the material to be counted, contained in a glass dish at a standard distance from the end-window. Immediately before and after each counting operation the background count was determined and the mean value subtracted from the observed count. The usual counting time was 10 min. and the readings were then corrected to number of counts per minute.

Radioactive Count of Pure Tetraethylammonium Radiochloride.—A 1-ml. sample of a 0.0286 *M* solution of NEt_4Cl^{36} in acetonitrile was counted by the above procedure. The over-all count was found to be 3075 counts per min., which after correction for the background count of 33 counts per min., gave an actual solution count of 3042 per min.

Extent of Exchange Accompanying Chloride Ion-promoted Elimination from Bromotetralone I.—A 50-ml. portion of an acetonitrile solution 0.0300 *M* in bromotetralone I and 0.0263 *M* in NEt_4Cl^{36} was maintained at 24.5° for 80 min. A 5-ml. sample was removed and found to require 5.50 ml. of 0.0090 *M* sodium methoxide for neutralization. The acid formation corresponded to 33% elimination. To the remainder of the solution petroleum ether was added and the solution washed well with water until the washings were found to be nonradioactive. The petroleum ether solution was then evaporated to dryness under reduced pressure. A solution containing 0.0180 g. of product per ml. of acetonitrile was counted by the standard technique. The actual count on the sample was found to be only 6.0 per min. The product was redissolved in petroleum ether and again washed well with water; a repeat of the above procedure then led to an actual count of 7.0 per min. showing the small count to be due to an actual incorporation of radiochlorine into the organic residue and not due to a trace of radiochloride ion impurity.

Since the radiochlorine count is extremely low we can to an excellent approximation assume the organic residue to be a mixture of bromotetralone I (contaminated with a trace of chlorotetralone III) and endocyclic α,β-unsaturated ketone II. To 0.0180 g. of residue was added a little acetonitrile and excess piperidine and the mixture allowed to stand for 24 hr. Then 30 ml. of acetone and excess nitric acid were added and the bromide ion concentration determined by potentiometric titration was equivalent to 3.68 ml. of 0.0100 *M* silver nitrate. This corresponds to a bromotetralone I mole fraction of 0.63 in excellent agreement with the 33% elimination as determined by acid titration.

The concentration of bromotetralone I in the counted solution was 0.0378 *M* and for a concentration of 0.0286 *M* the count would have been 4.9 per min. The percentage uptake of radiochlorine into the bromotetralone is therefore 4.9/3042 × 100%; *i.e.*, 0.16%. When 33% elimination has occurred the remaining bromotetralone I has 0.16% of its bromine atoms replaced by radiochlorine atoms and for every act of substitution about 200 of elimination have taken place.

Extent of Exchange Accompanying Chloride Ion-promoted Elimination from Chlorotetralone III.—A 60-ml. portion of solution 0.0167 *M* in chlorotetralone III and 0.0182 *M* in NEt_4Cl^{36} was maintained at 90.6° for 95 min. A 5-ml. portion was found to require 4.62 ml. of 0.00900 *M* sodium methoxide for neutralization. This corresponds to 50% elimination reaction having taken place. To the remainder of the solution petroleum ether was added and the solution water washed until the washings were nonradioactive. The petroleum ether solution was then evaporated to dryness under reduced pressure.

A solution containing 0.0170 g. of product per ml. of acetonitrile was counted by the standard technique. The actual count on the sample was found to be 20.9 per min. To 0.0173 g. of sample was added a little acetonitrile and excess piperidine; the solution was maintained at 90.6° for 24 hr. and then 30 ml. of acetone was added and the solution acidified with nitric acid. The chloride ion was found by potentiometric titration to be equivalent to 2.90 ml. of 0.0100 *M* silver nitrate; this corresponds to a chlorotetralone III mole fraction of 0.47, in excellent agreement with the 50% elimination as determined by acid titration.

