TABLE I

Reactants	Product	Yield	M.p.[a]	Analysis for[b]		C	H	N
IV + trimethylsilylmethylamine (TMSMA)	I	48%	126–127	$C_{19}H_{22}N_4Si$	Calcd.	68.22	6.64	16.75
					Found	67.82	6.47	16.89
IV + Na alcoholate of trimethylsilylmethanol[c]	II	43	94–95	$C_{19}H_{21}N_3OSi$	Calcd.	68.02	6.32	12.53
					Found	68.14	6.51	12.10
IV + Na thiolate of trimethylsilylmethylthiol[d]	III	50	103–104	$C_{19}H_{21}N_3SSi$	Calcd.	64.91	6.04	11.95
					Found	65.07	6.35	11.19
2,4-Diamino-6-chloro-*s*-triazine[e] + TMSMA	V	34	153–155	$C_7H_{16}N_6Si$	Calcd.	39.60	7.60	39.58
					Found	39.40	7.30	39.39
2,4,6-Trichloro-*s*-triazine[f] + TMSMA	VI	48	136–137	$C_{15}H_{36}N_6Si_3$	Calcd.	46.85	9.43	21.83
					Found	47.20	9.92	21.59

[a] Fisher-Johns—uncorrected. [b] Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. Mary Aldridge, American University, Washington, D. C. [c] J. L. Speier, B. F. Daubert, and R. R. McGregor, *J. Am. Chem. Soc.*, **70**, 1119 (1948). [d] D. C. Noller and H. W. Post, *J. Org. Chem.*, **17**, 1395 (1952). [e] J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikner, F. C. Schaefer, and D. Holm-Hansen, *J. Am. Chem. Soc.*, **73**, 2981 (1951). [f] Eastman Practical grade cyanuric chloride.

the residue from 95% ethanol, I was obtained in 48% yield.

In general, all preparations were conducted in a manner similar to that used for compound I. Compounds II and III were prepared directly from the products of the reaction of sodium and the alcohol or thiol without isolating the intermediate. All products were white needles except I and III; these were light yellow. Ethanol (95%) was the recrystallization solvent except for compound III which was recrystallized from methanol, and VI, for which 60:40 mixture of benzene and *n*-hexane was employed. Table I shows the reactants, yields, analysis, etc.

Each of the compounds reported here shows strong infrared absorption at 860 cm.$^{-1}$ and 1243 cm.$^{-1}$, frequencies considered characteristic of the $(CH_3)_3$ Si—CH_2 — group.[8]

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(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1954, pp. 274–281.

Polyphosphoric Acid in the Bernthsen Reaction[1]

FRANK D. POPP

Department of Chemistry, University of Miami, Coral Gables, Florida

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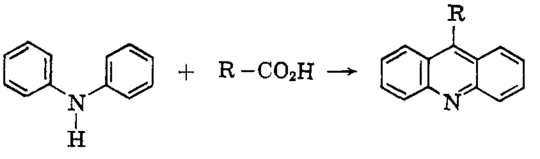
The Bernthsen reaction, one of the earliest used for the synthesis of acridines, (II) consists in heating a mixture of an aromatic or aliphatic carboxylic acid with a diphenylamine (I) and zinc chloride at 200–270° for about twenty hours.[2]



I II

The wide use of polyphosphoric acid[3] as a reagent in organic chemistry has led to this study of the use of polyphosphoric acid as a catalyst in the Bernthsen reaction. In a previous study of this type Elston[4] has reported that the reaction of diphenylamine and an excess of benzoic or *p*-toluic acid, in the presence of polyphosphoric acid at 160° for fifteen minutes, led to the formation of a diacyldiphenylamine (probably bis-*p*-) in a 12–15% yield, rather than a 9-substituted acridine.

It was felt that perhaps by changing the reaction conditions, particularly the ratio of amine and acid, one could successfully apply polyphosphoric acid to the Bernthsen reaction.

