Table I

Yields of Cystine and Hydrogen Peroxide upon X-Irradiation of Aqueous Cysteine Solutions[a]

[Cysteine], mM	[H_2SO_4], mM	pH	G_0 (cystine)	G_0 (H_2O_2)
30		~2.5	8.0	6.7
30		2.2	9.9	7.6
10		~2.5	6.6	5.6
10		2.4	8.4	5.6
3		~3	4.9	3.9
3	1.5	~3	4.8	3.7
3		2.8	5.3	3.5
3	3.0	2.5	4.6	3.4
1		3	3.1	2.9
1		3.25	3.0	2.3
1	1.0	3.0	2.7	2.6
1	0.5	3.2	2.4	2.7

[a] See Experimental Section for conditions.

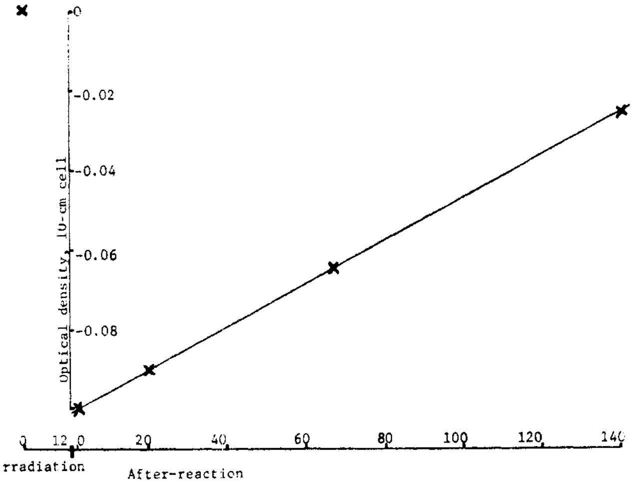

Figure 1.

results are not unequivocal; thiols are susceptible to oxidation by hydrogen peroxide and even by dissolved oxygen at pH 7 or above. In attempts to clarify the situation, we have examined solutions irradiated at intermediate pH (4–5). Moderately concentrated cysteine solutions (30 mM, pH 4) gave disulfide and peroxide yields little, if at all, greater than those obtained at pH 3. More dilute solutions, however, showed quite anomalous behavior. Thus, the optical densities at 255 mμ of 1 mM solutions (pH 4.5) *decreased* markedly during irradiation and then increased steadily, albeit slowly, when the solutions were allowed to stand after irradiation (Figure 1). However, when such irradiated solutions were acidified to pH 3 or below, the optical densities rose immediately to values which would have been observed had the irradiations been effected at pH 3. Yields of hydrogen peroxide were similar to those obtained at pH 3. The values may not represent the quantities actually present at pH 4.5, however, since the determination of peroxide involves acidification of the solution.

Clearly, little cystine is produced during irradiation in 1 mM solution at pH 4.5. Tentatively, we suggest that consumption of thiol (reactions, 3, 4, and 5a) proceeds readily, but that production of disulfide and peroxide (reactions 5b and 6a) is suppressed, plausibly because protonation of an oxygen atom of the sulfenyl peroxide must occur concomitantly with nucleophilic attack by the undissociated thiol (rate α[RSH][H^+]). The product under these conditions, then, would be the sulfenyl hydroperoxide. It is reasonable to suppose that this, like cysteic acid and cysteinesulfinic acid, might be even more transparent than the thiol at 255 mμ. First-order dependence of reaction 5b on hydrogen ion and thiol would then account for the nonproduction of disulfide, the slow after-reaction, and the disappearance of the anomaly at pH 3 and 1 mM, at pH 4 and 30 mM, and upon acidification. In more basic solution, the slow acid-dependent process would be superseded by rapid acid-independent reaction of the sulfenyl peroxide with the powerful nucleophile, thiolate ion (rate α[RS^-]). The termination reaction (7) should be essentially pH independent, and the nucleophilic substitution step is probably rate determining in the propagating sequence. Thus, the chain length and the yield of disulfide should increase with increasing alkalinity, as they are reported to do.

