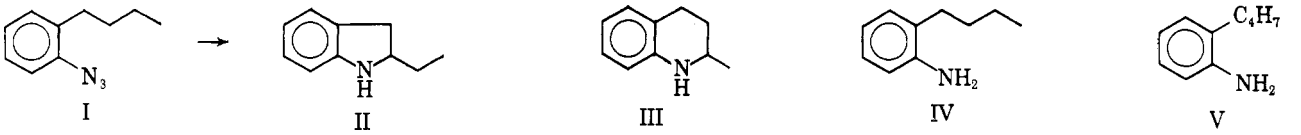
SCHEME I



	% COMPOSITION OF DISTILLATE				
	I	II	III	IV	V
Vapor phase reaction		43	11	1	46
Soln. reaction		37	10	29	25

ture of 2-methyl-1,2,3,4-tetrahydroquinoline (III) on the basis of its infrared (NH absorption), ultraviolet (λ_{max} 300 mμ), and n.m.r. spectra as well as its elemental analysis.

Experimental

2-Butylazidobenzene (I) was prepared *via* *o*-butylnitrobenzene as described previously.[1] G.p.c. (20-ft. by $^3/_8$-in. column packed with 25% 5-ring polymetaphenylether on 60–80-mesh Chromosorb W) of the nitro compound showed the presence of less than 1% of the *meta* and *para* isomers.

Pyrolysis of 2-Butylazidobenzene (I). **A.**—The vapor phase reaction was carried out essentially as described previously[1] with a modification in that the azide was introduced at the top of the reaction tube by suction through a very fine capillary. The crude pyrolysate was distilled. The fraction boiling at 114–118° at 12 mm. accounted for 70% of the material.

B.—Solution phase pyrolysis of II was achieved by employing the procedure used for the pyrolysis of *o*-azodiphenylcyclohexene.[2] After separating the solvent, the crude pyrolysate was distilled (b.p. 118–120° at 15 mm.). The distillate amounted to 63% of the material.

Product Analysis.—The total distilled product mixture from each of the above pyrolysis reactions as well as the catalytically (5% palladized carbon) hydrogenated product mixture were subjected to g.p.c. analysis at 250° on a 20-ft. by $^3/_8$-in. column packed with 25% five-ring polymetaphenyl ether on 60–80-mesh Chromosorb W. The product distribution is listed in Table I.

TABLE I

PRODUCT DISTRIBUTION

Reaction	Component, % A (IV)	B (II)	C (V)	D (III)
Vapor phase	1	72	7	19
Soln.	29	52	8	12
Vapor phase, H_2–Pd	47	43	0	11
Soln., H_2–Pd	54	37	0	10

Component A exhibited an infrared spectrum and g.p.c. retention time identical with that of 2-butylaniline (IV).

Component B exhibited a single sharp band at 2.95 μ (NH[7]) in the infrared region (determined neat) and a λ_{max} 290 mμ in the ultraviolet region (ethanol solution[8]). Its n.m.r. spectrum (acetone-d_6 solution) exhibited a four-proton multiplet centered at τ 3.30, a diffuse single-proton absorption at 5.06, a single-proton multiplet at 6.34, a two-proton multiplet at 7.22, a two-proton multiplet at 8.49, and a three-proton triplet at 9.06. Tetramethylsilane was used as an internal reference with τ 10.0.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.12; H, 9.07; N, 9.72.

Component D had a single sharp band in the infrared (neat) at 2.90 μ (NH[7]) and λ_{max} 300 mμ (ethanol solution[8]) in the ultraviolet. Its n.m.r. spectrum (acetone-d_6 solution) showed a four-proton multiplet centered at τ 3.35, a diffuse single proton at 5.27, a one-proton multiplet at 6.68, a two-proton multiplet at 7.31, a very complex two-proton multiplet at 8.28, and a clean, three-proton doublet at 8.85.

Anal. Calcd. for $C_{10}H_{13}N$: C, 81.58; H, 8.90; N, 9.52. Found: C, 81.71; H, 8.66; N, 9.71.