The concentration of chlorotetralone III in the counted solution was 0.0290 *M* and the percentage of Cl^{36} present was 20.9/3042 × 100%; *i.e.*, 0.69%. In determining the amount of exchange allowance must be made for dilution of the Cl^{36} by hydrogen chloride eliminated from the chlorotetralone. At 50% elimination $[NEt_4Cl^{36}]$ is 0.0182 *M* and [HCl] is 0.00835 *M*. The true percentage of chlorine exchange is, therefore, $0.69[0.0182 + 0.00835/2]/0.0182$; *i.e.*, 0.85%. When 50% elimination has occured the remaining chlorotetralone III has 0.85% of its chlorine atoms exchanged with those present as chloride ion in solution and for every act of substitution 59 of elimination have taken place.

Kinetics of the Chloride Ion-promoted Elimination from Chlorotetralone III.—All runs were carried out by the sealed bulb technique using 5.05-ml. aliquots. Titration of acid production was in 30 ml. of acetone previously rendered neutral to lacmoid indicator, against a standard solution of sodium methoxide in methanol. One run was followed by potentiometric titration against standard silver nitrate in a titration medium consisting of 30 ml. of acetone containing about 1 ml. of 1 *N* nitric acid. A silver wire electrode and a potassium nitrate–agar bridge to a diptype calomel reference electrode were used.

Throughout each individual run the first-order rate coefficients with respect to chlorotetralone III fell in value as reaction proceeded. Such a fall was observed and discussed for the bromide ion-promoted elimination from bromotetralone I.[2]

TABLE I

INITIAL SECOND-ORDER RATE COEFFICIENTS, k_2, FOR ACID PRODUCTION IN THE REACTION OF 2-BENZYL-2-CHLORO-4,4-DIMETHYL-1-TETRALONE WITH TETRAETHYLAMMONIUM CHLORIDE IN SOLVENT ACETONITRILE

t, °C.	[Chlorotetralone]	$[NEt_4Cl]$	10^3k_2, l. moles^{-1} sec.$^{-1}$
61.3	0.0200	0.0769	0.45
75.5	.0100	.00398	2.01[a]
75.5	.0200	.00961	1.93
75.5	.0200	.0769	1.86
90.6	.0200	.00961	8.9

[a] Initial second-order rate coefficient for bromide ion production is 2.06×10^{-3} l. moles^{-1} sec.$^{-1}$; $k_2 = Ae^{-E/RT}$; $A = 10^{12.7}$ l. moles^{-1} sec.$^{-1}$; $E = 24.6$ kcal./mole.

An illustrative run is given below; the first-order rate coefficients, k_1 (sec.$^{-1}$), are with respect to chlorotetralone III.

TEMPERATURE: 90.6°; 5.05-ML. ALIQUOTS AT 24°; [CHLOROTETRALONE]: 0.0200 *M*; $[NEt_4Cl]$: 0.00961; TITERS ARE IN ML. OF 0.00900 *M* NAOME

Time, min.	0	10	20	30	40	50	60
Titer	0.25	0.76	1.20	1.60	1.97	2.30	2.58
10^5 k_1:	..	7.98	7.58	7.31	7.12	6.90	6.64

Initial k_1 is 8.55×10^{-5} sec.$^{-1}$, corresponding to an initial second-order rate coefficient of 8.9×10^{-3} l. moles^{-1} sec.$^{-1}$.

Acknowledgment.—The authors wish to thank Mireille Coppens for preparation of the 2-benzyl-2-chloro-4,4-dimethyl-1-tetralone. This work was supported in part by grant no. G-14469, National Science Foundation.

Decomposition of Aryldiazonium Hexafluorophosphates in Tetramethylurea. A New Deamination Procedure

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Interest in this laboratory in the thermal decomposition of aryldiazonium hexafluorophosphates to the corresponding aromatic fluorocarbons[2] has led to the discovery of a new deamination procedure. It has

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[1] Supported by a grant from the National Research Council of Canada.

[2] Kenneth G. Rutherford, William Redmond, and James Rigamonti, C. S. B., *J. Org. Chem.*, **26**, 5149 (1961).

