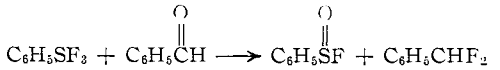
SF_5OF[1b] and SF_5Cl[2] are known, efforts to prepare alkyl- and arylsulfur pentafluorides have been unsuccessful.[1b,3] The only alkyl- or arylsulfur trifluoride known is 2,4-dinitrophenylsulfur trifluoride, prepared by Chamberlain and Kharasch[4] by the reaction of fluorine with the corresponding disulfide in anhydrous hydrogen fluoride solution.

We have found that phenylsulfur trifluoride is obtained in 50 to 60% yield by the exothermic reaction of silver difluoride with a solution of phenyl disulfide in a "Freon" solvent, 1,1,2-trichloro-1,2,2-trifluoroethane. Phenylsulfur trifluoride is a colorless liquid, b.p. 60° (5 mm.), that is hydrolyzed rapidly by water to benzenesulfinic acid and slowly attacks "Pyrex" glass.

$$(C_6H_5S)_2 + 6AgF_2 \longrightarrow 2C_6H_5SF_3 + 6AgF$$

Anal. Calcd. for $C_6H_5F_3S$: F, 34.3; S, 19.3. Found: F, 33.5; S, 19.9.

Phenylsulfur trifluoride fluorinates carbonyl compounds: for example, benzaldehyde is converted to benzal fluoride (80%) by being heated with phenylsulfur trifluoride for 5 minutes at 100°.[5]



$$C_6H_5SF_3 + C_6H_5\overset{\overset{\displaystyle O}{\|}}{C}H \longrightarrow C_6H_5\overset{\overset{\displaystyle O}{\|}}{S}F + C_6H_5CHF_2$$

Substituted arylsulfur trifluorides, $XC_6H_4SF_3$, where $X = NO_2$ or CH_3, are prepared in a similar manner.

When phenylsulfur trifluoride is heated gradually to 130° with silver difluoride in a reactor made of copper or Teflon [polytetrafluoroethylene], phenylsulfur pentafluoride is obtained in about 10% yield. Phenylsulfur pentafluoride is a colorless liquid, b.p. 149°, $n^{25}D$ 1.4290, that is comparable in thermal and hydrolytic stability to benzotrifluoride.

$$C_6H_5SF_3 + 2AgF_2 \longrightarrow C_6H_5SF_5 + 2AgF$$

Anal. Calcd. for $C_6H_5F_5S$: C, 35.3; H, 2.47; F, 46.5; S, 15.7. Found: C, 35.5; H, 2.74; F, 46.7; S, 15.6.

The n.m.r. (fluorine and proton), infrared and ultraviolet spectra are consistent with the structure $C_6H_5SF_5$. The compound is hydrolyzed slowly to benzenesulfonyl fluoride by heating at 100° with 100% sulfuric acid. *m*- and *p*-nitrophenylsulfur pentafluorides are also prepared (15–30% yield) by heating the corresponding disulfide with silver difluoride, first in the "Freon" solvent, CCl_2FCClF_2, and then at 130° in a copper reactor with fittings of "Teflon." Anilines substituted by a sulfur pentafluoride group in the *meta*- or *para*-position are prepared by catalytic hydrogenation of the corresponding nitro derivatives, and react in the manner typical of anilines; thus, they can be acylated or diazotized.

The above series of arylsulfur trifluorides and pentafluorides are unique in providing key compounds necessary for determination of the properties of the SF_3 and SF_5 groups in comparisons with other substituents. Thus, we have determined that the sulfur pentafluoride group is strongly electron-withdrawing and is *meta*-directing to electrophilic substitution.

A detailed report of the method of synthesis and chemistry of the arylsulfur trifluorides and pentafluorides, as well as quantitative measurements on the inductive and resonance effects of the sulfur pentafluoride group, will be published in the near future. We are indebted to Drs. B. C. McKusick and T. L. Cairns for helpful discussions and suggestions during the course of the work.

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WILMINGTON, DEL.

RECEIVED JULY 18, 1960

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[2] H. L. Roberts and N. H. Ray, *J. Chem. Soc.*, 665 (1960).

[3] H. J. Emeleus and H. G. Heal, *ibid.* 1126 (1946).

[4] D. L. Chamberlain and N. Kharasch, THIS JOURNAL, **77**, 1041 (1955).

