

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 67.76; H, 6.36; N, 4.65. Found: C, 67.94; H, 6.34; N, 4.84.

Oxidation of Camphenol to Ketone 13.—A solution of 0.35 g. of camphenol in 10 ml. of pyridine was added to 1.0 g. of chromic anhydride in 10 ml. of pyridine, and the mixture was stirred for 22 hr. Water was added, and the mixture was extracted with ether. The ether solution was washed with dilute hydrochloric acid, with water, and with dilute sodium bicarbonate solution, and was dried over sodium sulfate. Most of the solvent was removed through a small distillation column, and the remaining solution subjected to g.l.p.c. One large peak was observed in addition to the ether peak and a very small peak that had the retention time exhibited by camphenol. Collection of the material from the large peak furnished a solid, m.p. 65–70°, lit.^{12,13} m.p. 77–78°. The infrared spectrum showed strong absorption (carbonyl) at 1750 cm^{-1} . Without further purification, this material was converted to a semicarbazone derivative which was recrystallized from ethanol–water: m.p. 201–203°; lit. 205 m.p. dec.¹³ 213.5.¹²

Anal. Calcd. for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27. Found: C, 63.94; H, 8.35.

Wolff-Kishner Reduction of Ketone 13.¹⁶—Sodium (1.2 g.) was added to 20 ml. of diethylene glycol and then 0.29 g. of the ketone (prepared as described above but not purified by g.l.p.c.) and 2 ml. of hydrazine hydrate were added. The solution was refluxed for 18 hr. Then 2 ml. more of hydrazine hydrate was added, and refluxing was continued for an additional 18 hr. Benzene was used to extract the solution and to rinse out the apparatus. Portions of this benzene solution were subjected to g.l.p.c. The retention time of the only significant peak (except for benzene) was the same as that exhibited by camphene, and collected material gave an infrared spectrum identical with that of camphene. The yield of camphene in this reduction was about 20%.

(16) A similar reduction of this ketone has been reported (ref. 12).

Nitrene Chemistry. An Analysis of the Products from the Pyrolysis of 2-Butylazidobenzene

GERALD SMOLINSKY AND BERNICE I. FEUER

Bell Telephone Laboratories, Inc.,
Murray Hill, New Jersey 07971

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Previously we reported¹ that pyrolysis of 2-butylazidobenzene (I) led to the formation of a nitrene intermediate which cyclized to give only 2-ethylindoline (II) and no 2-methyl-1,2,3,4-tetrahydroquinoline (III). We concluded that when given a choice an aryl nitrene will ring close to a five-membered ring. Only in a reaction such as the pyrolysis of 2-azido-2',4',6'-trimethylbiphenyl,² where five- and six-membered ring closure must involve quite different types of mechanisms, do we find six-membered ring formation. These observations agree with a mechanism put forward by Barton³ in which it was assumed that nitrenes, like the presumed intermediates in the Hofman-Freytag-Loeffler reaction, the photochemically induced cyclization of ketones, and the photolysis of nitrites and hypochlorites, require a six-membered transition state.



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(2) G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 4717 (1960).

(3) D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 626 (1962).

However, photolysis of acid azides leads to acyl nitrenes which are reported⁴ to form both γ - and δ -lactams. These results, as well as our finding that (*S*)(+)-1-azido-2-(2-methylbutyl)benzene on pyrolysis definitely forms a small amount of 2,3-dimethyl-1,2,3,4-tetrahydroquinoline⁵ caused us to experience some doubt about the completeness of our earlier work.¹

Accordingly we have reinvestigated the pyrolysis of I both in the vapor phase¹ and in solution.⁶ The products obtained were analyzed by gas phase chromatography (g.p.c.) and shown to consist of five components. The g.p.c. trace of the total distillable pyrolysate indicated the presence of at least four compounds (A, B, C, and D; see Table I) while the trace of the hydrogenated distilled pyrolysate showed only three compounds present (A, B, and D). Furthermore, after hydrogenation the relative proportions of the various components changed markedly: A increased, B and D decreased, and C vanished completely.

