dropping funnel, and a solution of 150 g. of phenyl cyclohexyl ketone in 200 ml. of ether was added dropwise with stirring, followed by addition of another 500 ml. of absolute ether to bring the resulting precipitate largely into solution. After 5 hours, the Dry Ice condenser was replaced by a water-cooled condenser. An additional 500 ml. of absolute ether was added to replace the ammonia lost, and the mixture allowed to stir slowly overnight. The remaining ammonia was then removed by warming the solution until ether could be seen to reflux vigorously, and the reaction mixture was brought to *p*H 4–5 by addition of aqueous (25%) acetic acid. The ether layer was separated, washed once with acetic acid and once with aqueous sodium bicarbonate. The aqueous layers were re-extracted with ether and the combined ether layers were distilled. The 167 g. of moderately viscous clear liquid product boiled at 109° (0.5 mm.) on slow distillation, at 115° (0.05 mm.) on rapid distillation. It had $n^{25}D$ 1.5469, and 1.03 acetylenic H/mole.[13]

Phenylcyclohexylvinylcarbinol.—The reduction of 33 g. of phenylcyclohexylethinylcarbinol, run according to Lindlar (ref. 11), became too slow to detect after 1.05 moles of H_2 was taken up per mole of the ethinylcarbinol. The product was worked up by filtration, extraction with dilute acetic acid to *p*H 4, and distillation, and 30.8 g., b.p. 100–101° (0.2 mm.), was obtained. This had no detectable acetylenic H, $n^{25}D$ 1.5453.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.23; H, 9.31. Found: C, 82.77; H, 9.04.

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[13] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley & Sons, Inc., New York, N. Y., 1949, p. 55.

TUCKAHOE, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Molecular Complex Formation of 2,5-Diphenyl-1,4-dithiadiene

BY H. HARRY SZMANT AND LUIS M. ALFONSO[1]

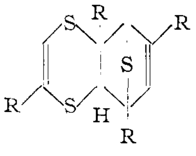
RECEIVED AUGUST 3, 1955

The previously reported substance obtained during the oxidation of 2,5-diphenyl-1,4-dithiadiene is shown to be a complex of the starting material and 2,4-diphenylthiophene which exists only in the solid state. A similar complex is formed with 2,4-diphenylfuran but not with 2,5-diphenylthiophene. The monosulfone of 2,5-diphenyl-1,4-dithiadiene is proven not to be the intermediate in the formation of 2,4-diphenylthiophene contrary to a recent claim to that effect.

The substance I isolated[2] during the oxidation of 2,5-diphenyl-1,4-dithiadiene II with equimolar quantities of hydrogen peroxide was carefully investigated in order to determine its structure. It was soon found that, when subjected to various reactions, this material gave derivatives of either II or of 2,4-diphenylthiophene III. Thus, on further oxidation of I under mild conditions there was isolated the monosulfone of II and unreacted III, and on more vigorous oxidation I gave the previously reported disulfone of II.[2] Bromination of I led to a dibromo derivative of II identical with the product of direct bromination of II. On the other hand, chloromercuration of I was shown to give the chloromercuri derivative of III.

The redetermination of the molecular weight of I gave a value which agreed with the average of the molecular weights of II and III, and the ultraviolet spectrum of I was shown to be identical with the curve calculated for an equimolar mixture of II and III. Finally, it was shown that crystallization of an equimolar mixture of II and III gave essentially quantitative yields of I.