[5] The use of SF_4 for fluorination of carbonyl compounds is described by W. R. Hasek, W. C. Smith and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

THE SYNTHESIS OF PHENYLATED AZIRIDINONES[1]

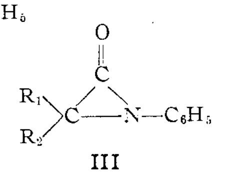
Sir:

This communication describes the preparation of a new class of cyclic amides, α-lactams, previously postulated as an intermediate in the sodamide-promoted conversion of α-chloro-α-phenylacetanilide (Ia) into α-anilinophenylacetamide[2] (II). Ia(λ_{max}^{EtOH} 247–250 mμ (4.19); λ_{max}^{KBr} (cm.$^{-1}$) 3306, 3150, 1667) was caused to react with sodium hydride in a manner described[2] (this time with a *complete* exclusion of oxygen from the reacting system), giving two compounds: (1) 2,5-diketo-1,3,4,6,-tetraphenylpiperazine (12% yield), and (2) 1,3-diphenyl-2-aziridinone, IIIa, (78–85% yield) as colorless crystals, (sintering at 115°) melting at 145–150° (dec.) (λ_{max}^{EtOH} 243–247 mμ (4.02); $\lambda_{max}^{CHCl_3}$ (cm.$^{-1}$) 1720, 1704, 1689; *anal.* found for $C_{14}H_{11}ON$: C, 79.9; H, 5.6; N, 6.4; mol. wt., 212 (ebullioscopic, benzene).[3] Alkaline hydrolysis of IIIa was slow even at 78°, consuming approximately 0.4 equivalent of alkali on being refluxed with 0.1 *N* ethanolic potassium hydroxide during six hours. However, ammonolysis of IIIa by means of sodamide in liquid ammonia provided II as the only isolable product.

$$R_1R_2ClCCONHC_6H_5 \xrightarrow[-H_2,\ -NaCl]{NaH}$$

I

Ia and IIIa, $R_1 = H$; $R_2 = C_6H_5$



III

Ib and IIIb, $R_1 = R_2 = C_6H_5$

α-Chloro-α,α-diphenylacetanilide[4] (Ib, m.p. 86°, λ_{max}^{EtOH} 245 mμ (4.24)) was brought to reaction

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[1] May otherwise be termed α-lactams or *azacyclopropanones*, the above systematic name, illustrating a carbonyl containing derivative of aziridine (otherwise termed ethyleneimine) is to be preferred. See Patterson and Capell "The Ring Index," Reinhold Publishing Corp., New York, N. Y., 1940.

[2] S. Sarel and A. Greenberger, *J. Org. Chem.*, **23**, 330 (1958).

[3] Measurements were taken with a Gallenkamp semimicro ebulliometer, No. 7665K.

[4] H. Klinger, *Ann.*, **389**, 253 (1912).

with sodium hydride in a fashion described here, affording IIIb (85% yield) as colorless crystals m.p. 202°; λ_{max}^{EtOH} 255 mμ (4.02); λ_{max}^{KBr} (cm.$^{-1}$) 3419, 1736, 1720, (*anal.* found for $C_{20}H_{15}ON$: C, 84.3; H, 5.8; N, 4.86; mol. wt., 290 (ebullioscopic, benzene)[3]). IIIb showed no identity with a sample of 2,5-diketo-1,3,3,4,6,6-hexaphenylpiperazine (IV), m.p. 224°; λ_{max}^{EtOH} 250–255 mμ (4.10); λ_{max}^{KBr} (cm.$^{-1}$) 3226, 1727, 1689 (*anal.* found for $C_{40}H_{30}O_2N_2$: C, 84.4; H, 5.5), prepared as described.[5] IIIb readily dissolved in cold concd. sulphuric acid (scarlet-red coloration), giving on dilution with water an immediate precipitate of colorless α-anilino-α,α-diphenylacetic acid, m.p. 174–177° (reported[6] m.p. 174.5°); λ_{max}^{KBr} (cm.$^{-1}$) 3419, 3367, 1733 (*anal.* found for $C_{20}H_{17}O_2N$: N, 4.4).[7] The physical and chemical evidence presented here clearly suggest that the azacyclopropanone, in analogy with cyclopropenone system,[8] has presumably a remarkable resonance stabilization to set off its internal strain. The observed low reactivity of (III) toward nucleophilic reagents seems to be parallel to that of substituted 2-azetidinones (β-lactams) with alkalies.[9]

Acknowledgment.—H. L. is indebted to Abrahm and Herbert Sive Memorial Research Fellowship, Johannesburg, South Africa, for financial aid.

[5] H. Klinger and Nickell, *Ann.*, **390**, 367 (1912).

[6] W. Schlenk, J. A. Appenrodt, A. Michael and A. Thal, *Ber.*, **47**, 484 (1914).

[7] By contrast (IV) was sparingly soluble in concd. sulfuric acid (brown coloration), giving unchanged starting material upon dilution with water.