We interpret the g.p.c. findings as follows. Pyrolysis of I leads to five products: II, III, IV, and at least two isomers of V. G.p.c. (before hydrogenation) component A corresponds to amine IV, B partially to indoline II, C is one isomer of V, and D is III. If we assume that one of the isomers of V is eluted from the column together with II (component B), then we can account for the fact that the relative proportion of B decreased after hydrogenation. Furthermore, it seems reasonable to assume that V consisted merely of a mixture of side-chain unsaturated derivatives of IV. This assumption is consistent with the fact that the infrared spectrum of component C shows NH_2 absorption,⁷ and further, that on hydrogenation the relative proportion of component A, component IV, markedly increased while C vanished.

Scheme I shows the distribution of products from both the solution and vapor phase reactions. The total yield, and relative proportions of compound II and III are essentially the same from both reactions, however, large differences are found in the proportions of IV and V. It appears that the aryl nitrene is prone to abstract hydrogen atoms and form a primary amine. When the nitrene is generated in the vapor phase, practically all of the hydrogen abstraction occurs intramolecularly; when generated in solution, however, a large portion of hydrogen is abstracted intermolecularly. From a synthetic point of view, the vapor phase reaction is by far the more desirable procedure.

The identity of the g.p.c. components was established as follows. Component A was shown to be 2-butylaniline (IV) by a comparison of its infrared spectrum with that of an authentic sample. Component B was assumed to be 2-ethylindoline (II) because its infrared spectrum exhibited secondary amine⁷ absorption, its ultraviolet spectrum in ethanol had a maximum at 290 $m\mu$ (indoline absorbs at 290.5 $m\mu$ while tetrahydroquinoline absorbs at 300 $m\mu$), and its elemental analysis and n.m.r. spectrum were consistent with that expected for structure II. Component D was assigned the struc-

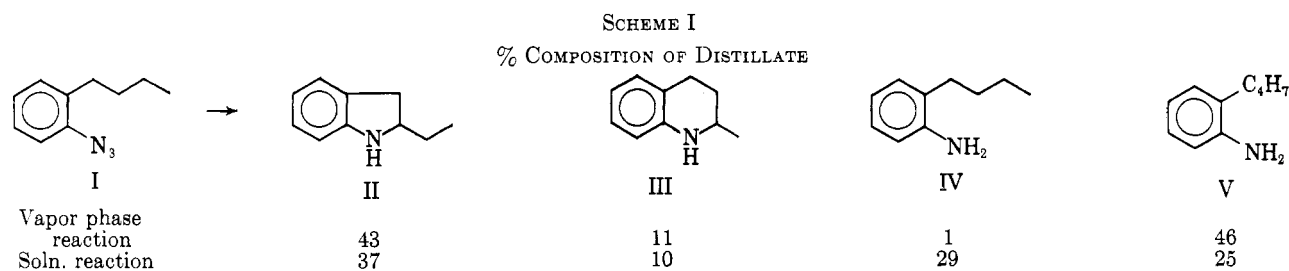
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(5) G. Smolinsky and B. I. Feuer, *J. Am. Chem. Soc.*, in press.

(6) G. Smolinsky, *ibid.*, **83**, 2489 (1961).

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 214.

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ture of 2-methyl-1,2,3,4-tetrahydroquinoline (III) on the basis of its infrared (NH absorption), ultraviolet (λ_{\max} 300 m μ), 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 previously¹ 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. }	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 (NH⁷) in the infrared region (determined neat) and a λ_{\max} 290 m μ in the ultraviolet region (ethanol solution⁸). 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 C₁₀H₁₃N: 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 (NH⁷) and λ_{\max} 300 m μ (ethanol solution⁸) 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 C₁₀H₁₃N: 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

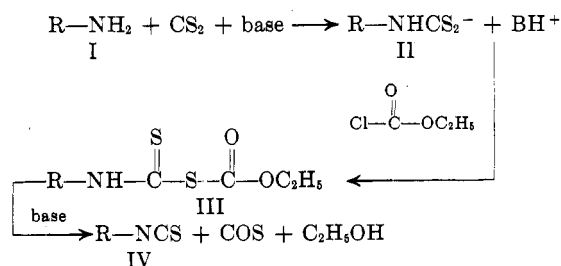
JOE E. HODGKINS AND W. PRESTON REEVES

The Departments of Chemistry of Texas Christian University, Fort Worth, Texas, and Arlington State College, Arlington, Texas

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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 chlorocarbamate; 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 aryl dithiocarbamates



(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 aryl dithiocarbamates 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 dithiocarbamate 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

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