solved at the end of 3 days. At the end of 7 days a new precipitate had formed. The mixture was then poured into water and extracted with chloroform to give 1.0 g. (83%) of acetanilide, m.p. 113–114°.

*p-Nitroacetanilide from p-nitro-N-sulfinylaniline.* To 5 ml. of glacial acetic acid and 0.1 ml. (0.17 g., 0.0015 mole) of thionyl chloride was added 1 g. (0.005 mole) of *p*-nitro-*N*-sulfinylaniline.[3] Immediate formation of crystals was noted, and after 15 min. of heating the mixture was completely solid. An additional 5 ml. of acetic acid was added and the mixture was allowed to stand for 30 min. The reaction mixture was then diluted with 100 ml. of water and extracted with chloroform. The solid which did not dissolve was removed by filtration and combined with that obtained from evaporation of the chloroform to give 0.9 g. (92%) of *p*-nitroacetanilide, m.p. 215–216°.[6]

*N-Cyclohexylacetamide.* A mixture of 5 ml. of acetic acid, 1.09 g. (0.0075 mole) of *N*-sulfinylcyclohexyl amine[7] and 0.1 ml. (0.17 g., 0.0015 mole) of thionyl chloride was refluxed for 2 hr., cooled, and extracted with chloroform to give 0.33 g. (31%) of *N*-cyclohexylacetamide, m.p. 103–104°.[8]

*Aniline hydrochloride from N-sulfinylaniline.* To a solution of 1.2 g. (0.009 mole) of *N*-sulfinylaniline in 5 ml. of acetic acid at 25° was added 1.65 g. (0.017 mole) of thionyl chloride. There was an immediate vigorous reaction resulting in the precipitation of 0.85 g. (74%) of aniline hydrochloride, m.p. 195–198°, undepressed by mixture with an authentic sample.

In another experiment a slow stream of dry hydrogen chloride was passed for 1 hr. into 10 g. (0.07 mole) of *N*-sulfinylaniline dissolved in 30 ml. of dry xylene at 25° to give 8.2 g. (88%) of aniline hydrochloride.

*Detection of thionyl chloride.* Solutions of *N*-sulfinylaniline in cyclohexane and in acetic acid were exposed to dry hydrogen chloride for 15 min. and then distilled. Vapor phase chromatography of both distillates and of authentic mixtures showed the presence of thionyl chloride.

LEXINGTON, KY.

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(6) A. Kaufmann, *Ber.*, **42**, 3482 (1909).

(7) Donald Trimnell, Thesis, University of Kentucky, 1958.

(8) A. Baeyer, *Ann.*, **278**, 104 (1894).

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[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

# Reaction of an Isocyanate and a Carboxylic Acid in Dimethyl Sulfoxide

W. R. SORENSON

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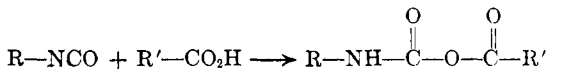
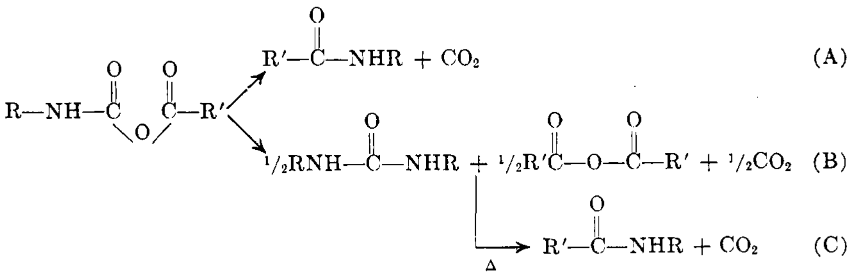
The reaction of an aromatic isocyanate or diisocyanate with benzoic acid in dimethyl sulfoxide as solvent has been found to give the urea or high molecular weight polyurea derived from the amine or diamine precursor of the isocyanate. The dimethyl sulfoxide takes part in the reaction also, forming the methylthiomethyl ester of benzoic acid. This fact, plus the observed stoichiometry of the reaction (2:1:1 for isocyanate:carboxylic acid:sulfoxide), precludes the operation in this case of the usual isocyanate-carboxylic reaction. A mechanism is proposed which accounts for the products formed.

