a) it was much more intense than that of a similarly diluted but neutral sample of the reaction mixture and (b) the coloring material had the indicator properties of nitrophenols.

(5) One-hundred cc. of 60% nitric acid containing 0.1 m./l. of nitrous acid was mixed with 0° with 1 g. of anisole. Reaction occurred instantly and proceeded autocatalytically. These conditions are probably not very different from those which were used for the preparation nitration of anisole to a mixture of ortho and para nitroanisoles.[2]

(6) Five-hundred cc. of 60% nitric acid was allowed to stand for an hour with 8 g. of urea; the solution was cooled to 0°, where urea nitrate crystallized. Three grams of anisole was then added. After two hours at 0°, 200 cc. of water was added and the mixture extracted with three 50-cc. portions of benzene. The benzene extract was washed and then fractionated through a short (10″) distilling column (tantalum-wire spiral type). After all the benzene was removed, the residue was distilled from a small Claisen flask. Anisole (1.9 g. distilling at 152–155°) was recovered. A small high boiling residue presumably contained nitro anisoles. At room temperature, 60% nitric acid containing urea gives no evidence of reaction for several minutes; then vigorous and autocatalytic nitration (with evolution of oxides of nitrogen) occurs.

The Reaction of *p*-Nitroanisole with Nitric Acid in the Presence of Nitrite.—Nine grams of *p*-nitroanisole was stirred at 50° for four and a half hours with 200 cc. of 50% nitric acid which contained 0.017 m./l. of sodium nitrite. When the mixture was filtered, 8.5 g. of *p*-nitroanisole, m. p. 50–52°, was recovered.

In a second experiment, *p*-nitroanisole (8.0 g.) was stirred at 50° for four and one-half hours with 200 cc. of 70% nitric acid containing 0.034 m./l. of nitrous acid. The reaction mixture in this case was homogeneous, whereas a slurry was obtained in the first experiment. When the mixture was cooled, diluted with water and filtered, 7.5 g. of *p*-nitroanisole, (identified by melting point and by the melting point of a mixture with an authentic sample) was recovered.

The Products of the Reaction of Anisole and of *p*-Nitrosoanisole with Nitric Acid and Nitrite.—Anisole (or *p*-nitrosoanisole) was added dropwise to about 200 cc. of a reaction mixture composed of nitric and nitrous acids (see Table I and II). During the addition, the reaction mixture was stirred vigorously and maintained at 50°. The amount of anisole or *p*-nitrosoanisole added was in each case between 3 and 4 g. After the addition was complete, the reaction mixture was heated long enough[1] to convert any mononitrophenols which had been formed into the more readily isolated 2,4-dinitrophenol. The mixture was then cooled and extracted with four successive 100-cc. portions of benzene. The benzene extract was concentrated to a volume of about 100 cc., and was then extracted with about 100 cc. of aqueous triethanolamine solution. Acidification of the aqueous extract threw down a precipitate of 2,4-dinitrophenol, which was filtered off, dried in a vacuum desiccator and weighed. The nitroanisole fraction was obtained from the residual benzene solution by removing the benzene under reduced pressure at room temperature.

In several instances, the above procedure was slightly varied. When the yield of nitroanisoles was relatively high, practically pure *p*-nitroanisole crystallized from the reaction mixture when it was cooled, and was recovered by filtration. This product was identified by its melting point and by the melting point of a mixture with an authentic sample of *p*-nitroanisole. In the reaction with *p*-nitrosoanisole, the nitroanisole isolated from the benzene extract was also practically pure *p*-nitroanisole. In the reactions with anisole, however, the product similarly isolated was an oil, probably a mixture of *o*- and *p*-nitroanisoles. These mixtures were usually worked up for *p*-nitroanisole, but were tested for the presence of nitrophenols only by their color reaction with alkali. In no case was an appreciable amount of nitrophenol found. The presumption that these oils were actually mixtures of *o*- and *p*-nitroanisoles was based first on the comparison with similar preparations previously reported.[2] In addition (in one instance), 1.40 g. of pure *p*-nitroanisole was isolated from 3.13 g. of the oil by recrystallization from aqueous alcohol. In another experiment, where the reaction with anisole gave a high yield of nitroanisoles, the initial yield of crystals from the reaction mixture was collected and found to be practically pure *p*-nitroanisole. In this case, 2.00 g. of *p*-nitroanisole was obtained from a total yield of 2.96 g. of crude oil.

Summary

The nitration of anisole in 40, 50 and 60% nitric acid is nitrite-catalyzed. The reaction product is a mixture of nitroanisoles and nitrophenols, in which the former compounds predominate when

60% acid is used and the latter when 40% acid is used. Under the same experimental conditions the same products can be obtained in roughly the same proportions from both nitrosoanisole and from anisole. This fact strongly indicates that the nitrosoanisoles are intermediates in the nitrite-catalyzed nitration of anisole.

