TABLE I

THIOSEMICARBAZONES

Condensing aldehyde	Recrys. solvent	M.p.,[d] °C. (uncor.)	Yield, %	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfur, % Calcd.	Sulfur, % Found
Benzaldehyde	Aqueous ethanol	193–194.5	80	13.4	13.5	..	...
p-Nitrobenzaldehyde	Aqueous acetone[a]	203–204	85	15.6	15.6	..	...
Nicotinaldehyde	None[b]	237–238	86	17.7	17.9	10.1	9.9
Cinnamaldehyde	Aqueous acetone	194.5–195.3	88	12.3	12.4	9.4	9.3
5-Nitro-2-furaldehyde diacetate	Aqueous acetone[c]	205.5	55	16.0	15.7		

[a] After dissolving in base and reprecipitating with concd. hydrochloric acid. [b] Purified by continuous extraction with absolute ethanol. [c] First triturating with water at 65°. [d] All decomposed with gas evolution.

product filtered. Purification of these thiosemicarbazones proved very difficult. See Table I for complete details.

2-(4-Carboxy-3-hydroxyanilino)-1,3,4-thiadiazole.—A mixture of 4-(4-carboxy-3-hydroxyphenyl)-thiosemicarbazide (1.5 g.) and an excess of 85% formic acid was refluxed for 48 hours. The mixture was filtered while hot, the filtrate cooled and cold water added to aid in precipitating the crude product. The white solid produced weighed one gram (64%) and, after recrystallization (aqueous formic acid), melted from 241–242° (dec.).

Anal. Calcd. for $C_9H_7N_3O_3S$: N, 17.7; S, 13.5. Found: N, 17.7; S, 13.9.

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The Synthesis of Heterocyclic Compounds from Aryl Azides. III. Some Six-membered Rings and Some Azidobiaryls

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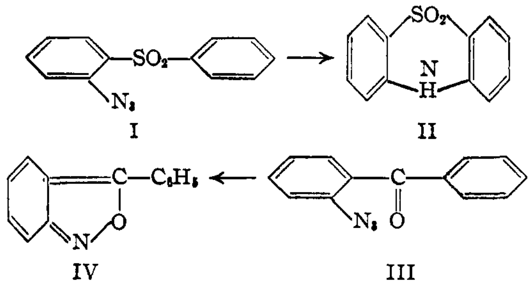
RECEIVED AUGUST 4, 1953

The formation of the pyrrole nucleus component of fused-ring systems has been reported by the pyrolysis and photolysis of aryl azides[1,2] of the *o*-azidobiaryl type. We now report the extension of this method to some compounds in which the two aryl groups are separated by one other atom. In addition, α-(*o*-azidophenyl)-furan and *o,o'*-diazidobiphenyl have been investigated.

o-Aminodiphenyl ether and *o*-aminodiphenyl sulfide both yielded azides by diazotization and treatment with sodium azide. *o*-Azidodiphenyl ether lost nitrogen when heated in inert solvents, but the product was largely an intractable tar, from which was obtained only a small amount of an impure picrate, resembling that reported from the expected phenoxazine. *o*-Azidodiphenyl sulfide, very sensitive to sunlight but otherwise stable, lost nitrogen between 140 and 180° to give 32% of phenothiazine. *o*-Azidodiphenylamine could not be prepared directly, because diazotized *o*-aminodiphenylamine cyclizes spontaneously to form 1-phenylbenzotriazole; however, *o*-amino-N-acetyldiphenylamine yielded an azide in the usual way. Although it lost nitrogen when heated, the product was intractable, and could not be made to yield any phenazine or its dihydro derivative.

o-Azidodiphenylsulfone (I) and *o*-azidobenzophenone (III) both lost nitrogen when heated in decalin solution. The sulfone gave a fair yield of phenothiazine dioxide (II) by cyclization to the adjacent benzene ring, accompanied by some *o*-aminodiphenyl sulfone arising from reduction by the solvent. The ketone underwent cyclization to the carbonyl oxygen atom instead, giving 3-phenylanthranil (IV). This is analogous to the cyclization of *o*-azido nitro compounds to the oxygen of the nitro group, giving furoxans, even when a benzene ring is also available.[1]