[8] R. Breslow, R. Haynie and J. Mirra, THIS JOURNAL, **81**, 247 (1959).

[9] S. A. Ballard and D. S. Melstrom in Elderfield's "Heterocyclic Compounds," Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1950, pp. 107–110.

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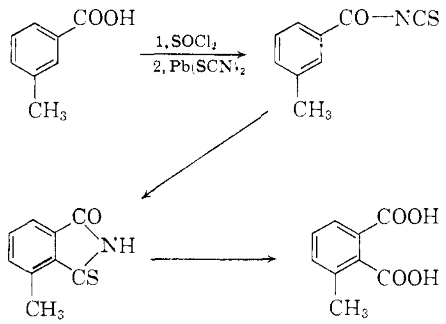
SPECIFIC *ortho*-CARBOXYLATION OF AROMATIC ACIDS AND ARALKYLAMINES: MONOTHIOIMIDES AND THIOLACTAMS

Sir:

We wish to report a simple reaction for converting benzoic acids to phthalic acids, arylacetic acids to homophthalic acids, and β-arylethylamines to *o*-carboxy-β-arylethylamines. The acids are converted through their chlorides by reaction with lead thiocyanate to acyl isothiocyanates,[1] which are cyclized to monothio-phthalimides or -homophthalimides by treatment with aluminum chloride in carbon disulfide for periods of several hours to several days. β-Arylethyl isothiocyanates, prepared from amines and carbon disulfide,[2] are similarly cyclized to thiolactams. Hydrolysis of the cyclized products then gives the acids corresponding to carboxylation of the starting materials. The cyclization of benzoyl isothiocyanates appears to require the presence of an activating *meta*-substituent, such as methyl; unsubstituted benzoyl isothiocyanate has up to now resisted cyclization, although β-naphthoyl isothiocyanate reacts successfully. Within this apparent limitation, the reaction provides a direct route for the synthesis of compounds heretofore available only with difficulty or not at all. The cyclization of benzoyl isothiocyanates appears to be selective when two *ortho*-positions are open, for *m*-toluyl isothiocyanate yielded only 3-methylphthalic acid, resulting from cyclization in the vicinal position.



Preliminary experiments indicate that the reaction also occurs with heterocyclic analogs, such as 3-thenoyl isothiocyanate, and with β,γ-unsaturated aliphatic acids such as cyclohexene-1-acetic acid. Examples of the closely related cyclization of β-arylethyl isocyanates have previously been reported,[3] although its utilization in an *ortho*-carboxylation procedure was not undertaken. Acyl isocyanates would presumably behave similarly, but we have not as yet investigated them, owing to the greater difficulties in preparing and handling them compared to the sulfur analogs.

The intermediate monothioimides, which can be isolated in moderate yields, constitute a class of compound of which only one example (monothiophthalimide[4]) has heretofore been reported, and to which no preparatively satisfactory general route has been available. All the monothiophthalimides we have prepared are red substances, while the monothiohomophthalimides are yellow (thioamides are usually colorless or straw-colored). Lithium aluminum hydride reduces both thioimides and thiolactams with removal of sulfur, giving tetrahydroisoquinolines. The potentialities for the synthesis of these and other classes of heterocyclic compounds from the thioimide intermediates are obvious.

Treatment of *m*-toluyl chloride with lead thiocyanate gave *m*-toluyl isothiocyanate, a colorless, unstable liquid, b.p. 78°(0.85 mm.) (N-*m*-toluyl-N′-phenylthiourea, m.p. 113°). (Since acyl isothiocyanates are in most cases unstable to short-term storage, most of those prepared in this work have been converted by reaction with aniline to N-acyl-N′-phenylthioureas for analysis and characterization).[5] Refluxing a mixture of *m*-toluyl

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[1] A. E. Dixon and J. Taylor, *J. Chem. Soc.*, **93**, 684 (1908).

[2] W. R. Vaughan, M. V. Anderson, H. S. Blanchard and D. I. McCane, *J. Org. Chem.*, **20**, 819 (1955); M. L. Moore and F. S. Crossley, *Org. Syntheses*, Coll. Vol. III, 599 (1955).

[3] L. M. Mohunta and J. N. Ray, *J. Chem. Soc.*, 1263 (1934); R. H. F. Manske and R. Robinson, *ibid.*, 240 (1927).

[4] J. C. Porter, R. Robinson and M. Wyler, *ibid* 620 (1941); H. D. K. Dtew and D. B. Kelly, *ibid.*, 625 (1941).

[5] Satisfactory analyses have been obtained for all new compounds reported here, with the noted exception of some of the less stable acyl isothiocyanates, all of which, however, showed infrared absorption at 1960 cm.$^{-1}$.