CHICAGO, ILLINOIS RECEIVED DECEMBER 13, 1947

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Vapor Pressures and Some Related Quantities of Pentene-1 from 0 to 200°

BY H. O. DAY AND D. E. NICHOLSON WITH W. A. FELSING

Introduction

The determination of the thermodynamic properties of hydrocarbons has been a part of the research program of this laboratory for a number of years. Thus, heat capacities, heats of vaporization, and compressibilities for a number of hydrocarbons have been determined and reported.[1] The increasing importance of olefinic hydrocarbons has indicated a study of the pentenes and this report covers a portion of the work on pentene-1. In determining *p–v–t* data on both gaseous and liquid pentene-1, it was found that adequate data on vapor pressures over the range of temperatures from room temperature to the vicinity of its critical temperatures were lacking. This paper, hence, reports the experimentally determined vapor pressures for the range 0 to 200°.

Previous Investigations

The existing vapor pressure data have been examined critically by Stull[2] and he has reported the most probable values for the temperature range of −80.4 to 30.1°.

The normal boiling points, as recorded in the literature, differ considerably, due probably to differences in the purity of the samples of pentene-1 used. The most probable value, as selected by Stull[2] and as reported by Sherrill and Walter[3] is 30.1°, though the value of 29.97° was chosen by the A.P.I. Project No. 44.[4]

Methods and Apparatus

The dead-weight piston gage apparatus used in this Laboratory in *p–v–t* investigations was limited to a low pressure value of about 5 atmospheres, as determined by the weight of the piston and scale pan. Hence, vapor pressures up to 7.5 atmospheres were determined by means of a glass-contained compound mercury manometer, as described by Wilson,[5] attached to a static vapor pressure determining apparatus used by Felsing and Thomas.[6] The loading device employed by Felsing and Durban[7] was used to introduce pure, air-free pentene-1 into the piezometer at about −65°. A reasonable fraction, usually one-third, of the liquid was then evaporated out of the piezometer into the vacuum system to insure complete freedom from dissolved gases. An internal stirrer, actuated by a solenoid and metronome, served to prevent temperature gradients in the liquid. The entire apparatus was constructed of Pyrex glass. Mercury levels in the manometer were determined by means of a Gaertner cathetometer which could easily be read to 0.05 mm. Temperatures within the Dewar-flask bath were measured by short range mercurial thermometers calibrated by the National Bureau of Standards. The over-all precision of these measurements was ±0.3%.

For vapor pressures from about 6 to 40 atmospheres, a dead-weight piston gage previously described,[8] was employed. Thermostat temperatures were controlled to ±0.005° by means of a platinum resistance thermometer in conjunction with a Mueller bridge and a photoelectric cell relay. The actual thermostat temperature was simultaneously determined by the resistance thermometer (calibrated by the National Bureau of Standards). In determining the vapor pressures, the volume of the vapor phase was varied from 0.2 to 15 cc.; this change in vapor volume had no effect on the observed pressures, indicating a high purity of the pentene-1. Three separate runs on three separate fillings gave closely agreeing values; the precision of the measurements was within ±0.1%.

The region above 200° is *not* considered in this paper, since the critical pressure is in the neighborhood of 201°; this critical region and liquid and vapor compressibilities will be reported in a later paper.

Material Used

The pentene-1 for this investigation was obtained from the Phillips Petroleum Company. The National Bureau of Standards, from freezing point data on representative samples of this lot, reported a purity of 99.34 ± 0.40 mole per cent. The most probable impurity was isopentane. The densities of the liquid under its own vapor pressure as a function of the temperature over the range 0–50° are represented by the equation

$$d(\text{g./cc.}) = 0.6630 - 0.001034t$$

where *t* is in degrees centigrade. The normal boiling point, as calculated from the vapor pressure equation, was found to be 30.07 ± 0.02°.

Treatment of Data

The experimental data were plotted to large scale as log *p* (mm.) against the reciprocal of the absolute temperature. Three linear equations were fitted by the method of least squares to separate portions of the line

(1) 0– 35°: $\log_{10} p\ (\text{mm.}) = 7.40607 - 1372.194/T$
(2) 40– 95°: $= 7.31561 - 1342.407/T$
(3) 100–170°: $= 7.26782 - 1324.730/T$

The ice-point was taken as 273.16°K.

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[1] (a) Lemons with Felsing, THIS JOURNAL, **65**, 46 (1943); (b) Dailey with Felsing, *ibid.*, **65**, 42 (1943); (c) Felsing and Watson, *ibid.*, **64**, 1822 (1942); **65**, 1889 (1943); **65**, 780 (1943); (d) Templeton and Davies with Felsing, *ibid.*, **66**, 2033 (1944); (e) Felsing, Cuellar and Newton, *ibid.*, **69**, 1972 (1947).

[2] Stull, *J. Ind. Eng. Chem.*, **39**, 517 (1947).

[3] Sherrill and Walter, THIS JOURNAL, **58**, 742 (1936).

[4] A.P.I. Res. Project 44 at NBS; "Selected Values of Properties of Hydrocarbons" Table 8a, dated May 31, 1947.

[5] Wilson, *Univ. of Illinois Eng. Exp. Sta. Bull.*, No. 146 (1925).

[6] Felsing and Thomas, *J. Ind. Eng. Chem.*, **21**, 1269 (1929).

[7] Felsing and Durban, THIS JOURNAL, **48**, 2885 (1926).

[8] Kelso with Felsing, *ibid.*, **62**, 3132 (1940).