The behavior of *o*-azidobenzophenone conforms to that predicted for it by Meisenheimer, Senn and Zimmermann.[3] They postulated that the conversion of 4-phenyl-5,6-benzotriazine-3-oxide, formed by the diazotization of *anti*-*o*-aminobenzophenone oxime, to phenylanthranil (IV) proceeded by initial isomerization to the azide III, which at the temperatures used lost nitrogen and cyclized. Since at higher temperatures phenylanthranil isomerizes to acridone, the behavior of *o*-azidobenzophenone and *o*-azidodiphenylsulfone should not be considered fundamentally different; the different types of product obtained at moderate temperatures appear to be a reflection of what need only be a small difference in stability of the parallel oxacyclic intermediates.

A series of reactions intended to lead to a furanoindole was initiated by the coupling of *o*-nitrobenzenediazonium chloride to furan. The *o*-nitrophenylfuran so obtained is tentatively assumed to be the α-isomer by analogy with the corresponding reaction with thiophene.[2] Reduction produced an amine which appeared to be a single substance, but an attempt to deaminate it to the known α-phenylfuran gave only tar. No pure compound could be obtained when the azide was sought, and the attempted preparation of an azo dye with β-naphthol gave a dye of a different composition. Diazotization thus appeared to be accompanied by additional changes, perhaps involving nitrosation of the furan nucleus.

o,o'-Diazidobiphenyl was prepared from the dinitro compound by way of the unisolated diamine, in the hope of preparing 4,5-pyrrolocarbazole from it. The stable azide indeed lost gas near 180°, but

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[1] P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2435 (1951).

[2] P. A. S. Smith and J. H. Boyer, *ibid.*, **73**, 2626 (1951).

[3] J. Meisenheimer, O. Senn and P. Zimmermann, *Ber.*, **60**, 1736 (1927).

from the residue there could be obtained only an amorphous, insoluble, high melting, brown substance. Acid-catalyzed decomposition[4] of the azide was more successful, and gave the interesting result that only one of the azide groups was attacked at moderate temperatures.

Acknowledgment.—The assistance of the du Pont Grant-in-Aid for Fundamental Research in Chemistry in supporting part of this work is gratefully acknowledged.

Experimental

Melting points are corrected, and analyses are by Microtech Laboratories or by Mr. Goji Kodama of this Laboratory.

***o*-Azidodiphenyl Ether**.—*o*-Aminodiphenyl ether[5] (10 g.) was diazotized in an excess of cold, dilute sulfuric acid, to which was then added 4.5 g. of sodium azide. After 12 hours, precipitation of crude *o*-azidodiphenyl ether was complete; yield 10.5 g. (84%), m.p. 34–36°. Recrystallization from aqueous methanol or sublimation at 60° (0.5 mm.) gave a colorless product which turned pinkish on standing, m.p. 36–37°. *Anal.* Calcd. for $C_{12}H_9ON_3$: C, 68.25; H, 4.27. Found: C, 68.36; H, 4.39.

When the azide was heated at 180° in tetralin, kerosene, or 1,2,4-trichlorobenzene, gas was evolved, and evaporation of the solvent left a dark, gummy residue. This gave a red color with concd. sulfuric acid and a green color with ferric chloride, but the only solid material that could be isolated was a small amount of an olive-green picrate which had no characteristic melting point. These properties are described for phenoxazine,[6] which was probably present in small amount. Decomposition of the azide with radiation in the near ultraviolet gave similar results. Acid-catalyzed decomposition with hydrogen bromide in glacial acetic acid[4] at 60° gave 2-amino-5-bromodiphenyl ether, m.p. 186°,[7] in 60% yield, further identified by conversion to the acetyl derivative, m.p. 140–142°, undepressed when mixed with an authentic sample.[7]

