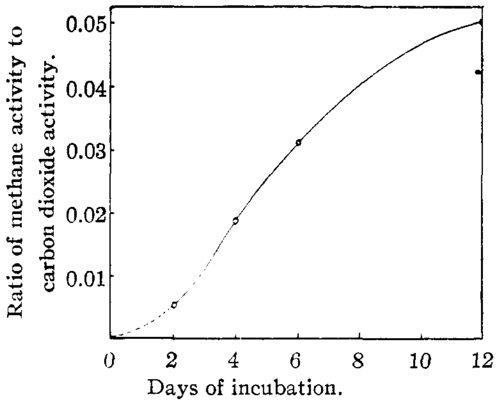


Fig. 1.—Relation of activity ratio to time of incubation.

material with later autolysis, or the formation of endogenous compounds, makes little difference. In any case we must conclude that the predominant reaction in the methane fermentation of acetic acid does not involve reduction of carbon dioxide.

This work indicates that the methane is produced by some mechanism other than the reduction of carbon dioxide, and must therefore be derived from the acetic acid. A simple decarboxylation seems to be the most likely mechanism, but is not definitely established. It is still possible that some preliminary condensation might take place, with subsequent decomposition of the condensation product, but this point cannot be proved by this method of attack.

Summary

It was suggested by previous workers that the methane fermentation of acetic acid might proceed by reduction of carbon dioxide to methane, as was shown to be the case for several alcohols.

In order to determine whether or not this was the case, radioactive C^{14} was used to mark the carbon atom of the carbon dioxide. The gases resulting from the fermentation were separated and converted to barium carbonate for measurement of the radioactivity.

By comparing the activity of the methane and the carbon dioxide, it was shown that only a very small portion of the methane was derived from the carbon dioxide. By studying the relation of the amount of methane formed by reduction of carbon dioxide to the time of incubation, a correlation was found which was interpreted as indicating a slow reduction unassociated with the general fermentation, such as the formation of cell substance and subsequent autolysis. From this it was concluded that the acetic acid was fermented entirely, or very nearly so, without reduction of carbon dioxide, and that the methane is predominantly derived from the acetic acid and not from carbon dioxide.

URBANA, ILLINOIS RECEIVED OCTOBER 27, 1947

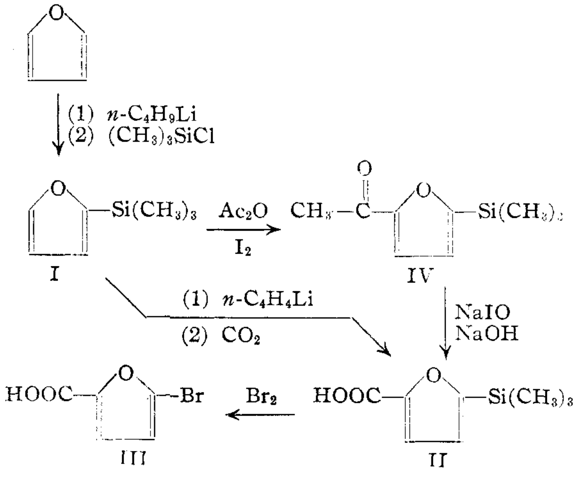
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY]

Acylation Reactions with Organosilicon Compounds[1]

BY ROBERT A. BENKESER AND ROBERT B. CURRIE[2]

Apparently, the only attempt to carry out a Friedel–Crafts reaction involving an organosilicon compound is the work of Kipping.[3] He reported that if a compound like tetraphenylsilane is heated with aluminum chloride the only product isolated is silicon tetrachloride (80% yield). Viewed from the generalized Lewis concept of acids[4] this is not surprising since it has long been known that the aromatic carbon–silicon bond is readily cleaved by acidic reagents.[5–7] The electropositive silicon atom tends to combine with a more electronegative element than carbon when given the opportunity.

It has now been found that using the mild catalyst iodine, an acylation reaction can be carried out with certain organosilicon compounds. In the experiments herein reported, 2-thienyltrimethylsilane and 2-furyltrimethylsilane were acetylated with acetic anhydride at 50°. The yields were of the order of 20–25%. The equations indicate the general sequence of reactions with furan



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[1] A portion of this work is abstracted from the thesis submitted by Robert B. Currie to Purdue University in partial fulfilment of the requirements for the degree of Master of Science, August, 1947.

