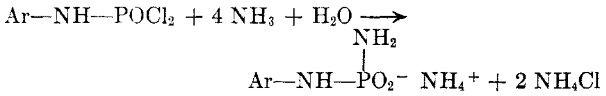
Sulfanilamides IVa–i were prepared by the following procedure, with minor modifications in individual cases. II was allowed to react with at least six equivalents of ammonia or of a primary or secondary amine in the presence of water. Since ammonia or the amine also serves as acceptor for the acid liberated in the reaction, it may be partially replaced by an inorganic base (such as sodium carbonate or sodium bicarbonate) or by a tertiary amine. After the initial reaction had subsided, heat was usually applied. The reaction mixture then was acidified and briefly warmed. On neutralization the sulfanilamide precipitated. The approximate yields, based on sulfanilic acid, obtained in our experiments are as follows: 70% for IVa and IVb, 60% for IVf, 50% for IVc, IVd and IVg, 30% for IVe, IVh and IVi. These yields do not include additional quantities of sulfanilamides obtainable by the hydrolysis of side-products which were formed in some of the reactions and are to be discussed later.

The formation of sulfanilamides is rationalized as proceeding by way of phosphorodiamidic acids (III).

The following facts support such a path:

1. The —$POCl_2$ group of N-phenylphosphoramidic dichloride and of N-(*p*-chlorophenyl)phosphoramidic dichloride is partly amidated and partly hydrolyzed by aqueous ammonia.[7,8]

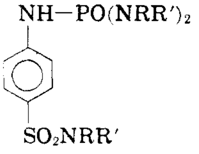


$$Ar—NH—POCl_2 + 4\,NH_3 + H_2O \longrightarrow Ar—NH—\overset{NH_2}{\overset{|}{P}}O_2^-\ NH_4^+ + 2\,NH_4Cl$$

2. Phosphorodiamidic acids, while stable to alkali, undergo acid hydrolysis very readily.[9] The free phosphate content of our reaction mixtures increased greatly during the acid treatment. No sulfanilamides were isolated when the reaction mixtures were neutralized without prior acid treatment. Phosphoric triamides, frequently obtained as side-products (see below), are only difficultly hydrolyzable by acid or alkali.

Some of the reactions yielded acid-insoluble side-products which were removable just before the final neutralization. They were phosphoric triamides (V) resulting from complete amidation of II.

Vd. R = R′ = C_2H_5. M.p. 152–153°. Calc'd for $C_{18}H_{35}N_4O_3PS$: C, 51.65; H, 8.43; N, 13.39; P, 7.40 S, 7.66. Found: C, 51.32; H, 8.59; N, 13.76; P 7.49; S, 7.54.



V

Ve. R = H, R′ = cyclohexyl. M.p. 205°. Calc'd for $C_{24}H_{41}N_4O_3PS$: C, 58.04; H, 8.32; N, 11.28; P, 6.24; S, 6.46. Found: C, 58.37; H, 8.08; N, 11.18; P, 6.08; S, 6.43.

Vf. R = H, R′ = benzyl. M.p. 179°. Calc'd for $C_{27}H_{29}N_4O_3PS$: C, 62.29; H, 5.62; N, 10.76; P, 5.91; S, 6.16. Found: C, 62.11; H, 5.47; N, 10.91; P, 6.09; S, 6.12.

Vg. R = H, R′ = phenyl. M.p. 257° (dec.). Calc'd for $C_{24}H_{23}N_4O_3PS$: C, 60.24; H, 4.84; N, 11.71; P, 6.47; S, 6.70. Found: C, 60.05; H, 4.86; N, 11.57; P, 6.38; S, 6.75.

Compounds of type V could be converted to the corresponding sulfanilamides by acid or alkaline hydrolysis under vigorous conditions. The sulfonamide group is thus more resistant to hydrolysis than is the phosphoric triamide group.

Phosphoric triamides in general are converted by alkaline hydrolysis to phosphorodiamidates, *i.e.*, only one P—N bond is cleaved, further hydrolytic break-down requiring a mild treatment with acid.[10] There are two ways in which the phosphoric triamide group of V can be cleaved by alkali. It appears that both possible modes of alkaline cleavage occur side by side, since a quantity of the corresponding sulfanilamide (IV) is obtained without acid treatment and an additional quantity after acid treatment.

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Mercury Derivatives of Fluorocarbon Carboxylic Acid Amides

Sir:

We have found that mercury derivatives of fluorocarbon carboxylic acid amides can be prepared readily by heating a small amount of the amide with an excess of red mercuric oxide to 150–170° for about five minutes. The mixture then is cooled, 10 ml. of 95% ethanol is added, and the

TABLE I

MERCURY DERIVATIVES OF FLUOROCARBON AMIDES

$(RCONH)_2Hg$ R	M.P., °C.	Mercury, % Theory	Mercury, % Found	Nitrogen, % Theory	Nitrogen, % Found
CF_3—	219	47.17	47.05	6.60	6.67
CF_3CF_2—	244	38.16	37.92	5.34	5.44
$CF_3CF_2CF_2$—	286	32.05	31.88	4.48	4.59

solution is brought to boiling, and filtered. The ethanol then is evaporated on a steam-bath. The yield of pure, white, granular product is almost quantitative. The results are summarized in Table I.

The mercury analysis was performed according to the procedure of Rauscher.[1]

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