***o*-Azido-N-acetyldiphenylamine**.—*o*-Nitro-N-acetyldiphenylamine[8] (3 g.) was dissolved in the minimum volume of warm, 50% aqueous ethanol and hydrogenated at 40 lb. pressure in the presence of 0.1 g. of platinum oxide catalyst in a Parr apparatus. The crude material weighed 2.33 g. (88%), m.p. 111–112°; recrystallization from petroleum ether (b.p. 60–75°) gave 2.0 g. (76%), m.p. 115–116°. When the hydrogenation was attempted in 95% ethanol, only 2-methyl-1-phenylbenzimidazole, m.p. 70–72°,[9] was formed.

Two grams of the amine was diazotized in 10 ml. of concd. hydrochloric acid and 25 ml. of water, and treated with sodium azide as before. The crude azide, wt. 1.61 g. (72%), had m.p. 95–97°; recrystallization from ethanol gave 1.4 g. (63%) of pale yellow crystals, m.p. 98–99°, raised to 99–99.5° by one more crystallization. *Anal.* Calcd. for $C_{14}H_{12}ON_4$: C, 66.66; H, 4.76. Found: C, 66.52; H, 4.81.

Photochemical or thermal decomposition in kerosene, tetralin or 1,2,4-trichlorobenzene gave dark red-brown gums from which nothing identifiable could be isolated. Acid-catalyzed decomposition with hydrogen bromide in glacial acetic acid was slow. From several experiments at different temperatures only an amorphous, brown solid was obtained, which possessed no definite melting point and could not be purified.

***o*-Azidodiphenyl Sulfide**.—Treatment of *o*-aminodiphenyl sulfide[10] in the manner described for *o*-azidodiphenyl ether gave the azide as pale yellow crystals, m.p. 30–31°, in 64% yield. Recrystallization from aqueous methanol gave nearly colorless blades, m.p. 30.5°.

Anal. Calcd. for $C_{12}H_9N_3S$: C, 63.41; H, 3.99. Found: C, 63.60; H, 4.20.

These turned deep yellow and then red in glass-filtered sunlight, and decomposed rapidly in direct sunlight to give an amorphous, dark brown material; in diffuse light, they were stable for more than a week.

Decomposition of 0.37 g. of azide in 25 ml. of resorcinol dimethyl ether began at 140°, and was completed at 190°, by which time the solution had turned black. After evaporation of the solvent in an air-stream and extraction with cold petroleum ether, the residue was treated with charcoal in hot ethanol and crystallized by the addition of water, to yield 0.105 g. (32%) of phenothiazine, shining leaflets, m.p. 182–185° (reported 180°,[11] uncor.), which gave the characteristic green color[11] with alcoholic ferric chloride.

***o*-Azidodiphenyl Sulfone**.—*o*-Aminodiphenyl sulfone[12] (3.15 g.) was diazotized in 15 ml. of 20% hydrochloric acid with a solution of 1.05 g. of sodium nitrite. After 1 hour, 1.0 g. of sodium azide was added, and the precipitate which formed during the next 12 hours was collected and washed with water; wt. 3.22 g. (92%), m.p. 130–163° dec. Recrystallization from 150 ml. of alcohol gave 2.79 g. (80%) of colorless needles, m.p. 161.5–163.5° dec., which turned pink on exposure to light.

Anal. Calcd. for $C_{12}H_9O_2N_3S$: C, 55.58; H, 3.50. Found: C, 55.53; H, 3.49.

Phenothiazine Dioxide.—To 100 ml. of nearly boiling decalin was added 1.00 g. of the foregoing azide in small portions. The initially yellow solution soon turned black, and gas evolution appeared to have ceased after 3 hours of boiling. The black residue obtained by filtration of the hot mixture was extracted with three 20-ml. portions of boiling ethanol, and the combined extracts were diluted with water until two layers appeared. The upper (decalin) layer was removed after cooling to −10°, and the remaining suspension was concentrated and the solid filtered off; wt. 0.39 g. (42%) of tan powder, m.p. 245–255°. Recrystallization from 15 ml. of ethanol gave 0.15 g. (16%) of colorless prisms, m.p. 254–255.5° (reported 257–259°[13]).