Experimental Section

A General Electric Co. Maximar II X-ray apparatus operated at 125 kV and 15 mA, unfiltered, was used for irradiations. Dose rates, determined by ferrous dosimetry and corrected for sulfuric acid concentration effects, were 1300–1400 rads min^{-1}. Typical times of irradiation were 4, 8, 12 and 20 min. All initial rates (G_0) were derived from three- or four-point yield *vs.* dose curves, all of which were linear from the origin. Optical densities of solutions were determined using a Bausch and Lomb "Precision" spectrophotometer.

Water for solutions to be irradiated was distilled successively from alkaline permanganate and a sodium dichromate–phosphoric acid mixture through 30-in. Vigreux columns. Vessels were preirradiated until brown while filled with such water. Cysteine solutions (chloride free) were prepared afresh for each experiment and were adjusted to about the desired pH with 50 mM sulfuric acid. The final acid concentrations in some of the solutions are recorded in Table I.

Eisenberg's[5] titanium sulfate procedure was used to determine hydrogen peroxide. Control experiments demonstrated fair reliability and no significant reaction of hydrogen peroxide (10 mM) with cysteine (50 mM) at pH 5 or below. Determinations of cysteine by the phosphotungstate color reaction were unreliable at thiol concentrations above 5 mM, presumably because of reaction with peroxide in the acetate buffer. However, the ultraviolet spectrum of cystine (like most simple disulfides) shows a strong shoulder at 255 mμ (ϵ 290) in the rising end absorbance, and so cystine production was measured directly. The extinction of cysteine, although variable owing to small amounts of cystine, is less than one-tenth of that of cystine at 255 mμ. Plausible minor radiolysis products (cysteic acid, cysteinesulfinic acid, and hydrogen sulfide) are essentially transparent.

Registry No.—Cysteine, 52-90-4.

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[5] G. E. Eisenberg, *Ind. Eng. Chem. Anal. Ed.*, **15**, 327 (1943).

Aromatic o-Diisocyanates. A New Class of Compounds

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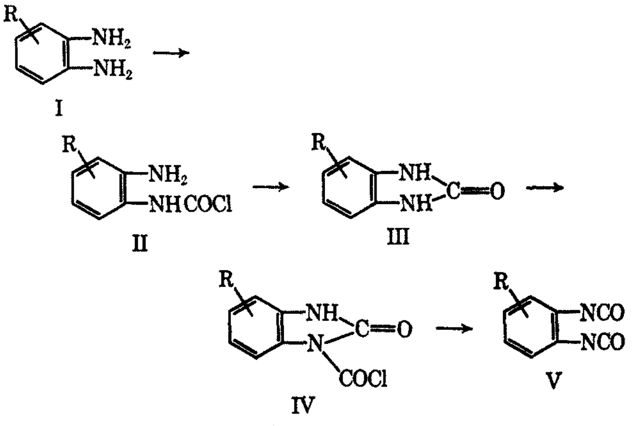
All recorded attempts to prepare representatives of the yet unknown class of aromatic o-diisocyanates by phosgenation of aromatic *o*-diamines have met with failure;[1] benzimidazolones have been reported as the principal reaction products. We have now found that prolonged phosgenation of *o*-tolylenediamines I at elevated temperature affords the corresponding *o*-tolylene diisocyanates V in moderate yields and believe that this method can also be utilized for the preparation of other aromatic *o*-diisocyanates.

As far as one can conclude from experimental data and reported analogies, the reaction proceeds *via* the tolyleneaminocarbamoyl chlorides (II), the methylbenzimidazolones (III), and the tolyleneallophanoyl chlorides (IV) (Scheme I).

SCHEME I



a, R = *o*-CH_3
b, R = *m*-CH_3

This reaction sequence is supported by (1) formation of carbamoyl chlorides II upon phosgenation of I at temperatures below 100° for short periods of time; (2) cleavage of hydrogen chloride from II upon purging with nitrogen at 150° to give III; (3) predominant formation of III upon phosgenation of I at 150° for short periods of time; (4) formation of V from either I or III upon prolonged phosgenation at 150°; (5) formation of IV upon prolonged phosgenation of III at 80° as indicated by cleavage of the isolated product to V and hydrogen chloride upon heating in *o*-dichlorobenzene at 175–180°.[2]