TABLE I

PER CENT YIELD OF DEAMINATION PRODUCT[a]

Amine	Ethanol	Hypophosphorous acid	Alkaline formaldehyde	Tetramethylurea
Aniline	5	60	60	25–30
o-Toluidine	*o*-Methylphenetole, *ca.* 50	70–75	80	
p-Toluidine	*o*-Methylphenetole, *ca.* 45	77–83	80	25–30
o-Anisidine	Amount unstated		75	33
Anthranilic acid	Ethyl benzoate, 53		25	80–85
p-Aminobenzoic acid	*p*-Ethoxybenzoic acid, 50 + ethyl benzoate			82
o-Nitroaniline	82	75–80	20	75
p-Nitroaniline	70	55–60	10	62
p-Chloroaniline	87		50	70
o-Bromoaniline	72–80			80
p-Bromoaniline	68–80			72
p-Aminoacetophenone				43

[a] Unless otherwise specified, the amino group has been replaced by hydrogen.

long been known that a primary aromatic amino group can be replaced by hydrogen by reduction of its intermediate diazonium compound.[3] The long established procedures involve reduction of the aromatic diazonium chloride with ethanol,[4] hypophosphorous acid,[5] or alkaline formaldehyde.[6] Sodium stannite,[7] stannous chloride, and sodium sulfite[8] have been reported as reducing agents in this reaction, but their use appears to be limited as a general procedure. Recently Meerwein[9] has reported the use of dioxane, dioxolane, diglyme, and tetrahydrofuran as hydride transfer agents in the reduction of aryldiazonium chlorides. The yield of reduction product in each case with the limited number of examples chosen was good. However, the author's attempts to reduce diazonium fluoborates in tertiary amines apparently did not show promise as a useful procedure even though *p*-chlorobenzenediazonium fluoborate and 2,4,6-trichlorobenzenediazonium fluoborate gave, respectively, 45% and 65% of reduction product. Nevertheless, this is the first case recorded in the literature of reduction of a diazonium salt in nonaqueous media. Hendrickson[10] has recently reported another nonaqueous reduction in fair yields of a limited number of aromatic diazonium fluoborates with sodium borohydride in methanol.

We wish to report the nonaqueous reduction of several aryldiazonium hexafluorophosphates in tetramethylurea. All of the available phosphate salts conveniently decomposed spontaneously and exothermically in this solvent, a phenomenon which was not experienced with several other nonaqueous solvents. Comparisons, where possible, with yields of identical reduction products obtained from the established methods can be observed in the chart.

A striking parallel can be observed between tetramethylurea and ethanol reductions. Both methods appear highly desirable as reducing procedures when electron withdrawing groups are present on the aromatic nucleus of the parent amine. However, in the case of the reduction of *ortho*- and *para*-substituted aminobenzoic acids, the tetramethylurea method has a distinct advantage. The yields of reduced product from this method are greater than 80% in the case of both amino acids whereas the aqueous ethanol procedure leads to the formation of benzoate and substituted benzoate ester.

As can be seen from Table I, hypophosphorous acid and alkaline formaldehyde procedures lend themselves more readily to the reduction of aromatic primary amines which contain electron donating groups on the ring.

Although the reduction of aryldiazonium hexafluorophosphates in tetramethylurea could conceivably follow either an ionic or a free radical path, the former would appear more likely in view of the work of Meerwein[9] and DeTar.[11] Meerwein has obtained very good evidence of hydride transfer in the reaction of 2,4,6-trichlorobenzenediazonium fluoborate with 2-phenyl-1,3-dioxolane to give a 55% yield of trichlorobenzene and an 80% yield of 2-phenyl-1,3-dioxolenium fluoborate. DeTar has presented strong evidence for a hydride transfer reaction in ethanolic deaminations. The strong parallel of inductive influences between ethanolic and tetramethylurea deaminations would indicate that a similar mechanism is operative. The aryldiazonium hexafluorophosphate presumably breaks down in tetramethylurea ionically according to equation 1.

$$ArN_2PF_6 \longrightarrow Ar^{\oplus} + N_2 + PF_6^{\ominus} \qquad (1)$$

The aryl cation, depending on its reactivity can either abstract hydride from the solvent (equation 2), couple with it to form a salt (equation 3), or react with $PF_6^{\ominus}$ to yield the fluoroaromatic and PF_5 (equation 4).

