TABLE I

	Aminophenyltrimethylsilanes							Acetyl derivatives		
	B.p. (10 mm.)	$n^{20}D$	d^{20}_4	M_D (obsd.)	M_D (calcd.)	Si, % Calcd.	Si, % Found	M.p., °C.	Si, % Calcd.	Si, % Found
Ortho	101	1.5388	0.952	54.38	54.45	16.98	16.99	130–130.5	13.53	13.70
Meta[a]	111	1.5362	.947	54.44	54.45	16.98	16.96	114–115	13.53	13.83
Para	113	1.5393	.947	54.73	54.45	16.98	16.57	169–170	13.53	13.72

[a] It must be kept in mind that the nitro compound here was adjudged to be only 95% pure.

	β-Naphthol coupling products							
	M.p., °C.	Si, % Calcd.	Si, % Found	N, % Calcd.	N, % Found	Yield, %	Color	Crystallizing solvent
Meta	94–95	8.76	8.68	8.74	8.95	58	Red needles	Acetic acid
Para	94–95	8.76	8.48	8.74	8.94	50	Red-orange	Acetic acid

TABLE II

	Aminobenzyltrimethysilanes							Acetyl derivatives		
	B.p. (10 mm.)	$n^{20}D$	d^{20}_4	M_D (obsd.)	M_D (calcd.)	Si, % Calcd.	Si, % Found	M.p., °C.	Si, % Calcd.	Si, % Found
Ortho	114	1.5345	0.939	59.41	59.01	15.66	15.47	117–117.5	12.69	12.40
Para	119	(m.p. 33.5–34°)		...	...	15.66	15.85	132–133	12.69	12.84

	β-Naphthol coupling products							
	M.p., °C.	Si, % Calcd.	Si, % Found	N, % Calcd.	N, % Found	Yield,[a] %	Color	Crystallizing solvent
Ortho	97–98	8.39	8.15	8.38	8.31	12	Orange	Acetic acid
Para	126–127	8.39	8.25	8.38	8.82	19	Red	Acetic acid

[a] It is entirely possible that these yields can be improved since the optimum conditions were not investigated.

p.s.i. After absorption of the calculated amount of hydrogen, the catalyst was removed by filtration through a layer of Celite and the alcohol was removed by distillation. The residual amine was fractionally distilled through an efficient column at 10 mm. pressure. All amines were initially clear colorless liquids, but darkened on standing. The properties of these amines are given in Tables I and II.

The reduction of *o*-nitrophenyltrimethylsilane required careful control, in order to avoid excessive cleavage to give aniline. By carrying out the reduction in 95% ethanol, wrapping the reduction bottle in damp cloths, and terminating the reduction as soon as the calculated amount of hydrogen was absorbed, it was possible to obtain an 83% yield of *o*-aminophenyltrimethylsilane, with minor amounts of aniline and tarry pot residue.

The reduction of *m*-nitrophenyltrimethylsilane (95% pure)[1] and *p*-nitrophenyltrimethylsilane was carried out with no unusual precautions to give 75–85% yields of *m*-aminophenyltrimethylsilane and *p*-aminophenyltrimethylsilane, respectively. Very small amounts of aniline and tars were formed.

The reduction of *o*-nitrobenzyltrimethylsilane was found to take place very slowly, requiring 20 to 50 hours to obtain complete reduction. A maximum yield of 90% of *o*-aminobenzyltrimethylsilane was obtained from 39 g. of the nitrosilane in 50 ml. of absolute ethanol.

The reduction of *p*-nitrobenzyltrimethylsilane proceeded in a normal manner, requiring about 4 to 8 hours and giving about 85% yields of *p*-aminobenzyltrimethylsilane.

Acylation of Aminosilanes.—Small portions (0.5 g.) of the amines were dissolved in 3 to 5 ml. of acetic anhydride, with slight cooling. After solution was complete, 20 to 30 ml. of water was added and the mixture was cooled in an ice-bath. The waxy solids obtained were crystallized from hot petroleum ether (90–100°). Virtually quantitative yields of the acetyl derivatives were obtained, with properties as shown in Tables I and II.