Anal. Calcd. for $C_{12}H_9O_2NS$: C, 62.32; H, 3.92. Found: C, 62.60; H, 4.08.

The hot, red decalin filtrate was evaporated to a tarry residue, which was treated with charcoal in hot ethanol and then diluted with water until cloudy and chilled to −10°. The supernatant liquid was decanted from the tar which separated, and then diluted further with water and chilled. Filtration gave 0.10 g. of yellow solid, m.p. 95–105°, which by extraction with concd. hydrochloric acid and reprecipitation by dilution gave 0.03 g. of crude *o*-aminodiphenyl sulfone, m.p. 111–117°. Reworking the tarry residues gave a further 0.01 g., m.p. 107–112°, undepressed when mixed with pure authentic material.

***o*-Azidobenzophenone**.—*o*-Aminobenzophenone[14] (2.66 g.) was diazotized in the manner described for *o*-aminodiphenyl sulfone, and the cold, filtered diazonium solution was treated with sodium azide; a yellow oil separated overnight. The aqueous layer was extracted with five 5-ml. portions of ether, and the combined oil and extracts were neutralized with sodium bicarbonate and dried over magnesium sulfate. Evaporation of the ether left a gum, which crystallized when chilled with Dry Ice in methanol; wt. 2.24 g. (74%), m.p. 33–36°. The first crop from two crystallizations from absolute ethanol was 0.37 g. of pale yellow needles, m.p. 36–38°, unchanged on further recrystallizations (the isomeric phenylbenzotriazine oxide obtained by Meisenheimer, Senn and Zimmermann[3] melts at 154° dec.).

Anal. Calcd. for $C_{13}H_9ON_3$: C, 69.93; H, 4.07. Found: C, 70.25; H, 4.29.

o-Azidobenzophenone decomposes with a puff when added to concd. sulfuric acid at room temperature. An attempt to prepare an oxime gave a yellow solid, m.p. 116–140°, which decomposed more readily than the ketone, turned pink on exposure to light, and could not be purified readily to a melting point better than 131–140°.

3-Phenylanthranil.—Gas evolution from 0.48 g. of *o*-azidobenzophenone in 50 ml. of decalin appeared to be com-

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(4) P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2438 (1951).

(5) F. Ullmann, *Ber.*, **14**, 29 (1881).

(6) F. Kehrmann, *Ann.*, **322**, 9 (1902).

(7) H. McCombie, W. G. McMillan and H. A. Scarborough, *J. Chem. Soc.*, **133**, 1202 (1930).

(8) F. Kehrmann and E. Baumgartner, *Helv. Chim. Acta*, **9**, 673 (1926).

(9) M. A. Phillips, *J. Chem. Soc.*, 2820 (1929).

(10) E. Bourgeois and P. Huber, *Rec. trav. chim.*, **31**, 30 (1912).

(11) A. Bernthsen, *Ber.*, **16**, 2896 (1883).

(12) F. Ullmann and G. Pasdermadjian, *ibid.*, **34**, 1150 (1901).

(13) A. Bernthsen, *ibid.*, **39**, 1807 (1906).

(14) C. Graebe and F. Ullmann, *Ann.*, **291**, 8 (1896).

plete in 30 minutes at 140°; in a preliminary run, the mixture turned deep red if heated longer. Evaporation of the solvent left a yellow gum, which was repeatedly triturated with petroleum ether and further evaporated to remove the last traces of decalin. Crystallization from 2 ml. of absolute ethanol in a Dry Ice–methanol-bath gave 0.12 g. of yellow solid, m.p. 43–50°; two more crystallizations gave colorless crystals of pure phenylanthranil, m.p. 53–53.5° (reported[3] 53°). The filtrates and residues gave 0.54 g. (53%) of the colorless mercuric chloride addition product from alcoholic mercuric chloride; m.p. 170–194° dec. Two crystallizations from acetone and one from ethanol raised the m.p. to 195–198° (reported[3] 200°).