With the highly reactive aryl cations, the activation energy requirement for hydride transfer would be met more readily. The resultant urea carbonium ion could conceivably react with the $PF_6^{\ominus}$ ion to yield PF_5 and fluorinated tetramethylurea, although no attempt has been made thus far to isolate and characterize such a compound. The less reactive cations would not be sufficiently energetic for predominant hydride transfer and competing reactions 3 and 4 become more likely. No evidence of reaction 4 has been observed with any of the parent amines studied, although this does not preclude the possibility of traces of fluoroaromatic present. Evidence for reaction 3, however, is concrete

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(3) Nathan Kornblum, *Org. Reactions*, **II**, 262 (1944).

(4) P. Griess, *Phil. Trans. Roy. Soc. London*, Ser. A, **154**, 683 (1864).

(5) J. Mai, *Ber.*, **35**, 163 (1902).

(6) R. Q. Brewster and J. A. Poje, *J. Am. Chem. Soc.*, **61**, 2418 (1939).

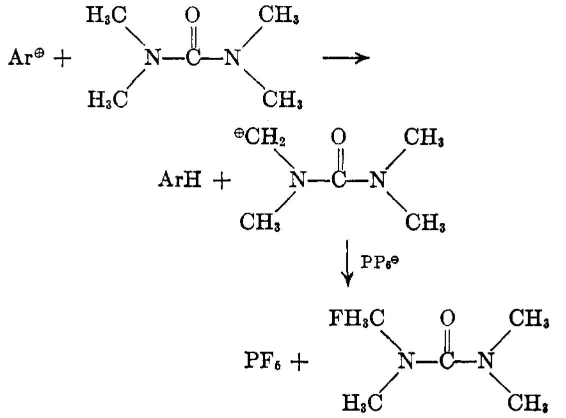
(7) P. Friedlander, *Ber.*, **22**, 587 (1889).

(8) A. Haller, *ibid.*, **18**, 90 (1885).

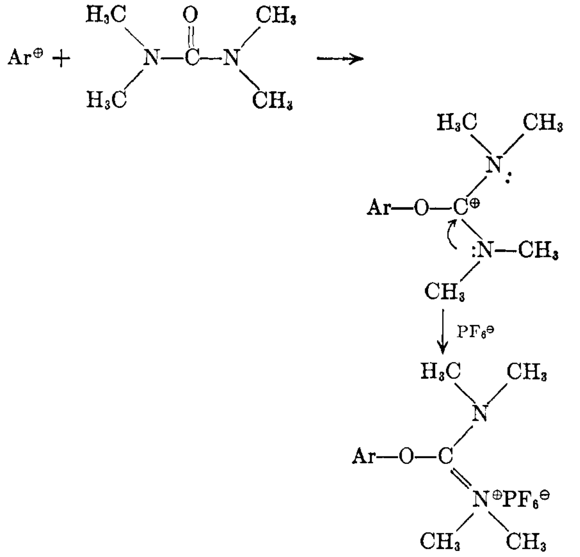
(9) H. Meerwein, *et al.*, *Angew. Chem.*, **70**, 211 (1958).

(10) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 1251 (1961).

(11) D. F. DeTar and T. Kosuge, *ibid.*, **80**, 6072 (1958).



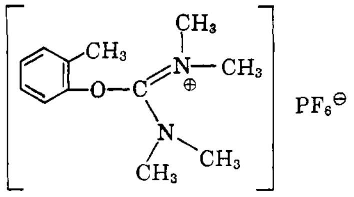
(2)



(3)

$$Ar^{\oplus} + PF_6^{\ominus} \longrightarrow ArF + PF_5 \quad (4)$$

in the case of at least one amine studied in detail thus far. The diazonium hexafluorophosphate derived from *o*-toluidine gives on decomposition in tetramethylurea a 61% yield of *o*-methylphenoxytetramethylamidinium hexafluorophosphate I. The structure of this salt was

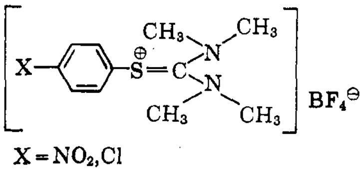


proved by elemental analysis, and vigorous base hydrolysis to *o*-cresol, and dimethylamine. The $PF_6^{\ominus}$ ion was determined quantitatively by tetraphenylarsonium chloride reagent.[12] An amidinium structure is proposed since the infrared spectrogram showed a strong absorption at 5.90 μ.