Previous work[1] on the reaction of an isocyanate with a carboxylic acid in equimolar amounts has shown that the first product of the reaction is a mixed carbamic-carboxylic anhydride, which, in most cases, is not stable but in some instances can be isolated:



$$\mathrm{R{-}NCO + R'{-}CO_2H \longrightarrow R{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}R'}$$

The decomposition of the mixed anhydride proceeds by two paths to give an amide in A (below), and in B a symmetrical urea and the anhydride of the acid.[2] Carbon dioxide is evolved in both cases. The products of path B, on heating to higher temperatures (135° or more) can react with each other to give the amide, path C.[2] Thus, under forcing conditions, the ultimate product of the reaction is the amide:



This over-all reaction has been used to prepare amides in good yields.[3]

We would like to report here an unusual variant of the above reactions. If two moles of phenyl

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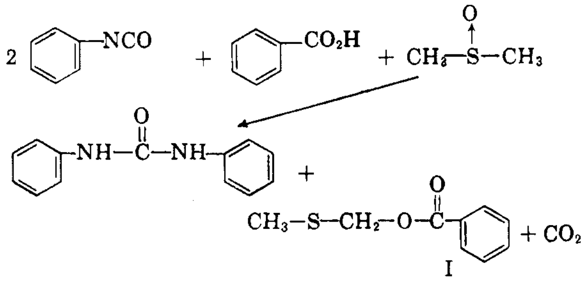
(1) W. Dieckmann and F. Breest, *Ber.*, **39**, 3052 (1906).

(2) C. Naegli and A. Tyabji, *Helv. Chim. Acta*, **17**, 931 (1934); **18**, 142 (1935).

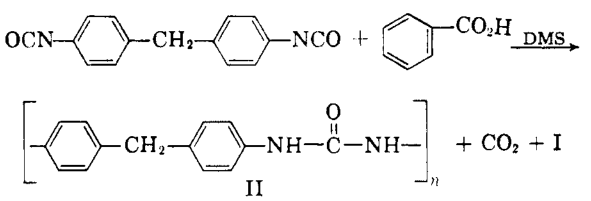
(3) C. L. Ayre, G. Dinga, and R. Pflaum, *J. Org. Chem.*, **20**, 695 (1955).

isocyanate, one mole of benzoic acid and one mole of dimethyl sulfoxide (DMS) are warmed together in benzene, *sym*-diphenyl urea, carbon dioxide and $\alpha$-benzoyloxydimethyl sulfide I may be isolated.



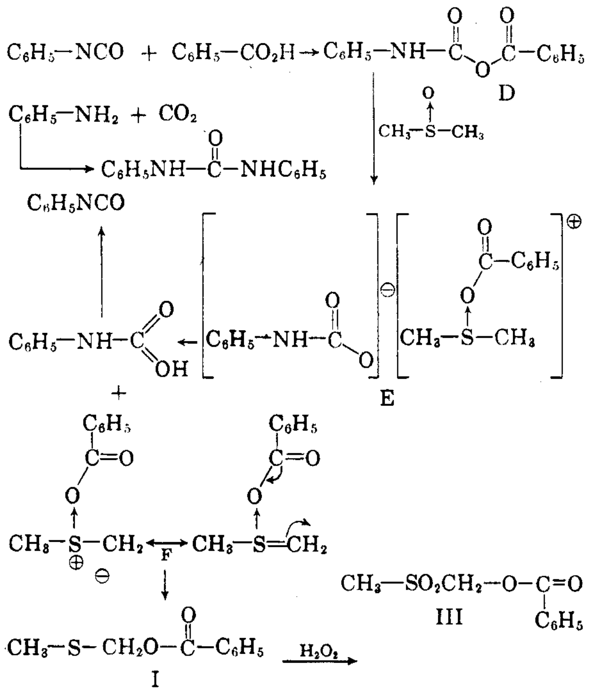
The sulfide-ester I was identified by elementary analysis, saponification equivalent, infrared absorption, oxidation to the corresponding sulfone (III). The melting point of the urea was undepressed in mixed melting with an authentic sample of *sym*-diphenyl urea. The yield of the urea was 70%, of I, 50%.