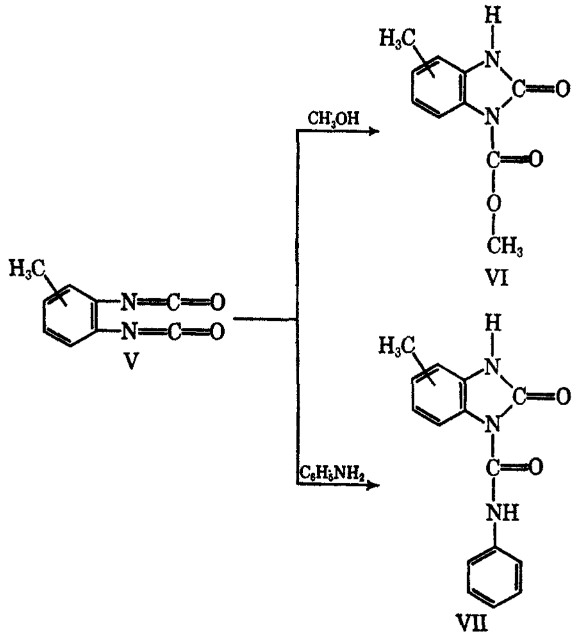
o-Tolylene diisocyanates V are very unstable, a fact which impedes their preparation in high yields and makes their isolation and precise characterization difficult; they polymerize readily to form solids, but can be depolymerized and isolated by heating and distillation. Repeated polymerization–distillation cycles tend to increase the stability of V slightly, indicating that trace amounts of impurities, contained in the original samples, may act as polymerization catalysts.

A sample of V, subjected to mass spectroscopy, showed a strong molecular ion at *m/e* 174 and a fragmentation pattern which is in general agreement with that found for 2,4- and 2,6-tolylene diisocyanate. Refractive indices were close to values reported in the literature[3] for *m*-tolylene diisocyanates. Vapor phase chromatography showed the same elution for the 2,3- and 3,4-tolylene diisocyanates as for the 2,4 and 2,6 isomers, yet boiling points of the *ortho* isomers are slightly lower as shown by their enrichment in the forecuts upon fractionation of a mixture of the various tolylene diisocyanate isomers. The infrared spectra of both *o*-tolylene diisocyanates V are characterized by strong NCO absorption at 4.45 μ. Absorption in the 6.0–9.0-μ region is identical with that of the 2,4 and 2,6 isomers. *o*-Methyl isomer Va shows also absorption at 12.9 and 13.9 μ, which is typical for 1,2,3-substituted benzene derivatives, whereas absorption at 11.4 and 12.3 μ, characteristic for 1,2,4-substituted benzenes, is displayed by *m*-methyl isomer Vb. The spectrum of the 2,3 isomer Va did not show any carbonyl or NH absorption, thus providing another proof for the existence of monomeric *o*-tolylene diisocyanate.

The *o*-tolylene diisocyanates react readily with water at room temperature to give the corresponding methylbenzimidazolones (III); linear ureas are not formed.

Reactions with methanol or aniline proceed under ring formation to give allophanoyl derivatives VI and VII (Scheme II).

SCHEME II



Polymers derived from *o*-tolylene diisocyanates are rapidly and completely soluble in concentrated sulfuric acid without degradation, thus indicating a linear structure. The intrinsic viscosity (0.12–0.18), measured in 100% sulfuric acid at 30°, is of the same magnitude as observed for polymers obtained from aliphatic α,ω-diisocyanates.[4] It is proposed that polymerization of the *o*-tolylene diisocyanates V proceeds *via* an alternating intraintermolecular chain growth mechanism, analogous to that postulated for aliphatic 1,2-diisocyanates,[5] to give a polymer of structure VIII. Assignment of this structure is also favored by the infrared spectrum of the polymer which shows split carbonyl absorption of equal intensity at 5.65 and

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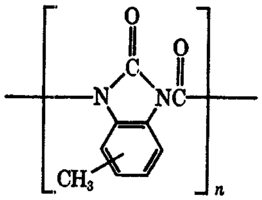
[1] W. Siefken, *Ann.*, **562**, 75 (1949), see p 92.

[2] An analogous reaction, *i.e.*, the thermal decomposition of ethyleneallophanoyl chloride to ethylene diisocyanate and hydrogen chloride, has been reported by A. A. R. Sayigh, J. N. Tilley, and H. Ulrich, *J. Org. Chem.*, **29**, 3344 (1964).