The presence of $PF_6^{\ominus}$ ion in this salt renders a free radical reaction highly unlikely. A free radical breakdown of the aryldiazonium hexafluorophosphate would occur according to equation 5.

$$ArN_2PF_6 \longrightarrow Ar\cdot + :N{\equiv}\overset{\oplus}{N}\cdot + PF_6^{\ominus} \quad (5)$$

To explain the evolution of nitrogen (97% of the theoretical amount), one must envisage at least in part an electron transfer from the $PF_6^{\ominus}$ ion to the positively charged N_2 species. This would leave phosphorus pentafluoride and a fluorine atom. Regardless of the fate of the fluorine atom, reformation of the hexafluorophosphate anion would be very unlikely. Again, an electron transfer from the solvent to the $N_2^{\oplus}$ species would render the solvent positively charged. This would have a stronger tendency to react with the $PF_6^{\ominus}$ ion than the aromatic free radical, again producing PF_5. Similar salts as well as reduction products have been isolated from the decomposition of the diazonium hexafluorophosphates derived from *p*-nitroaniline, *p*-toluidine, and aniline. It is interesting to note that Meerwein[13] decomposed the diazonium fluoborates derived from *p*-nitroaniline and *p*-chloroaniline in tetramethylthiourea. No reduction product was reported—instead there were obtained in high yields tetramethylthiouronium fluoborate salts of the proposed structure:



Evidently the much higher nucleophilic property of the sulfur atom over oxygen as well as its greater size makes it more susceptible to attack by the aryl cation and hence a reaction analogous to equation 3 becomes predominant. Thus tetramethylthiourea is not a hydride transfer agent even with the more active aryl cations.

Experimental[14]

Decomposition of Aryldiazonium Hexafluorophosphates.—The aryldiazonium hexafluorophosphates were prepared as previously reported.[2]

The dry salts were decomposed by the portionwise addition of 50 g. to a beaker which contained tetramethylurea (200 ml.) at room temperature. Usually a rapid evolution of nitrogen was noted and the temperature of the reaction mixture rose quite rapidly. In cases where the reaction was only moderately exothermic, the mixture was warmed to increase the rate. The temperature was not allowed to rise above 65° in any of the runs. When all sign of reaction had ceased as evidenced by the lack of nitrogen evolution (about 1.5 hr.), the solution was poured into 1 l. of water. The reduction product in most cases was recovered by distillation with steam followed by separation from the water layer and fractionation. In the case of the reduction of the amino benzoic acids, the reaction mixture was poured on a mixture of cracked ice and hydrochloric acid. The benzoic acid was recovered by filtration.

***o*-Methylphenoxytetramethylamidinium Hexafluorophosphate (I).**—*o*-Toluidinediazonium hexafluorophosphate was decomposed in the manner described above. The reaction mixture was poured on a mixture of ice and hydrochloric acid. The precipitate obtained was recovered by filtration and air dried. The red color was removed by treatment of a chloroform solution of the compound with Norite. Recrystallization from a chloroform-petroleum ether (b.p. 30–60°) solvent pair gave an average of 61% yield on several runs of colorless *o*-methylphenoxytetramethylamidinium hexafluorophosphate, m.p. 144–145°.

Anal. Calculated for $C_{12}H_{19}ON_2PF_6$: C, 40.90; H, 5.44; N, 7.95; PF_6, 41.16. Found: C, 40.57; H, 5.24; N, 7.75; PF_6, 41.04.

Hydrolysis of I.—The hydrolysis of I (15 g., 0.043 mole) was accomplished in 100 ml. of 4 *N* sodium hydroxide in a 250-ml.