[2] Present address: Merck and Company, Rahway, New Jersey.

[3] Evison and Kipping, *J. Chem. Soc.*, 2774 (1931).

[4] Lewis, *J. Franklin Inst.*, **226**, 293 (1938).

[5] Ladenburg, *Ann.*, **173**, 143 (1874).

[6] Kipping and Lloyd, *J. Chem. Soc.*, **79**, 449 (1901).

[7] Kipping, *ibid.*, **91**, 223 (1907).

The proof of structure of 2-acetyl-5-trimethylsilylfuran (IV) was accomplished by the hypoiodite degradation to the corresponding acid. This acid was identical with that obtained by the metalation of 2-furyltrimethylsilane (I) with *n*-butyllithium. Finally this acid (II) was converted to the known 5-bromo-2-furoic acid by treatment with bromine.

The thiophene sequence was essentially the same as that indicated above for furan except that metalation of thiophene with *n*-butyllithium is known to occur in the 2-position.[8] This established the structure of 2-thienyltrimethylsilane. The acid obtained from the metalation of this compound with *n*-butyllithium and from the hypoiodite degradation of 2-acetyl-5-trimethylsilylthiophene was shown to be 5-trimethylsilyl-2-thiophenecarboxylic acid by cleaving it with hydrogen chloride to the known 2-thiophenecarboxylic acid.

Experimental

2-Thienyltrimethylsilane.—To 84 g. (1.0 mole) of thiophene[9] was added 325 ml. of an ethereal solution of *n*-butyllithium[10] containing 0.98 mole of the organometallic.[11] The addition was made as rapidly as the evolved butane would allow. The mixture was refluxed three hours and then permitted to stand overnight at room temperature. Eighty grams (0.74 mole) of trimethylchlorosilane was added slowly and when the addition was complete the mixture was refluxed an additional three hours. After hydrolyzing with 10% sulfuric acid, the ether layer was separated and shaken with 10% sodium hydroxide. After drying over Drierite the ether was removed, and the residue was fractionated through a short, glass-spiral column. Eighty-six grams (75%) of a colorless oil was collected boiling at 159–160° (748 mm.), $n^{20}\text{D}$ 1.4966, $d^{20}{}_4$ 0.945.

Anal. Calcd. for $C_7H_{12}SSi$: C, 53.8; H, 7.70. Found: C, 53.3; H, 7.78.

If the thienyllithium prepared above is carbonated the acid can be shown to be 2-thiophenecarboxylic acid[8] thus establishing the position of the trimethylsilyl group.

2-Acetyl-5-trimethylsilylthiophene.—A mixture of 30 g. (0.19 mole) of 2-thienyltrimethylsilane, 30 g. (0.29 mole) of acetic anhydride, and 0.25 g. of iodine[12] was heated for one hour at 50°. The dark solution was shaken with 10% potassium hydroxide until the washings were basic. Ether was added; the residue was washed several times with water and then with a concentrated solution of sodium thiosulfate. After drying over anhydrous sodium sulfate, the ether was removed and the residue was fractionated through a small glass-spiral column. Five grams (13%) of a yellow oil boiling at 104–105° (4 mm.) was collected, $n^{20}\text{D}$ 1.5289, $d^{20}{}_4$ 1.028.

Anal. Calcd. for $C_9H_{14}OSSi$: Si, 14.1; C, 54.5; H, 7.07. Found: Si, 13.7; C, 54.3; H, 7.08.

The semicarbazone of this ketone was prepared in the conventional manner and it melted with decomposition at 217–220°.

Anal. Calcd. for $C_{10}H_{17}ON_3SSi$: N, 16.46. Found: N, 16.30 and 16.47.

5-Trimethylsilyl-2-thiophenecarboxylic Acid.—To 8 g. (0.05 mole) of 2-thienyltrimethylsilane was added 54 ml. of an ethereal solution of *n*-butyllithium[10] containing 0.05 mole of the organometallic.[11] The mixture was refluxed four hours and then carbonated by pouring jet-wise onto powdered Dry Ice. After allowing the mixture to warm to room temperature, water was added with vigorous stirring. The clear ether layer was discarded and, upon acidifying the basic water layer with concentrated hydrochloric acid, 6.3 g. (62%) of 5-trimethylsilyl-2-thiophenecarboxylic acid separated and after crystallization from dilute ethanol it melted at 134–135°.