[3] J. H. Saunders and K. C. Frisch, "Polyurethanes, Chemistry and Technology," Part I, Interscience Publishers, New York, N. Y., 1962, p 348.

[4] Y. Iwakura, K. Uno, and K. Ichikawa, *J. Polm. Sci., Part A*, **2**, 3387 (1964).

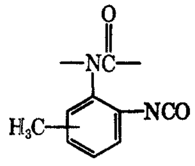
[5] C. King, *J. Amer. Chem. Soc.*, **86**, 437 (1964).



VIII

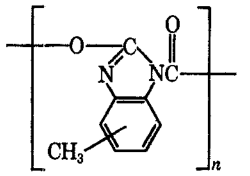
5.75 μ; this doublet appears to be characteristic for 1,2-diisocyanate-derived polymers.[4] The predominant occurrence of unit VIII in the polymer is also indicated by hydrolysis in aqueous hydrogen chloride which gave methylbenzimidazolones III in high yield.

The presence of some free isocyanate groups is indicated by absorption at 4.45 μ; this could either be due to physical occlusion of a small amount of unpolymerized diisocyanate or may be indicative of partial 1-nylon-type polymerization[6] to give units of structure IX. The infrared spectrum, however, did not display absorption at 5.58 μ, reported for such polymers.



IX

The infrared spectra of the polymers did not indicate the presence of units of structure X,[4] since the stretching absorption band of the C=N group, expected to appear at about 6.0 μ, is not present. The absence of any absorption at 7.05 μ excludes also the presence of isocyanurate moieties in the polymer, although depolymerization by heating the polymers resulted—besides in an 80% yield of the distillable monomers V—in about 20% of undistillable isocyanurates, as indicated by strong infrared absorption at 5.9 and 7.05 μ found for the residue. Obviously, partial trimerization (isocyanurate formation) occurs upon depolymerization of the polymer chain by heating.



X

The polymers formed from o-tolylene diisocyanates, especially that formed from the o-methyl isomer, are nearly identical with a material which, at times, causes turbidity in commercial tolylene diisocyante. The latter differs from the former merely by the presence of some 2,4 isomer, very likely as part of the polymer chain although physical encapsulation cannot be excluded.

Experimental Section[7]

2,3-Tolylenediamine (I).—A methanolic solution of 2-amino-3-nitrotoluene was hydrogenated, in the presence of Raney nickel, in a stirred autoclave at 200 psig and 100°. The diamine was isolated by fractional distillation: mp 60–61.5° (lit.[8] mp 61–62°); purity by vpc >99%.

3,4-Tolylenediamine (I).—Commercial material was distilled prior to use: mp 87–89° (lit.[9] mp 88.5°); purity by vpc >99%.

Preparation of 2,3-Tolylenecarbamoyl Chloride (II) and Cleavage to 4-Methylbenzimidazolone (III).—Dry o-dichlorobenzene (500 ml) was charged in a round-bottomed flask and saturated with phosgene at 100°. Introduction of phosgene was continued, while 2,3-tolylenediamine (10 g), dissolved in 100 ml of dry o-dichlorobenzene at 60–70°, was added dropwise over a period of 1.5 hr. The reaction mixture was then cooled to room temperature. The formed solids were filtered, washed with petroleum ether, and dried *in vacuo* at room temperature to give 14.8 g of product which melted under decomposition between 190 and 210°. The infrared spectrum of this product showed strong carbonyl absorption at 5.75 μ. Recrystallization attempts with various solvents failed and resulted in partial cleavage of hydrogen chloride.

A sample of the product was stirred in o-dichlorobenzene at 150°, while nitrogen was passed through the slurry. The off-gases were passed through water; titration of the water indicated an hydrogen chloride content corresponding to the amount calculated for the cleavage of 2,3-tolylenecarbamoyl chloride (II) into hydrogen chloride and 4-methylbenzimidazolone (III). The solids, obtained after purging and cooling, were filtered and identified by melting point and infrared spectrum as 4-methylbenzimidazolone (III).