The Modified Kaluza Synthesis. III. The Synthesis of Some Aromatic Isothiocyanates

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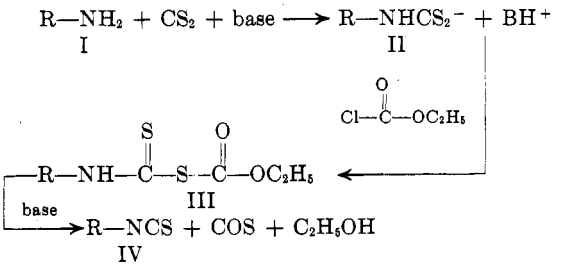
In the first paper of this series the preparation of aliphatic isothiocyanates by the modified Kaluza synthesis was reported.[1] Further study elucidated the mechanism of decomposition of the intermediate carboethoxy alkyl dithiocarbamates.[2] We now wish to report extension of the modified Kaluza synthesis to include several aromatic isothiocyanates.

The synthesis of isothiocyanates (mustard oils) by the modified Kaluza method may be divided into three parts: first, the formation of the dithiocarbamate salt (II) from an amine (I), carbon disulfide, and a base; secondly, formation of the carboethoxy dithiocarbamate (III) by treatment of the salt with ethyl chlorocarbonate; and thirdly, decomposition of III with base to yield the isothiocyanate (IV). The first step of the synthesis proved to be more difficult with aromatic amines than with aliphatic amines owing to their lower basicity. In order to prepare the aryldithiocarbamates



(II, R = aryl), it was necessary to use nonaqueous solvents such as benzene or ether and a strong organic base such as triethylamine.[1] Under these conditions the aryldithiocarbamates precipitate from solution. With aniline and higher base strength amines, precipitation of the dithiocarbamate began within about 5 min. at 0°. The lower base strength amines, *e.g.*, *p*-chloroaniline, required several hours under the same conditions for appearance of the dithiocarbamates derivative. Yields of this first step ranged from 83 to greater than 90%. The *p*-nitro- and *p*-cyanoanilines gave no precipitation of dithiocarbamate salt. It might be

(1) J. E. Hodgkins and M. G. Ettlinger, *J. Org. Chem.*, **21**, 404 (1956).
(2) J. E. Hodgkins, W. P. Reeves, and Y. T. Liu, *J. Am. Chem. Soc.*, **83**, 2532 (1961).

TABLE I

FORMATION OF ARYL ISOTHIOCYANATES BY THE MODIFIED KALUZA SYNTHESIS

IV	Structure	Time for dithiocarbamate formation	Yield of II, %	Yield of IV, %	B.p., °C. (mm.)	M.p., °C.	M.p. of aniline derivative Lit.	M.p. of aniline derivative Found
a	C_6H_5NCS	24 hr.	90	81	105–108 (14)		154[a]	153
b	o-CH_3—C_6H_4NCS	24 hr.	89	80	126–129 (12)		136[b]	136
c	m-CH_3—C_6H_4NCS	24 hr.	94	78	129–132 (12)		94[b]	99
d	p-CH_3—C_6H_4NCS	24 hr.	92	81	130–133 (25)		141[b]	140
e	p-Cl—C_6H_4NCS	72 hr.	83	70		46.5	152[b]	152
f	p-Br—C_6H_4NCS	3–4 days	88	73		50	148[b]	155[c]
g	o-CH_3O—C_6H_4NCS	3 hr.	88	82	156–158 (24)		136[b]	131
h	p-C_2H_5O—C_6H_4NCS	3 hr.	89	88		53–54	136[b]	135
i	p-$(CH_3)_2N$—C_6H_4NCS	15 min.	95	60[d]		69	...	149[e]
j	β-$C_{10}H_7NCS$	7 days	90	73		58–59	129	155[f]
k	p-CH_3O—C_6H_4NCS	3 hr.	95	92	167–168 (18)		143[g]	141
l	p-CN—C_6H_4NCS	None	0	...	...		...	...
m	p-NO_2—C_6H_4NCS	None	0	...	...		...	...