Diazotization of Aminosilanes and Coupling with β-Naphthol.—The following procedure is typical of that employed in the diazotization and coupling of the amines.

Weighed portions (4 to 12 g.) of the aminosilanes were added to a mixture of 50 to 100 g. of crushed ice and a slight excess of dilute hydrochloric acid. In all cases the amine hydrochloride separated as a white solid. A dilute ice cold solution of the calculated amount of sodium nitrite was added rapidly (2 to 5 min.) with vigorous stirring. Most of the precipitated hydrochloride reacted in a short time, giving an orange diazonium solution. The solution darkened rapidly and formed dark tarry material. Within 10 min. of the start of the reaction, the diazonium solution was filtered rapidly through a glass wool plug into a cold dilute solution of the calculated amount of β-naphthol, containing a slight excess of sodium hydroxide. This reaction mixture was stirred rapidly and red solid particles separated usually along with dark tarry material. After about 20 min., acetic acid was added, if required, to give a slightly acid solution, and the product was filtered. The red gummy solid was dissolved in a small amount of benzene and poured into a chromatographic column, packed with activated alumina and Celite (50–50 by volume). The silicon-containing dye was collected in the first red area carried through the column by the benzene used as the elution solvent. Subsequent fractions obtained from the column contained mixtures of cleavage products, tars and unreacted β-naphthol. The product was crystallized from acetic acid, containing small amounts of water. Properties and yields of the azo compounds are given in Tables I and II.

Several attempts to obtain a coupling product from the ortho amine were not successful.

Action of Nitrosyl Chloride on *o*-Aminobenzyltrimethylsilane.—An ethereal solution of 25.6 g. (0.14 mole) of *o*-aminobenzyltrimethylsilane was cooled to −10° in an ice-salt-bath. With mechanical stirring, a cold solution of 9.6 g. (0.15 mole) of nitrosyl chloride in ether was added through a condenser cooled with Dry Ice. Addition was carried out slowly, the reaction mixture becoming orange and cloudy and finally forming black tar. After reaction was complete, the ether and any unreacted nitrosyl chloride were removed by vigorous suction with a water-pump. Ice cold water was added and one portion of the black solution resulting was added to boiling water in an attempt to form the phenol. The remainder of the diazonium solution was added to a solution of excess potassium iodide. Steam distillation of both portions of the reaction gave small amounts of dark oil and some yellow solid. Distillation of the organic material from either phase of the reaction gave no identifiable material other than this solid. Combination of the solid from both phases gave 2.7 g. (16%) of indazole, m.p. 147–148°, identified by an undepressed melting point with an authentic sample.[3]

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(3) See *Org. Syntheses*, **20**, 73 (1940).

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The Ethanolysis of Allyl Benzenesulfonate

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In connection with another investigation[1] information on the kinetics of the ethanolysis of allyl

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[1] C. G. Bergstrom and S. Siegel, THIS JOURNAL, **73**, 145 (1951).

benzenesulfonate was needed. The displacement of the benzenesulfonate group from a saturated carbon atom is analogous to the displacement of the chloro group[2] and the ethanolysis of allyl benzenesulfonate was expected to be faster than ethyl benzenesulfonate[3] and to be markedly accelerated by the ethoxide ion.[4] This was found to be the case.