All of these experimental facts still did not seem definitive in distinguishing with complete certainty between the possibilities that I is a molecular complex of II and III, or that I is a Diels–Alder adduct of structure IV which, because of the sulfur bridge and the generally recognized inhibition of thiophene derivatives to form Diels–Alder adducts,[3] could easily dissociate into the original components. Such a dissociation would explain the ultraviolet spectrum of I and the molecular weight data since these determinations are performed with solutions of high dilution. For this reason an attempt to separate the components of I by chromatography seemed to be particularly significant since this technique involves the use of concentrated solutions. This experiment proved successful and it is thus concluded that I is a molecular complex of II and III which exists only in the solid state.[4]



IV, R = C_6H_5

In view of the apparent absence in II and III of electron-donating and electron-accepting properties which ordinarily are associated with complex formation,[5,6] it was of interest to examine possible complex formation of II with other substances. The isomer of III, namely, 2,5-diphenylthiophene was shown not to form a complex, while 2,4-diphenylfuran gave a molecular complex the ultraviolet spectrum of which was again identical with that calculated for an equimolar mixture of the two components. These facts indicate that successful complex formation of II depends on the location of the phenyl groups in the five-membered

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[1] From the M.S. thesis of L.M.A., Duquesne University, 1955.

[2] H. H. Szmant and J. Dixon, THIS JOURNAL, **75**, 4354 (1953).

[3] See the discussion by O. Dann, M. Kokorudz and R. Gropper in *Ber.*, **87**, 140 (1954).

[4] While this work was in progress Parham and Traynelis (THIS JOURNAL, **76**, 4960 (1954)) also concluded that I was a complex on the basis of ultraviolet absorption data, chloromercuration and formation from the components.

[5] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[6] L. N. Ferguson, *J. Chem. Ed.* **31** 626 (1954).

heterocycle rather than on the nature of the hetero atom.[7] Thus, one is led to the conclusion that in the molecular complexes of II isolated so far, the molecules are "stacked like a pack of cards"[5] and that the overlapping of the π-orbitals of the phenyl rings of both components plays a decisive role in the stabilization. The latter type phenomenon has been invoked to explain preferential *exo* and *endo* orientation in the formation of Diels–Alder adducts.[8]

The preparation of I during the oxidation of II raises the question of the precursor in the formation of III. Parham[9] has concluded that the elimination of sulfur during the oxidation of II or of its nitro derivative occurs by the loss of sulfur dioxide from an intermediate monosulfone. We were able to prepare the monosulfone of II and showed it to be stable on heating to 200°, on refluxing a mixture of the monosulfone and II in glacial acetic acid, and on refluxing the monosulfone in glacial acetic acid in the presence of catalytic amounts of sulfuric acid. The last conditions are similar to those employed during the oxidation of II by means of peracetic acid except that they are even more vigorous. Thus, it can be stated with some certainty that the formation of III does not occur by the elimination of sulfur dioxide from the monosulfone of II. It is more likely that III is formed from a monosulfoxide of II and work investigating the possibility of this reaction path is in progress.[10]

Experimental[11]

Preparation of I. (A) By Oxidation of II.—The following is an improvement of the previously published procedure.[2] A solution of 7.45 g. of II in 100 cc. of ethyl acetate was brought to reflux and 12 cc. of 40% peracetic acid was added dropwise. The resulting mixture was refluxed for 3–4 minutes and the ethyl acetate was distilled with simultaneous addition of isopropyl alcohol. On cooling there was obtained a yellow solid which upon crystallization from isopropyl alcohol had a m.p. 126–128°. Yields as high as 70% were obtained.

(B) **From II and III.**—II (58 mg.) and III (51 mg.) were dissolved in 10 cc. of benzene. Upon concentration of the solution and addition of isopropyl alcohol there was obtained an essentially quantitative yield of I.

Molecular weight (f.t. depression of benzene solution): 252, 264. Calcd. for equimolar mixture of II and III: 252.

The ultraviolet absorption curve of I (259 mμ, ϵ 57,300; 295 mμ, ϵ 16,700) coincides with the sum of the curves of II (260 mμ, ϵ 22,400; 308 mμ, ϵ 8,800) and III (258 mμ, ϵ 34,800).