From the results of the reaction of benzoic acid and diphenylamine in polyphosphoric acid under a variety of conditions it appears that a ratio of one mole of acid to two moles of amine and a temperature of about 200° for fifteen minutes are the best conditions. Use of benzoic anhydride and ethyl benzoate gave results similar to benzoic acid. It is of interest to note that in one run the reaction was scaled up from 0.03 to 0.1 mole and the yield increased from 18 to 48%.

Table I lists the results obtained. No attempts were made to find the ideal reaction conditions in these cases. The use of *p*-nitro- and *p*-aminobenzoic acids did not lead to acridines by the use of zinc chloride.[5] With polyphosphoric acid the latter gave 9-(*p*-aminophenyl)acridine while *p*-nitrobenzoic acid did not lead to any acridine.

The use of polyphosphoric acid, rather than zinc chloride, is more convenient, particularly in regard to reaction times, and in view of the ready availability of starting materials this may be a worthwhile procedure in many cases, despite the poorer yields.

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(1) Presented in part at the Combined Southeastern-Southwestern Regional American Chemical Society Meeting, New Orleans, Louisiana, December, 1961.

(2) For references see: (a) R. M. Acheson, "Acridines," A. Weissberger, ed., Interscience Publishers, New York, N. Y., 1956, pp. 19–25; (b) A. Albert, "Heterocyclic Compounds," Vol. 4, R. C. Elderfield, ed., J. Wiley and Sons, Inc., New York, N. Y., 1952, pp. 502–503.

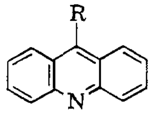
(3) (a) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958); (b) F. D. Popp and W. E. McEwen, *Proc. Kansas Acad. Sci.*, **63**, 169 (1960).

(4) C. T. Elston, Ph.D. thesis, University of Illinois, 1954; quoted in ref. 3a.

(5) W. Hess and A. Bernthsen *Ber.*, **18**, 689 (1885).

Table I

Polyphosphoric Acid-Catalyzed Bernthsen Reaction



R[a]	Yield,[b] %	M.p.[c]	Reported m.p.[d]	Reported yields[d]
C_6H_5	18[e]	184–185°[f]	184°	48
$C_6H_5CH_2$	11	170–173°	173°	50
$C_6H_5CH_2CH_2CH_2$	8	101–103°	104°	25
$CH_3(CH_2)_{16}$	Trace	66–68°	69–70°	?
p-BrC_6H_4	6	239–240°[g]	234°	?
p-$CH_3C_6H_4$	18	188–189°	189–190°	40
p-$NH_2C_6H_4$	24	270–272°[h]	...	0
p-$NO_2C_6H_4$	0	...	...	0

[a] All reaction were 0.03 mole acid to 0.06 mole amine with 230–250 g. PPA at 195–205° for 15 min. [b] Yield of material purified to within 2–3° of reported m.p. [c] M.p. of purified product (from ethanol or aqueous ethanol). [d] See ref. 2a for original literature reference. [e] 48% in a 0.1 mole run. [f] Phosphate salt, m.p. 194–196°. Calcd. for $C_{19}H_{16}NPO_4$: C, 64.58; H, 4.56; N, 3.97; P, 8.77. Found: C, 64.43, 64.64; H, 4.65, 4.63; N, 3.94, 4.04; P, 8.72. [g] Calcd. for $C_{19}H_{12}NBr$: C, 68.28; H, 3.62; N, 4.19. Found: C, 68.15; H, 3.81; N, 4.43. [h] Calcd. for $C_{19}H_{14}N_2$: C, 84.41; H, 5.22; N, 10.37. Found: C, 84.07; H, 5.40; N, 10.38.

In several instances a small amount of ketonic material, which is probably similar to the diacyldiphenylamine of Elston,[4] was noted.

Experimental[6]

Preparation of 9-Substituted Acridines.—A mixture of diphenylamine, a carboxylic acid, and polyphosphoric acid[7] was heated, with stirring, to the desired temperature and held at this temperature for the stated time. The reaction mixture was then poured onto ice and filtered or decanted. Examination of the infrared spectra of the gummy solid indicated that it contained mainly diphenylamine, a small amount of ketonic product,[8] and possibly some 9-substituted acridine.[9] Treatment of the solution with 25% sodium hydroxide solution caused the precipitation of a solid (while the solution was still acidic) which was apparently the phosphate salt of the 9-substituted acridine.[10] After filtration the solution was made strongly basic with sodium hydroxide and extracted with chloroform. Concentration of the chloroform generally gave a trace of the 9-substituted acridine. The phosphate salt was shaken with 25% sodium hydroxide and chloroform and the chloroform concentrated to give the 9-substituted acridine as listed in Table I.