4- and 5-Methylbenzimidazolone (III). Procedure 1.—Phosgene was passed through an agitated slurry of the respective o-diamine I in o-dichlorobenzene at 100° for 3 hr. The filtered product was dissolved in 10% aqueous NaOH and insolubles were removed by filtration. Precipitation with HCl, followed by a recrystallization from ethanol-water, gave pure 4- and 5-methylbenzimidazolone, respectively: 5-methylbenzimidazolone, mp 299–300° (lit.[10] mp 299–301°) and λ(infrared) 3.1–3.2, 5.7, 6.0, 9.7, 11.7, 12.7, 13.5, 14.0 μ; 4-methylbenzimidazolone, mp 297–300° and λ(infrared) 3.1–3.2, 5.7, 6.0, 9.3, 9.9, 11.3, 12.4, 13.1, 13.7 μ.

Anal. Calcd for $C_8H_8N_2O$: C, 64.85; H, 5.44; N, 18.91. Found: C, 64.83; H, 5.66; N, 19.45.

Procedure 2.—Dry o-dichlorobenzene (200 ml) was saturated with phosgene at 150°. 3,4-Toylenediamine (10 g), dissolved in 200 ml of dry o-dichlorobenzene, was added at 140–150° over a period of 2 hr, while simultaneously passing phosgene into the reaction mixture. The reaction mixture was then purged with nitrogen at 150° for 2 hr and subsequently allowed to cool to room temperature. After standing overnight, the formed solids were filtered and washed with petroleum ether (bp 30–60°). Recrystallization from ethanol gave white crystals (6.1 g) which were identified by melting point and infrared spectrography as 5-methylbenzimidazolone.

2,3-Tolyleneallophanoyl Chloride (IV).—A moderate stream of phosgene was passed through a slurry of 6.0 g of 4-methylbenzimidazolone (III) in 500 ml of o-dichlorobenzene at 80° for 8 hr. The reaction mixture was cooled to 10° and filtered. The filter cake was washed with petroleum ether and dried *in vacuo* at room temperature to give 6.2 g (72.4% of theory) of IV, mp 214–218°. The infrared spectrum of this compound was characterized by a broad carbonyl band at 5.6–5.9 μ; absorption at 6.0 μ, characteristic for the starting material III, had disappeared. Hydrolysis of the product, followed by titration, indicated 16.00% of hydrolyzable chloride (calcd 16.84%). Attempts to purify the product by recrystallization from hot o-dichlorobenzene resulted in cleavage of hydrogen chloride.

o-Tolylene Diisocyanates V.—Phosgenation of o-tolylenediamines I and the methylbenzimidazolones III was conducted in a round-bottomed flask equipped with paddle stirrer, reflux condenser, subsurface gas inlet, dropping funnel and thermometer.

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[6] V. E. Shashoua, *J. Amer. Chem. Soc.*, **81**, 3156 (1959); V. E. Shashoua, W. Sweeny, and R. F. Tietz, *ibid.*, **82**, 866 (1960).

[7] Infrared spectra were determined with a Perkin-Elmer 137 spectrophotometer as smears (liquids) or KBr pellets (solids) from 4000–1300 cm^{-1}. Mass spectra were obtained with a Consolidated Electrodynamics Corp. mass spectrometer, Model 21-103C equipped with an all-glass heated inlet system, scanning from *m/e* 13 to 400. Vapor phase chromatography was conducted with a F & M Scientific Division gas chromatograph, Model 700, equipped with hot filament detector, 1 m × 6.4 mm o.d., column packed with 15% SE-30 on Chromosorb W 80/100 (column temperature 175°, detector 210°, injection part 220°, helium flow 55 cc/min).

[8] E. Lellmann, Ann., **228**, 243 (1885).

[9] F. Beilstein and A. Kahlberg, *Ann.*, **158**, 351 (1871).

[10] E. Lellmann and O. Bonhoeffer, *Ber.*, **20**, 2124 (1887).

A. 2,3-Tolylene Diisocyanate (Va) from 2,3-Tolylenediamine (Ia).—Dry *o*-dichlorobenzene (150 ml) was heated at 150° in a round-bottomed flask under a blanket of nitrogen and saturated with phosgene, while agitating. 2,3-Tolylenediamine (20 g) was dissolved in 200 ml of dry *o*-dichlorobenzene at 90–100° and added slowly at this temperature through a dropping funnel over a period of 4 hr, while simultaneously passing phosgene into the flask. The molar ratio of phosgene to *o*-TDA was approximately 20:1. Feeding of phosgene and rapid stirring of the reaction mixture at 150° was continued for 14 hr after addition of the diamine had been completed. Hydrogen chloride, formed during the reaction, and excess phosgene were withdrawn through a water-cooled reflux condenser.