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(12) The $PF_6^{\ominus}$ ion is determined quantitatively as tetraphenylarsonium hexafluorophosphate.

(13) H. Meerwein, *et al.*, *Ber.*, **90**, 851 (1957).

(14) All melting points are uncorrected.

round-bottomed flask fitted with a condenser. A rubber connecting tube was led from the top of the condenser into a gas washing bottle which was fitted with a sintered glass disk. To the washing bottle was added 150 ml. of anhydrous ether. While heating the reaction flask at reflux temperature, a gas was evolved which dissolved in the ether. After 4 hr. the apparatus was disassembled and dry hydrogen chloride gas was bubbled through the ethereal solution. The precipitate which formed was isolated by rapid filtration and dried *in vacuo*. A yield of 3.2 g. (48.4%) of dimethylamine hydrochloride, m.p. 168–171°, was obtained.

Addition of Dry Ice to the reaction mixture resulted in the formation of a pink organic layer which when separated yielded 7.5 g. (83%) of *o*-cresol. The *p*-bromobenzenesulfonate derivative melted at 78°. A mixture melting point determination with an authentic sample showed no depression. The dibromo derivative (m.p. 56°) likewise showed no depression in melting point when mixed with an equal portion of authentic material.

Acknowledgment.—The authors wish to thank the Ozark-Mahoning Co. of Tulsa, Oklahoma, for supplies of hexafluorophosphoric acid and the Grand River Chemical Division of John Deere and Co., Pryor, Oklahoma, for supplies of tetramethylurea.

The Solvolysis of Stigmasteryl Tosylate

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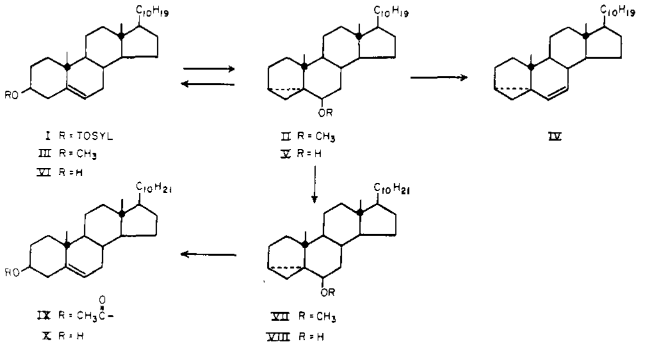
In connection with studies on the identification of an unknown house-fly sterol,[2a] a sample of high purity β-sitosterol was required. All commercial samples of the sterol showed, by gas chromatography, a major impurity[2b] varying, in content, from 10–30%. We therefore converted stigmasterol to β-sitosterol according to published procedures[3] but, again, could not obtain a preparation of satisfactory purity.



In repeating the solvolysis of stigmasteryl tosylate (I) in methanol and chromatography on alumina,[3b] the product obtained could be resolved further by rechromatography on Florisil into *i*-stigmasteryl methyl ether (II) and, as minor components, stigmasteryl methyl ether (III), stigmasterol and a hydrocarbon (IV). Riegel and co-workers[4] described a similar hydrocarbon in the *i*-cholesterol series to which they assigned the Δ^6-*i*-cholestene structure on the basis of its physical and chemical behavior. The structure 3,5-cyclo-6,22-sitostadiene has been assigned to hydrocarbon IV by analogy.[5] Since chromatography of the reaction mixture on Florisil directly gave only *i*-stigmasteryl methyl ether, stigmasteryl methyl ether, and stigmasterol, it would appear that the hydrocarbon IX is an artifact resulting from contact of II with an alumina column. Hydrogenation of *i*-stigmasteryl methyl ether followed by rearrangement with zinc acetate in boiling acetic acid gave, after one recrystallization, 22,23-dihydrostigmasteryl acetate. Hydrolysis of acetate IX gave pure 22,23-dihydrostigmasterol.