Bimolecular rate constants for the reaction of the ester with sodium ethoxide in anhydrous ethanol were obtained at three temperatures. The constants were reproducible to ±2%. There was no noticeable drift in the constants calculated for a run, which suggests that the reaction of the ester with the solvent was negligible. However, at the concentrations of sodium ethoxide used in this study, the first-order reaction with the solvent, measured independently, does contribute about 4 to 5%[5] to the over-all solvolysis of allyl benzenesulfonate. This indicated correction was not made in calculating the second-order rate constants because the correction would be of the order of magnitude of the uncertainty in the measurements. Furthermore, the correction is small compared with the variation in the constant (k_2) which is expected if the initial concentration of reactants was varied over a wider range.[5] The rate was essentially unchanged in a medium containing one per cent. of water. This is a behavior typical of the S_N2 type of displacement reaction.[4]

The preparation of allyl benzenesulfonate from allyl alcohol and benzenesulfonyl chloride was improved by the use of 2,4,6-collidine in place of pyridine.[6] Apparently the formation of quaternary ammonium salts is minimized by the use of a more sterically hindered base.

Experimental

Allyl Benzenesulfonate.—Allyl alcohol, obtained from the Paragon Chemical Company, was dried by an azeotropic distillation with carbon tetrachloride. The physical properties of the purified material were b.p. 95.0°; d^{25}_4 0.850; n^{25}D 1.4113; (lit.[7] b.p. 96–97°; d^{20}_4 0.857; n^{20}D 1.4134). Benzenesulfonyl chloride was distilled *in vacuo* before it was used; b.p. 85.0–86.5° (1.5 mm.).

To a mixture of allyl alcohol (19.2 g.) and 2,4,6-collidine (80 ml.) cooled to −4°, benzenesulfonyl chloride (53.0 g.) was added dropwise, at a rate which permitted the temperature of the reactants to remain between 0 and −5°. The mixture was stirred for one hour after the acid chloride had been added and the internal temperature dropped to −10°. Sulfuric acid (75 ml. of 10 *N*) was added at such a rate that the temperature remained between −10 and 0°. The ester separated from the solution and was taken up in chloroform, was washed with 2.5 *N* sulfuric acid and was dried over anhydrous potassium carbonate. The chloroform was evaporated and the ester was distilled; b.p. 98° (0.4 mm.); $d^{25.3}_4$ 1.204; n^{25}D 1.5177; yield 39.6 g. (66% theoretical). The product gave no precipitate with an alcoholic solution of silver nitrate; sapn. equiv. calcd., 198.2; found, 196.2, 195.9.

Measurement of the Reaction of Allyl Benzenesulfonate with Sodium Ethoxide.—All volumetric apparatus was calibrated at the various temperatures used in the usual manner. The temperature, controlled to ±0.05°, was measured by thermometers calibrated by comparison with a platinum resistance thermometer. The solvent, anhydrous ethanol, was prepared from a commercial grade of absolute alcohol and was distilled from a mixture of sodium ethoxide and diethyl phthalate[8] directly into the volumetric flasks in which the various solutions were prepared. All exits of the distilling apparatus were closed with tubes containing indicating Drierite. A solution of sodium ethoxide in absolute alcohol was prepared by dissolving sodium in 100 ml. of alcohol to give a solution of double the concentration desired for the rate study. To standardize this solution, two samples were removed with a 10-ml. pipet and titrated against 0.02 *M* hydrochloric acid using phenolphthalein as the indicator. Fifty ml. of the standardized solution was transferred by pipet to a 100-ml. volumetric flask, and alcohol was distilled into the flask until the calibration mark was almost reached. The sodium ethoxide solution was then brought to the desired temperature in the thermostat. The sample of ester was injected into the flask from a weight pipet. The time at which the ester sample was injected was taken as the starting time of the reaction. After the sample was added, the contents of the flask were mixed and alcohol was added to bring the liquid to the calibration mark. One-tenth aliquots were withdrawn and the samples were placed in stoppered six-inch test-tubes which had previously been brought to the temperature of the thermostat.

The reaction was quenched when the contents of a tube was poured into an iodine flask containing a cold mixture of 10 ml. of carbon tetrachloride, phenolphthalein indicator and a slight excess of standard 0.02 *M* hydrochloric acid solution. The excess acid was titrated as rapidly as possible with 0.04 *N* sodium hydroxide. The end-point faded slowly.