α(?)-*o*-Nitrophenylfuran.—A suspension of 28 g. of *o*-nitroaniline in 125 ml. of 10% hydrochloric acid was diazotized slowly at 0–5° with a solution of 14.5 g. of sodium nitrite. Furan (400 g.) was then added, followed by the dropwise addition of 80 g. of sodium acetate in 200 ml. of water. After stirring for 3 hours at 0–5° and 72 hours at room temperature, the furan layer was separated, and the alkalized aqueous layer was extracted with ether. After distillation of the furan and ether from the combined extracts, steam was used to remove the slightly volatile reaction product, which was taken up with ether from the large volume of distillate. Evaporation of the dried ether solution left a yellow oil, wt. 5.9 g. (15.5%). Part of this was distilled for analysis at 108–110° (0.8 mm.); it partially crystallized on cooling below room temperature.

Anal. Calcd. for $C_{10}H_7O_3N$: C, 63.49; H, 3.73. Found: C, 63.61; H, 3.83.

α(?)-*o*-Aminophenylfuran.—α(?)-*o*-Nitrophenylfuran (*ca.* 2 g.) in 100 ml. of boiling methanol was reduced by the dropwise addition of 40 g. of sodium sulfide nonahydrate and 5 g. of sodium bicarbonate in 50 ml. of water dropwise. The filtered solution was concentrated to remove methanol, and then extracted repeatedly with ether. The addition of concd. hydrochloric acid to the combined extracts precipitated 1.10 g. of colorless needles, m.p. 195–210° with sublimation. This substance gave no color with ferric chloride, but could be diazotized to give an orange solution which coupled with β-naphthol to give a scarlet azo dye, m.p. 132–134°.

Anal. Calcd. for $C_{10}H_{10}ONCl$: C, 61.37; H, 5.14. Found: C, 61.56; H, 5.16.

The **benzenesulfonyl derivative** formed colorless crystals from aqueous alcohol, m.p. 95–96°.

Anal. Calcd. for $C_{16}H_{13}O_3NS$: C, 64.20; H, 4.38. Found: C, 63.98; H, 4.47.

The diazotized amine hydrochloride (0.56 g.) reacted with sodium azide to evolve gas and form a red-brown oil which may have been *o*-azidophenylfuran. Thermal decomposition in decalin at 180° gave a deep red solution, from which by evaporation, treatment with charcoal in methanol, and precipitation with water there was obtained 0.8 g. of a dull red powder, m.p. 105° dec. Recrystallization from hot methanol with the aid of charcoal gave 0.08 g. of pale red powder, m.p. 218–220° dec., which did not appear to be the expected furanoindole.

Anal. Found: C, 72.89; H, 4.71.

An attempt to deaminate the aminophenylfuran by the procedure of Kornblum and Iffland[15] gave at first an orange solution, from which only black tar could subsequently be isolated.

***o*,*o*′-Diazidobiphenyl.**—*o*,*o*′-Dinitrobiphenyl[16] (10 g.) in 50 ml. of 95% ethanol was hydrogenated on a Parr shaker at 35 lb. pressure in the presence of 0.2 g. of platinum oxide catalyst. The solution was then filtered, acidified with hydrochloric acid, evaporated *in vacuo* to a turbid, orange residue, and treated with charcoal in water solution. The resulting yellow solution was tetrazotized and treated with sodium azide much as described for *o*-azidodiphenyl ether, giving 8.63 g. (89.5%) of tan crystals, m.p. 70–72°. Recrystallization from alcohol gave 7.94 g. (82.5%) of tan needles, m.p. 72–73°, and 72.5–73.5° after a second crystallization.