The reaction mixture was then purged with nitrogen at 150° for 2 hr, insolubles were removed by filtration, and the filtrate worked up by distillation. After removal of the solvent, a liquid distilled slowly into the receiver, where it polymerized rapidly to a solid material, 8.19 g or 28.6% of theory calculated for Va. Heating of the polymer between 250 and 300° under 15 mm pressure resulted in gradual depolymerization and distillation of 6.5 g of 2,3-tolylene diisocyanate (Va), $n^{25}\text{D}$ 1.5650 (2,4-tolylene diisocyanate, lit. $n^{25}\text{D}$ 1.5654). When subjected to vapor phase chromatography, this product eluted at the same retention time as standard solutions of the 2,4- and 2,6-tolylene diisocyanates in *o*-dichlorobenzene under identical conditions. The infrared spectrum of compound Va displayed absorption at 4.45 μ, indicative for isocyanato groups and had peaks at 12.9 and 13.9 μ, characteristic for 1,2,3-substituted benzene derivatives: mass spectrum (70 eV) *m/e* (relative intensity of 2,3 isomer, relative intensity of 2,4/2,6 isomer mixture) 174 (100, 100), 146 (26.5, 25.0), 132 (18, 17.5), 118 (33, 17), 91 (40, 16), 39 (15.5, 12.5). The observed differences at 118 and 91 are believed to be due to the different isomer configuration. A molecular ion observed at *m/e* 148 and fragment ions associated with this molecular ion must be due to small amounts of a protonated entity in the product, very likely 4-methylbenzimidazolone, which could have been formed by traces of moisture. The residue (about 1.6 g) obtained by thermal cleavage of the polymer showed strong infrared absorption at 5.85 and 7.05 μ, indicating that partial, irreversible trimerization to isocyanurates had occurred.

Polymerization of the freshly distilled sample of Va proceeded relatively slowly and could be followed by the increase in the infrared absorption at 5.65 and 5.75 μ. The sample had completely polymerized after 2 hr.

Reaction of Va with water at room temperature resulted in the formation of 4-methylbenzimidazolone (IIIa), identified by melting point and infrared spectrum.

B. 3,4-Tolylene Diisocyanate (Vb) from 3,4-Diaminotolylene (Ib).—The procedure described for the preparation and isolation of Va was repeated, except that 300 ml of *o*-dichlorobenzene were saturated with phosgene and 20 g of 3,4-diaminotolylene was dissolved in 500 ml of *o*-dichlorobenzene. The yield of distilled diisocyanate Vb was 1.6 g or 5.5% of theory, $n^{25}\text{D}$ 1.5615. When subjected to vapor phase chromatography, Vb displayed the same retention time as Va. The infrared spectrum of this product displayed strong absorption at 4.45 μ, indicative for isocyanato groups, and had peaks at 11.4 and 12.3 μ, characteristic for 1,2,4-substituted benzene derivatives. A freshly distilled sample of Vb polymerized completely within 20 min.

C. *o*-Tolylene Diisocyanates V from 4- and 5-Methylbenzimidazolone (III).—A stirred solution of 10 g of 4-methylbenzimidazolone (IIIa) in 1000 ml of dry *o*-dichlorobenzene at 150° was treated with phosgene for 9 hr. Excess phosgene was then removed by passing nitrogen through the reaction mixture at 160° for 2 hr. The solvent was removed by distillation and the resulting residue subjected to vapor phase chromatography, which indicated a 3% yield of diisocyanate Va.

A solution of 10 g of 5-methylbenzimidazolone (IIIb) in 500 ml of dry *o*-dichlorobenzene was phosgenated at 155° for 6 hr. The reaction product was purged with nitrogen at 150° for 2 hr and the solvent was removed by distillation. Vapor phase chromatography of the residue indicated that diisocyanate Vb had been formed in 15% yield of the theory.