Anal. Calcd. for $C_8H_{12}O_2SSi$: Si, 14.0. Found: Si, 13.7.

This same acid was isolated (mixed m. p.) when 2-acetyl-5-trimethylsilylthiophene was treated with sodium hydroxide and iodine in a typical iodoform reaction.

2-Thiophenecarboxylic Acid.—Approximately 0.5 g. of 5-trimethylsilyl-2-thiophenecarboxylic acid was dissolved in 15 ml. of benzene, and while refluxing the solution, hydrogen chloride was bubbled through for one hour. Extraction with 10% sodium hydroxide, followed by acidification of the water layer gave a crystalline solid melting at 126–127° which showed no depression with an authentic sample of 2-thiophenecarboxylic acid. This establishes the position of both the carboxyl and acetyl group.

2-Furyltrimethylsilane.—To 68 g. (1.0 mole) of furan[13] was added 325 ml. of an ethereal solution of *n*-butyllithium[10] containing 0.98 mole of the organometallic.[11] The remainder of the directions are identical with those described above for 2-thienyltrimethylsilane. Rectification of the residue gave 53 g. (52%) of a colorless oil boiling at 124–125° (750 mm.), $n^{20}\text{D}$ 1.4470, $d^{20}{}_4$ 0.880.

Anal. Calcd. for $C_7H_{12}OSi$: C, 60.0; H, 8.58. Found: C, 59.5; H, 8.71.

2-Acetyl-5-trimethylsilylfuran.—A mixture of 35 g. (0.25 mole) of 2-furyltrimethylsilane, 28.4 g. (0.27 mole) of acetic anhydride and 0.3 g. of iodine[12] was heated with stirring to an internal temperature of about 50°. At this point the reaction became exothermic and some cooling and later heating was necessary to keep the temperature between 45–55° for one hour. At the end of this time 15 ml. of water was added, and after stirring for a few minutes the dark solution was shaken with small quantities of 10% potassium hydroxide until the washings were basic. It was washed once with water and again with a concentrated solution of sodium thiosulfate. Upon removal of the solvent and rectification of the residue there was obtained 11.3 g. (25%) of a yellow oil (darkens rapidly on standing) boiling at 78.5–79° (3–4 mm.), $n^{20}\text{D}$ 1.4925, $d^{20}{}_4$ 0.978.

Anal. Calcd. for $C_9H_{14}O_2Si$: Si, 15.4. Found: Si, 15.0.

The semicarbazone of this ketone, prepared in the usual way, melted at 200–201°.

Anal. Calcd. for $C_{10}H_{17}O_2N_3Si$: N, 17.56. Found: N, 17.72 and 17.59.

5-Trimethylsilyl-2-furoic Acid.—To 10 g. (0.07 mole) of 2-furyltrimethylsilane was added 67 ml. of an ethereal solution of *n*-butyllithium[10] containing 0.07 mole of the organometallic.[11] The mixture was refluxed four hours, and then allowed to stand overnight at room temperature. The mixture was carbonated and worked up in a manner similar to that described for 5-trimethylsilyl-2-thiophenecarboxylic acid. After reprecipitating the acid from 10% potassium hydroxide and crystallizing it twice from dilute ethanol, 8 g. (62%) of a light tan solid was obtained melting at 110–111°.

Anal. Calcd. for $C_8H_{12}O_3Si$: Si, 15.2. Found: Si, 14.9.

This same acid was isolated (mixed m. p.) when 2-acetyl-5-trimethylsilylfuran was treated with sodium hydroxide and iodine.

5-Bromo-2-furoic Acid.—A mixture of 1 g. (0.005 mole) of 5-trimethylsilyl-2-furoic acid and 1.5 g. (0.009 g. atom) of bromine in 15 ml. of dry carbon tetrachloride was refluxed one hour. The solid which had separated was

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(8) Private communication from Dr. Henry Gilman.

(9) Purchased from Socony-Vacuum Oil Company.

(10) Gilman, Zoellner and Selby, THIS JOURNAL, **55**, 1252 (1933).

(11) Gilman and Haubein, *ibid.*, **66**, 1515 (1944).

(12) See Hartough and Kosak, *ibid.*, **68**, 2639 (1946).

(13) Kindly supplied by the E. I. du Pont Company

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

(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).