Measurement of the Reaction of Allyl Benzenesulfonate with Ethyl Alcohol.—The solutions were prepared in 100-ml. volumetric flasks in the manner described previously but omitting the sodium ethoxide. At suitable intervals a 10-ml. aliquot was removed by pipet and introduced into 20 ml. of cold carbon tetrachloride. This effectively stopped the reaction. Cold water (25 ml.) was added and the mixture shaken to extract the acid and alcohol from the carbon tetrachloride. The mixture was then titrated quickly with standard 0.04 *N* sodium hydroxide to the phenolphthalein end-point. To obtain a value of the titer for complete reaction, an aliquot was transferred to a flask containing 20 ml. of water and heated for eight hours at 70°. This value was taken to be equivalent to the initial concentration of the ester (a).

Treatment of Results.—The second-order rate constants k_2 were calculated from the formula

$$k_2(t_2 - t_1) = \frac{2.303}{(b - a)} \log \frac{(a - x_1)}{(a - x_2)} - \log \frac{(b - x_2)}{(b - x_1)}$$

where k is the rate constant, a and b the initial concentrations, x the transformation variable and t the time.

The rate constant is a weighted average of all of the possible point combinations and is given by

$$k_2 = \frac{k_i w_i}{w_i}$$

$$w = (t_2 - t_1)(x_2 - x_1)$$

Hydrolysis of the sample of allyl benzenesulfonate used shows that somewhat more than the theoretical amount of acid is produced. This is assumed to be due to the presence of benzenesulfonyl chloride. In calculating the rate constants, it was assumed that the benzenesulfonyl chloride reacted before the first point was taken to give ethyl benzenesulfonate, which was considered inert. The reaction of benzenesulfonyl chloride has the effect of decreasing the initial ethoxide concentration by an amount equal to the amount of benzenesulfonyl chloride in the ester sample. Actually, the correction was insignificant.

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[2] H. R. McCleary and L. P. Hammett, *ibid.*, **63**, 2254 (1941).

[3] M. S. Morgan and L. H. Cretcher, *ibid.*, **70**, 375 (1948).

[4] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 603 (1941).

[5] J. D. Roberts, W. G. Young and S. Winstein, THIS JOURNAL, **64**, 2157 (1942).

[6] R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

[7] R. Delaby and P. Dubois, *Compt. rend.*, **188**, 710 (1929).

[8] R. H. Manske, THIS JOURNAL, **53**, 1106 (1931).

TABLE I

RATE OF REACTION OF ALLYL BENZENESULFONATE WITH NaOEt IN ETHANOL AT 19.7°

Allyl benzenesulfonate, 0.0317 *M;* sodium ethoxide, 0.0398 *M*

Time, min.	Reacted, %	$k_2 \times 10^3$ (l. mole^{-1} sec.$^{-1}$)
39.2	19.6	2.67
52.7	27.9	3.07
69.3	32.2	2.80
83.5	35.0	2.62
101.7	41.0	2.73
151.2	52.1	2.75
220.3	61.6	2.67
307.1	71.2	2.73
	Weighted average	2.68
	Average	2.76 ± 0.09

The first-order rate constants were calculated from the equation

$$k_1 = \frac{2.303}{t} \times \log \frac{a}{(a - x)}$$

and the recorded value is an average of the individual values for k_1. The initial concentration of ester is represented by a, the other symbols are as given above. The variation in the rate constants for the runs at 20° was greater than those measured at higher temperatures. However, the estimated deviation in the constants is approximately 2 to 4%.