To demonstrate that the reaction is actually one of very high efficiency, one mole of methylene bis(4-phenyl isocyanate) and one mole of benzoic acid, were brought together under strictly anhydrous conditions in excess DMS as solvent at room temperature. The reaction proceeded exothermally with evolution of carbon dioxide and formation of a viscous solution. The polyurea (II) was formed quantitatively in high molecular weight (inherent viscosity of 1.0, see Experimental). Tough films could be formed from the as-made solution by casting on a glass plate and drying in vacuum. The polyurea was identical with authentic II (see Experimental) in its infrared spectrum. No attempt was made to isolate the sulfide-ester I from this reaction.

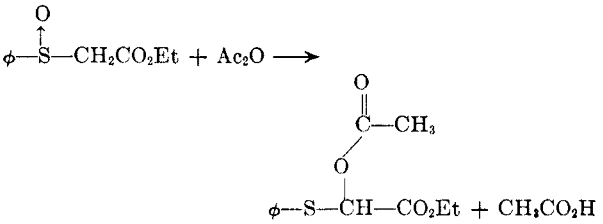


It is significant to note that the stoichiometry of the reaction reported here precludes the operation of path B of the usual isocyanate-acid reaction discussed originally in the formation of the products observed here. Where DMS is present, the stoichiometry of two $-NCO$ groups to one $-CO_2H$ is followed. Benzoic acid above this amount could be recovered from the polymer-forming reaction. A lesser quantity gave only low polymer. In the normal reaction one $-NCO$ to one $-CO_2H$ is required to form products in high yield. Unlike the normal reaction which produces an amide as the ultimate product, a urea is the ultimate product in our case. The quantitative formation of a high molecular weight polyurea in the case of the diisocyanate shows that the reaction must proceed uniformly by one course without side reactions, since high polymer-forming reactions are extremely sensitive to impurities, imbalances of reactants and chain terminating reactions. For example, any amide formation here would be a chain terminating reaction since a benzamide link would be the result.

A reasonable mechanism to account for the course of our reaction involves formation of a mixed carboxylic-carbamic anhydride, D, which subsequently reacts with DMS to give E, which decomposes to phenyl carbamic acid and resonance-stabilized F. The latter, by a cyclic process, rearranges to the sulfide ester (I). Phenyl carbamic acid decarboxylates to give aniline, which reacts with the second mole of isocyanate to form the urea. It is this part of the sequence that accounts for polymer formation in the case of the diisocyanate.



This reaction is similar to that of DMS with acid chlorides to give $\alpha$-chlorodimethyl sulfide as noted by Bordwell,[4] and also to the reaction of carbethoxymethylphenyl sulfoxide with acetic anhydride as found by Pummerer.[5]



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[4] F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955).

[5] R. Pummerer, *Ber.*, **43**, 1401 (1901).

## EXPERIMENTAL

*α-Benzoyloxydimethyl sulfide* (I). In 250 ml. dry benzene was placed 24.2 g. (0.2 mole) benzoic acid, 47.6 g. (0.4 mole) phenyl isocyanate, and 15.6 g. dimethyl sulfoxide. The mixture was refluxed overnight on a steam bath. After cooling, the solid was filtered and recrystallized from benzene-ether. It had a m.p. of 240–241° and was undepressed on admixture with authentic *sym*-diphenylurea. The melting point of the latter is given as 240° in the literature. The yield was 29.5 g. (70%).

The benzene filtrate was extracted once with 100 ml. of 10% sodium bicarbonate solution, and once with 100 ml. of water. Ten g. of benzoic acid was recovered by acidifying the extract. The benzene solution was dried over $MgSO_4$ and the benzene distilled off. The residue was distilled at reduced pressure to a slightly yellow liquid of b.p. 85–86°/0.1 mm. The weight was 10.5 g., or 50% yield based on unrecovered benzoic acid.

*Anal.* Calcd. for $C_9H_{10}O_2S$: C, 59.34; H, 5.48; S, 17.58; sapon. equiv., 182. Found: C, 59.4, 59.4; H, 5.2, 5.3; S, 17.6, 17.7; sapon. equiv., 176, 175.

The infrared spectrum of this compound had bonds at 3.3, 6.27, 6.34 and 6.74$\mu$, indicative of an aromatic ring; at 5.83, 8.0, and 9.2$\mu$ for an aromatic ester; at 3.4–3.48$\mu$ for aliphatic C—H.