Anal. Calcd. for $C_{12}H_8N_6$: C, 61.02; H, 3.41. Found: C, 60.67; H, 3.51.

Heating small portions of the azide in 1,2,4-trichlorobenzene, kerosene or tetralin resulted in copious gas evolution, but from the residue after evaporation there was obtained only a dark solid, m.p. indefinite above 200°, which could neither be crystallized nor sublimed. Decomposition of the azide with near ultraviolet radiation gave similar results.

Decomposition of 2.0 g. of the azide in 20 ml. of warm 15% hydrogen bromide in glacial acetic acid[4] proceeded readily. Evaporation left an oily, brown residue which crystallized in part when triturated with ether. Treatment with charcoal in methanol and two crystallizations from methanol gave 0.5 g. of colorless, matted needles, m.p. 113–115°.

Anal. Calcd. for $C_{12}H_8Br_2N_4$: C, 39.13; H, 2.16. Found: C, 38.94; H, 2.24.

A primary aromatic amino group was indicated by diazotization and coupling to β-naphthol. When heated above its melting point, the material gave the deflagration characteristic of azides, and with cold, concentrated sulfuric acid it gave a gas and a purple solution. Halogen could be detected by the copper wire flame test, but not by silver nitrate. These results are consistent with the structure **2-amino-3,5-dibromo-2′-azidobiphenyl.**

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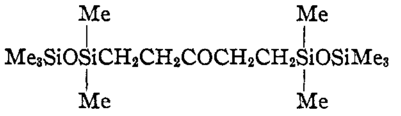
Aliphatic Organo-functional Siloxanes. II. Diesters with Dimethyl-(β-carboethoxyethyl)-siloxy End Groups[1]

BY LEO H. SOMMER AND RICHARD P. PIOCH

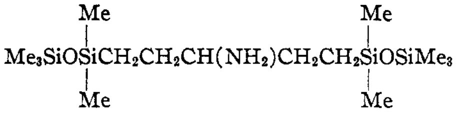
RECEIVED JULY 29, 1953

In the first paper of a series dealing with aliphatic organo-functional siloxanes (organo-siloxanes having functional groups linked to carbon)[2] we reported the synthesis of compounds I and II.



$$\mathrm{Me_3SiO}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{CH_2CH_2COCH_2CH_2}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{OSiMe_3}$$

(I)



$$\mathrm{Me_3SiO}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{CH_2CH_2CH(NH_2)CH_2CH_2}\underset{\mathrm{Me}}{\overset{\mathrm{Me}}{\mathrm{Si}}}\mathrm{OSiMe_3}$$

(II)

Compound I was prepared by equilibration of the appropriate polysiloxane–polyketone with hexamethyldisiloxane using concd. sulfuric acid as the reagent and following a procedure previously used for the preparation of trimethylsiloxy end-blocked dimethylpolysiloxanes.[3] Compound II resulted from equilibration of the appropriate polysiloxane–polyamine with hexamethyldisiloxane using potassium hydroxide in an isopropyl alcohol–water solvent.[4]

In both of the above compounds, the organo-functional polymer unit is difunctional and the monofunctional end-groups are the now conventional trimethylsiloxy units.

We now report the synthesis of *a series of new-type organosiloxanes having ester end-groups and dimethylsiloxy units as the difunctional portion of the*

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[15] N. Kornblum and D. Iffland, THIS JOURNAL, **71**, 2137 (1949).

[16] R. C. Fuson and E. A. Cleveland, *Org. Syntheses*, **20**, 45 (1940).

(1) Paper 35 in a series on organosilicon chemistry. For Paper 34, see THIS JOURNAL, **75**, 3765 (1953).

(2) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, **75**, 2932 (1953).

(3) W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 361 (1946).

(4) For the use of this reagent in the preparation of trimethysiloxy end-blocked dimethylpolysiloxanes see M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *ibid.*, **68**, 2284 (1946).