The solvolysis of stigmasteryl tosylate in acetone–water was carried out with slight modification of the procedure described for the preparation of *i*-ergosterol and *i*-dehydroergosterol.[6] Chromatography of the mixture on Florisil gave *i*-stigmasterol V and stigmasterol VI. Hydrogenation of *i*-stigmasterol V afforded i-22,23-dihydrostigmasterol (*i*-β-sitosterol) VIII. Rearrangement of this product with zinc acetate in boiling acetic acid gave 22,23-dihydrostigmasteryl acetate IX.

The over-all yield of 22,23-dihydrostigmasterol obtained *via* the *i*-sterol (70%) is better than that obtained *via* the *i*-stigmasteryl methyl ether (63%). In addition, the route *via* the *i*-sterol permits the recovery of reusable stigmasterol. The 22,23-dihydrostigmasterol obtained through either procedure gave only one peak in gas–liquid chromatography which differed from that of stigmasterol. Although there have been many examples of β-sitosterol isolated from plant sources, the purity of these materials may be open to question. The conversion of stigmasterol to β-sitosterol *via* the *i*-sterol is a convenient procedure, affording good yields and leading to a product of very high purity.

Experimental[7]

Stigmasteryl Tosylate (I).—To a solution of 15.0 g. of dry stigmasterol in 200 ml. of dry pyridine was added 18.0 g. of *p*-toluenesulfonyl chloride [freshly recrystallized from petroleum ether (b.p. 60–70°). The reaction mixture was allowed to stand overnight in the dark at room temperature and poured into 1 l. of ice-cold 5% aqueous potassium bicarbonate solution. The resulting solid tosylate was collected by filtration, washed with water, and dried in a vacuum oven at 60°. Recrystallization from dry acetone gave (I) as colorless crystals, m.p. 147–148°, $[\alpha]_D$ −49°.

***i*-Stigmasteryl Methyl Ether (II).**—To a refluxing solution of 8.0 g. of fused potassium acetate in 400 ml. of dry methanol was added 8.0 g. of finely pulverized stigmasteryl tosylate. The mixture was refluxed for 3 hr. After removal of the solvent *in vacuo*, the residue was extracted with ether, washed with water, 5% aqueous potassium bicarbonate, water, dried over potassium carbonate, and evaporated *in vacuo* leaving 6.0 g. of oily material. This oily residue was dissolved in petroleum ether, adsorbed on a

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[1] Deceased, May 31, 1962.

[2] (a) Dr. William Robbins and staff, Insect Physiology Laboratory, ARS, U. S. Department of Agriculture, Beltsville, Md.; (b) The nature of this impurity is the subject of a forthcoming publication by M. J. Thompson, S. J. Louloudes, W. Robbins, J. A. Waters, J. A. Steele, and E. Mosettig.

[3] (a) S. Bernstein and E. S. Wallis, *J. Org. Chem.*, **2**, 341 (1938); (b) E. Fernholz and W. L. Ruigh, *J. Am. Chem. Soc.*, **62**, 3346 (1940); (c) B. Riegel, E. W. Meyer, and J. Beiswanger, *ibid.*, **65**, 325 (1943).

[4] B. Riegel, G. P. Hager, and B. L. Zenity, *ibid.*, **68**, 2562 (1946).

[5] The ultraviolet spectrum of IX showed only end absorption, thus ruling out a 3,5-diene structure.

[6] W. R. Nes and J. A. Steele, *J. Org. Chem.*, **22**, 1457 (1957).

[7] All melting points were determined on a Kofler block and are uncorrected. Analyses are by the Analytical Service Laboratory of this Institute under the direction of Mr. Harold G. McCann. Rotations were taken in 1% chloroform solutions at 20° by Mrs. E. Peake. The infrared spectra were determined on a Perkin-Elmer double beam spectrophotometer (Model 21) in carbon disulfide by Mr. H. K. Miller with the assistance of Mrs. C. I. Wright. The gas chromatographic analyses were carried out on a Barber-Colman gas chromatograph with SE-30 support. "Woelm" neutral alumina, activity grade I, and Florisil (60–100 mesh) purchased from the Floridin Co., Tallahassee, Fla. were used for chromatography. Solvents were purified, distilled, and dried with the help of Mr. J. Lyons, with the exception of ethanol and chloroform which were the usual commercial grades of reagent material.