*α-Benzoyloxydimethyl sulfone* (III). Five g. of I was dissolved in 20 ml. *t*-butyl alcohol and heated to 85–90° in an oil bath. Ten ml. of 30% hydrogen peroxide was added and heating continued 1 hr. and 15 min. The *t*-butyl alcohol was distilled off at reduced pressure. The residue solidified on cooling. It was recrystallized three times from absolute ethanol to give 2.5 g. (43%) of the sulfone, melting at 105–106°.

*Anal.* Calcd. for $C_9H_{10}O_4S$: C, 50.46; H, 4.67; S, 14.95. Found: C, 50.4, 50.4; H, 4.5, 4.4; S, 14.7, 14.5.

*Poly-bis(4-aminophenyl)methane carbonamide* (II). In 20 ml. dry dimethyl sulfoxide was dissolved 2.42 g. (0.02 mole) benzoic acid. To it was added 5.0 g. (0.02 mole) methylene bis(4-phenylisocyanate). The reaction was allowed to proceed at room temperature with occasional shaking. The vessel was protected from moisture with a drying tube. In 3–4 hr., a clear, viscous yellow solution resulted. Clear, tough films were obtained by casting on glass plates and drying at 80° in a vacuum oven.

In another run, the polymer was precipitated into water, washed with water and methanol, then dried. The yield, 4.4 g., was quantitative. The inherent viscosity ($\eta$inh = $\frac{1}{c} \ln \frac{\eta}{\eta_0}$, where concentration is 0.5% in dimethyl sulfoxide at 25°) was 1.0.

The infrared spectrum obtained on a sample of the above film was identical to that of films of the polyurea obtained by mixing equimolar amounts of the diisocyanate and bis-(4-aminophenyl)methane in dimethylformamide and casting similarly.

If twice the amount of benzoic acid was used as given above, the reaction proceeded as above. The polymer was precipitated in methylene chloride, filtered, and washed thoroughly with more methylene chloride. The weight of polymer was again 4.4 g. The combined methylene chloride was extracted with 5% aqueous sodium bicarbonate solution, which was, in turn, extracted with ether. Acidification of the aqueous layer precipitated 2.2 g. of benzoic acid, virtually all that was in excess. When this procedure was carried out on a polymer solution made as described originally, with no excess benzoic acid present, no benzoic acid was recovered.

When benzoic acid was added portionwise to a solution of the diisocyanate in DMS, a maximum solution viscosity was achieved at 1:1 molar equivalence, beyond which no viscosity change occurred nor carbon dioxide evolved.

That carbon dioxide was evolved from the reaction was established by passing the evolved gas from a typical reaction through a calcium hydroxide solution. The familiar milky precipitate formed. No quantitative measure was made.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

# Synthesis of Urushenol, the Mono-olefinic Component of the Allergenic Principles of Poison Ivy and Japanese Lac

BERNARD LOEV[1] AND CHARLES R. DAWSON

*Received January 12, 1959*

The synthesis of urushenol has made available for clinical study for the first time one of the olefinic catechols that make up the allergenic principle of poison ivy and Japanese lac. The catechol hydroxyl groups are protected by benzylation during the construction of the olefinic side chain. The benzyl ethers are subsequently cleaved, and a double bond of the styrene type is simultaneously reduced, by means of sodium and butanol. The desired Δ8 olefinic bond is not altered during the reductive cleavage. It is believed that the method will be adaptable to the synthesis of the higher olefinic components of poison ivy urushiol.

It has been known for over twenty years that the toxic principle of poison ivy is chemically similar to Japanese lac urushiol.[2,3] Only recently, however, has the complete structure of each of these allergenic oils been elaborated.[4,5] Because of the extreme sensitivity of these compounds and for other

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[1] This paper is based on a portion of the thesis submitted by Bernard Loev in 1952 to Columbia University in partial fulfillment of the requirements for the Ph.D. degree in Chemistry. Present address: Smith Kline and French Laboratories, Philadelphia, Pa.

[2] R. Majima and co-workers, *Ber.*, **55**, 172 (1922) and preceding papers.

[3] G. A. Hill, V. Mattacotti, and W. D. Graham, *J. Am. Chem. Soc.*, **56**, 2736 (1934).

[4] W. F. Symes and C. R. Dawson, *J. Am. Chem. Soc.*, **76**, 2959 (1954).

[5] S. V. Sunthankar and C. R. Dawson, *J. Am. Chem. Soc.*, **76**, 5070 (1954).