TABLE II

FIRST ORDER REACTION OF ALLYL BENZENESULFONATE WITH ABSOLUTE ETHANOL AT 25.10°

Allyl benzenesulfonate, 0.0345 *M*

Time, min.	Reacted, %	$k_1 \times 10^6$ (sec.$^{-1}$)
165	7.4	7.71
495	21.5	8.15
1213	44.5	8.10
1707	56.1	8.03
2702	72.4	7.93
4109	86.1	8.00
	Average	8.00 ± 0.11

TABLE III

REACTION RATES FOR THE ETHANOLYSIS OF ALLYL BENZENESULFONATE

Temp., °C.	Ester, mole/l.	NaOEt, mole/l.	$k_1 \times 10^6$, sec.$^{-1}$	$k_2 \times 10^3$, l. mole^{-1} sec.$^{-1}$
25.36	0.0469	0.0432	..	4.90
25.36	.0287	.0440	..	5.18
25.36	.0346	.0430	..	5.23^a
19.70	.0317	.0398	..	2.68
19.70	.0304	.0445	..	2.63
19.70	.0317	.0422	..	2.73
14.70	.0250	.0448	..	1.57
14.70	.0287	.0418	..	1.52
34.79	.0344	....	23.3	..
34.79	.0492	....	23.8	..
25.10	.0345	....	8.0	..
25.10	.0419	....	7.9	..
20.15	.0408	....	4.5	..
20.15	.0332	....	4.2	..

[a] Solvent: 99% ethanol and 1% water.

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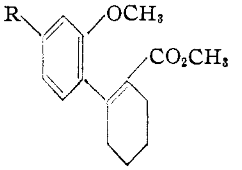
Coumarins as Possible Synthetic Intermediates[1]

BY V. BOEKELHEIDE AND A. P. MICHELS

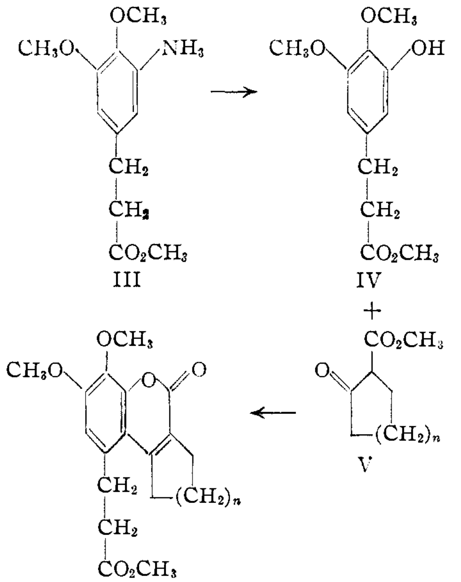
The von Pechmann coumarin condensation[2] is a convenient method for linking substituted aromatic compounds with alicyclic derivatives. Since the lactone ring of the resulting coumarins is susceptible to cleavage, intermediates can readily be obtained which would appear to have some value for the synthesis of certain natural products. It is the purpose of this note to describe some preliminary experiments directed toward this end.

As a model study directed toward the synthesis of morphine analogs, the intermediates I and II were prepared and treated with ethyl cyanoacetate in an attempt to obtain a Michael condensation. In each case the Michael condensation failed completely. Our work which was completed prior to recent publications on the limited reactivity of phenylcyclohexenone derivatives in the Michael condensation,[3,4,5] is further evidence of the limitations of the Michael reaction when applied to highly substituted molecules.



I, R = $-CH_3$
II, R = $-OCH_3$

Another possible application of coumarins as synthetic intermediates would be the synthesis of colchicine analogs. Thus, the condensation of a suitable phenol (IV) with β-keto esters, such as V, would yield intermediates of some promise for the synthesis of colchicine analogs in which the nature of ring C might readily be varied.[6] When



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(1) Abstracted from the M.S. Thesis of A. P. Michels, 1949.

(2) H. von Pechmann and C. Duisberg, *Ber.*, **16**, 2119 (1883).

(3) G. F. Woods, THIS JOURNAL, **69**, 2549 (1947).

(4) W. E. Bachmann and E. J. Fornefeld, *ibid.*, **72**, 5529 (1950).

(5) C. F. Koelsch, *ibid.*, **73**, 2951 (1951).

(6) For a discussion of ring C of colchicine, see H. R. V. Arnstein, D. S. Tarbell, G. P. Scott and H. T. Huang, *ibid.*, **71**, 2448 (1949).