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(6) All melting points are uncorrected. Analysis by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

(7) Victor Chemical Co.

(8) In the case of the benzoic acid reaction, this fraction had peaks identical to those reported by Elston[4] for his dibenzoyldiphenylamine. In addition, in the case of stearic acid treatment of this gum with sodium hydroxide and chloroform gave, on evaporation of the chloroform, a solid, m.p. 107–108.5° (from absolute ethanol), which was apparently distearyldiphenylamine (Calcd. for $C_{48}H_{79}NO_2$: C, 82.11; H, 11.34; N, 2.00. Found: C, 82.41; H, 11.26; N, 1.98, 2.11).

(9) Since we were interested in the convenience of the method, no attempt was made to isolate this acridine and include it in the yield.

(10) In the case of 9-phenylacridine this salt was washed with water and alcohol to give analytically pure material (see Table I). The same salt could be obtained by reacting 9-phenylacridine with 85% phosphoric acid.

Apparent *meta* Rearrangement of Benzoylsulfuric Acid

Stephen J. Tauber and Nancy N. Lowry

Department of Chemistry, Smith College, Northampton, Massachusetts

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Benzoylsulfuric acid was reported by Oppenheim[1] to rearrange to m-sulfobenzoic acid. Elliott, *et al.*,[2] described the rearrangement as yielding chiefly o-sulfobenzoic acid. They suggested that the difference in products is due to direct sulfonation under Oppenheim's conditions as opposed to chiefly rearrangement under their own. Oppenheim either let benzoylsulfuric acid stand in the presence of sulfuric acid or warmed sulfuric acid with an excess of benzoyl chloride; details of time, temperature,[3] and amounts are lacking. Elliott, *et al.*, heated benzoylsulfuric acid *per se* at 100°. We have established that if the reaction mixture from sulfuric acid and a large or small excess of benzoyl chloride is heated at 100° then the predominant product is m-sulfobenzoic acid.

Our evidence indicates that this product is not due to direct sulfonation. The presence of unchanged sulfuric acid was avoided by the use of an excess of benzoyl chloride, the size of the excess evidently being immaterial, and by drawing out with dry air the hydrogen chloride produced in the initial reaction. Even should a trace of unchanged sulfuric acid have been present we could argue against direct sulfonation by sulfuric acid either of benzoyl chloride or of benzoylsulfuric acid from the observation that neither ethyl benzoate nor benzoic acid is sulfonated by sulfuric acid at our temperature. We consider the comparison applicable because of the similarity of the electronic environment in the several compounds of the carbon atom attached to the benzene ring. Ethyl benzoate reacts with sulfuric acid only by cleavage to benzoic acid, in consonance with the scheme of Newman, *et al.*[4]

The difference between our results and those of Elliott, *et al.*, is presumably to be sought in the difference in conditions. They heated purified benzoylsulfuric acid, which might undergo an intramolecular rearrangement—a self-sulfonation constrained to reaction at the *ortho* position by steric requirements—as indeed suggested by Elliott, *et al.*[2] Our conditions evidently cause intermolecular sulfonation (involving a sulfonating agent other

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(1) (a) A. Oppenheim, *Ber.*, **3**, 735 (1870); (b) Ador and Oppenheim, *ibid.*, 738.

(2) G. A. Elliott, L. L. Kleist, F. J. Wilkins, and H. W. Webb, *J. Chem. Soc.*, 1219 (1926).

(3) Elliott, *et al.*, ascribed a temperature of 150°, which Oppenheim did not mention.

(4) M. S. Newman, R. A. Craig, and A. B. Garrett, *J. Am. Chem. Soc.*, **71**, 869 (1949).