D. 2,3-Tolylene Diisocyanate (Va) from 2,3-Tolyleneallophanoyl Chloride (IVa).—A sample of IV (1 g) was heated in 15 ml of dry *o*-dichlorobenzene at 175–180° for 20 min. After hydrogen chloride evolution had ceased, the solution was subjected to vapor phase chromatography, which indicated that 2,3-tolylene diisocyanate had been formed in a 35% yield. An infrared spectrum of the solution showed strong absorption at 4.45 μ, indicative for the presence of free isocyanato groups.

***o*-Tolylene Diisocyanate Polymers.**—Both the 2,3- and the 3,4-tolylene diisocyanate derived polymers are insoluble in the common solvents, but can be dissolved in 100% sulfuric acid. The intrinsic viscosity in sulfuric acid of the polymer derived from the 2,3 and 3,4 isomers were found to be 0.18 and 0.12, respectively. Mass spectroscopy showed the presence of tolylene diisocyanate as the predominant component (*m/e* 174). Combustion analyses were in good agreement with the values calculated for tolylene diisocyanate: λ(infrared) of 2,3-tolylene diisocyanate polymer 4.45, 5.65, 5.75, 7.5, 7.7, 9.6, 10.9, 12.9, 13.6; λ(infrared) of 3,4-tolylene diisocyanate polymer 4.45, 5.65, 5.75, 7.45, 7.8, 9.2, 9.3, 10.6, 11.85, 12.3, 13.1, 13.7, 14.4.

Anal. Calcd for $(C_9H_6O_2N_2)_n$: C, 62.07; H, 3.47; N, 16.09. Found: C, 61.42; H, 3.86; N, 15.79.

2,3-Tolyleneallophanic Acid Methyl Ester (VI).—A few drops of freshly distilled 2,3-tolylene diisocyanate were added to an excess of methanol. After a short time, crystals started to precipitate. Filtration and recrystallization of the filter cake from methanol gave VI: mp 207.5–209°; λ(infrared) 3.18, 5.75, 5.80, 6.98, 7.42 μ.

Anal. Calcd for $C_{10}H_{10}N_2O_3$: C, 58.24; H, 4.87; N, 13.60. Found: C, 57.66; H, 4.97; N, 13.72.

2,3-Tolyleneallophanoylanilide (VII).—A few drops of freshly distilled 2,3-tolylene diisocyanate were added to an excess of aniline. The resulting white crystals were recrystallized from methanol to give VII: mp 238–240°; λ(infrared) 3.12, 3.24, 5.80, 5.86, 7.4 μ.

Anal. Calcd for $C_{15}H_{13}N_3O_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.85; H, 5.36; N, 15.76.

Registry No.—4-Methylbenzimidazalone, 19190-68-2; IVa, 19190-69-3; Va, 7373-19-5; Vb, 13879-33-9; VIa, 19190-72-8; VIIa, 19190-73-9.

Acknowledgments.—The authors are indebted to Dr. R. W. Finch, Mr. W. W. Harple and Mr. H. Hoberecht for determination and interpretation of infrared and mass spectra.

Synthesis of the Dibenzo[*b*,*g*]oxocin System

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Received July 11, 1968

The medium-ring heterocyclic systems, like the corresponding carbocycles, are of considerable chemical interest for studies on aromaticity,[2] transannular interactions[3] and reactions,[4] conformation[5] and other properties. The partially or fully unsaturated molecules are of particular interest in this respect.[6] Much less is known of the heterocyclic systems than of the carbocycles, however, because of the lesser synthetic availability of the heterocycles. In this paper we wish to report a synthesis of the dibenzo[*b*,*g*]oxocin system.

The starting materials used in the synthesis were di-*o*-tolyl ether (**1a**) and 2-carboxy-2′-methyldiphenyl

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(1) Taken from the dissertation of D. Slobodin, submitted in partial fulfillment of the requirements for the Ph.D. degree, 1967.

(2) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **90**, 1527 (1968).

(3) N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, **82**, 4075 (1960).

(4) L. A. Paquette and R. W. Begland, *ibid.*, **87**, 3784 (1965).

(5) L. A. Paquette and R. W. Begland, *J. Org. Chem.*, **32**, 2723 (1967).

(6) L. A. Paquette, *Trans N. Y. Acad. Sci.*, **28**, 387 (1966).