[a] H. S. Fry, *J. Am. Chem. Soc.*, **35**, 1544 (1913). [b] T. Otterbacher and F. C. Whitmore, *ibid.*, **51**, 1909 (1929). [c] *Anal.* Calcd. for $C_{13}H_{11}BrN_2S$: C, 50.49; H, 3.61; N, 9.11. Found: C, 51.08; H, 3.51; N, 9.03. [d] This is the only entry in the table based on a single reaction. The reason for the low yield is probably due to the fact that the product was washed with acid and water (see Experimental). [e] *Anal.* Calcd. for $C_{15}H_{17}N_3S$: C, 66.38; H, 6.32; N, 15.48. Found: C, 66.37; H, 6.31; N, 15.37. [f] *Anal.* Calcd. for $C_{17}H_{14}N_2S$: C, 73.35; H, 5.16; N, 10.25. Found: C, 73.28; H, 5.09; N, 10.20. [g] K. N. Campbell, B. K. Campbell, and S. J. Patelski, *Proc. Indiana Acad. Sci.*, **53**, 119 (1943).

possible to prepare the dithiocarbamate derivatives of these two amines by first forming the lithium compounds before treatment with carbon disulfide, but this has not been investigated.

Carboethoxylation of the aryldithiocarbamate salts was accomplished in chloroform solution without difficulty. The decomposition of the intermediate carboethoxy aryldithiocarbamates was carried out in the same solution with triethylamine. This last reaction seemed much easier than with the aliphatic derivatives, probably because of the higher acid strength of the aromatic compounds. In some of the reactions it was observed that the mustard oils contained (infrared spectra) traces of phenylurethan or diphenylurea derivatives; this could usually be traced to the use of wet chloroform or to improper distillation of the final product. The yields of isothiocyanates ranged from 70 to 90%. Our results with various aromatic amines are summarized in Table I. The aniline derivatives were used for characterization. If the melting point of the aniline derivative differed significantly from the literature value or could not be found, the derivative was analyzed.

Thus, the modified Kaluza method is applicable to aromatic amines[3] with base strengthening, mild base weakening, and no substituents. The method is not applicable, in its present form, to the synthesis of isothiocyanates containing strong electron-withdrawing groups. The synthesis is slower for phenyl isothiocyanate than the generally accepted method, but the use of lead and a steam distillation procedure is avoided.[4] The present method seems more generally applicable than decomposition of thiourea derivatives,[5] does not employ phosgene[6] or thiophosgene,[7] and, overall, gives better yields than any available synthesis.

(3) The original Kaluza synthesis is not applicable to aromatic amines; see ref. 1.

(4) F. B. Dains, R. Q. Brewster, and C. P. Olander, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 447.

(5) F. Cymerman-Craig, M. Moyle, and R. A. White, *Org. Syn.*, **36**, 56 (1956).

(6) V. H. Slotta and H. Dressler, *Ber.*, **63**, 888 (1930).

(7) G. M. Dyson and H. J. George, *J. Chem. Soc.*, **125**, 1702 (1924). This procedure has been modified and employed extensively in the aliphatic series [A. Kjaer, F. Marcus, and J. Conti, *Acta Chem. Scand.*, **7**, 1370 (1953), and later articles].

Experimental

The following is the generalized procedure used for the preparation of all the aryl isothiocyanates. In Table I is shown the times required for salt formation and the melting or boiling point of the various isothiocyanates.

The amine (0.1 mole) was dissolved in the minimum amount of benzene and treated with 6.6 ml. (0.1 mole) of carbon disulfide and 14 ml. of (0.1 mole) of triethylamine, and the solution was cooled to 0°. After complete precipitation of the triethylammonium dithiocarbamate salt (see times in Table I), the solution was filtered; the solid was washed with anhydrous ether and air-dried for about 10 min. The salt was then dissolved in about 75 ml. of chloroform, treated with 14 ml. of triethylamine, and cooled again to 0°. To this solution was added 10.2 ml. (0.1 mole) of ethyl chlorocarbonate dropwise over a 15-min. period with hand stirring. The resulting solution was stirred at 0° for 10 min. and allowed to warm to room temperature during a 1-hr. period. The chloroform solution was washed with 3 *M* HCl and twice with water and was dried over sodium sulfate. The chloroform was evaporated *in vacuo* and the aryl isothiocyanate was either distilled or recrystallized from ethanol depending on the physical state of the compound.

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The Solvolysis of Acid Chlorides with *t*-Alkyl Hydroperoxides[1]

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We have shown recently[3] that *t*-alkyl and *t*-aralkyl chlorides undergo solvolysis with *t*-alkyl hydroperox-

(1) Paper XXXV on Organic Peroxides.

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(3) Paper XXXIV on Organic Peroxides: N. A. Milas, R. J. Klein, and D. G. Orphanos, *Chem. Ind.* (London), 423 (1964).