Experiments with I. (A) Oxidation to Monosulfone of II.—The treatment of 0.720 g. of I in 90 cc. of ethyl acetate with 10 cc. of 40% peracetic acid gave after standing at room temperature for 3 hours, addition of ethanol and concentration of the volume, 0.53 g. of material. The solid was washed with petroleum ether and crystallized from ethanol to give a white solid, m.p. 151.5–153°, identical with the monosulfone of II prepared by the direct oxidation of II (see below). The petroleum ether washings were concentrated and gave a small amount of III.

(B) **Bromination.**—The treatment of I with N-bromosuccinimide in the manner described below for the bromination of II gave a product which after several crystallizations from ethanol and benzene proved to be identical with the dibromo derivative of II described below.

(C) **Chloromercuration.**—An ethanolic solution of I was treated with mercuric chloride and a saturated solution of sodium acetate. After standing at room temperature for three days the solution deposited white silky needles which did not depress the melting point of the chloromercuri derivative of III prepared according to the procedure of Bogert and Herrera.[12]

(D) **Chromatography.**—A concentrated solution of 0.4 g. of I in a few cc. of benzene was deposited on activated alumina and eluted with a mixture of benzene and petroleum ether. The first fraction contained 0.05 g. of pure III while the remaining fractions upon concentration gave I.

Complex of II and 2,4-Diphenylfuran.—II (0.335 g.) and 0.410 g. of 2,4-diphenylfuran[13] were dissolved in 20 cc. of benzene. Upon concentration of the solution and addition of methanol there was obtained an essentially quantitative yield of solid, m.p. 111–112°, which depressed the m.p. of the starting materials.

Anal. Calcd. for $C_{32}H_{24}OS_2$: C, 78.68; H, 4.96; S, 13.16. Found: C, 78.37; H, 4.99; S, 13.43.

The ultraviolet absorption curve of this material (248 mμ, ϵ 38,200; 270 mμ, ϵ 39,400) coincides with the sum of the curves of II and 2,4-diphenylfuran (242 mμ, ϵ 19,800; 276 mμ, ϵ 21,800).

The Preparation of the Monosulfone of II.—A solution of 10 g. of II in ethyl acetate was treated with a mixture of 40% peracetic acid and ethyl acetate (1:1) at room temperature until the color almost faded. After additional stirring at room temperature for 40 minutes the solution was concentrated *in vacuo* and isopropyl alcohol was added. Upon cooling there was obtained a white solid in 67% yield which on crystallization from ethanol had a m.p. 152–154°.

Anal. Calcd. for $C_{16}H_{12}O_2S_2$: C, 63.98; H, 4.02; S, 21.35. Found: C, 63.28; H, 4.14; S, 21.36.

The infrared spectrum of this compound in chloroform showed very intense absorption at 1177 and 1331 cm.$^{-1}$ typical of sulfones and the complete absence of absorption characteristic of sulfoxides.[14]

Attempted Decomposition Reactions of the Monosulfone of II. (A). Thermal.—The compound upon heating to 200° for several minutes in the fused state showed no decomposition or change in m.p.

(B) **In the Presence of Sulfuric Acid.**—A solution containing 0.30 g. of the compound, 50 cc. of glacial acetic acid and 0.05 cc. of concd. sulfuric acid was refluxed for two hours and poured on ice. The starting material, 0.29 g., was recovered in a pure state.

(C) **In the Presence of II.**—A solution containing 0.90 g. of the compound, 0.80 g. of II and 50 cc. of glacial acetic acid was refluxed for two hours and poured on ice. The solid material was dried and recrystallized from a mixture of benzene and heptane to give 0.65 g. of the monosulfone of II. The filtrate from the crystallization was concentrated, diluted with ethanol and cooled, and 0.54 g. of II was precipitated.

Bromination of II. (A) Monobromo Derivative of II.—A mixture of 10 g. of II, 5.5 g. of N-bromosuccinimide, a few mg. of benzoyl peroxide and 250 cc. of carbon tetrachloride was allowed to stand at room temperature for five days. The solid was filtered and the filtrate was concentrated *in vacuo* with simultaneous addition of methanol, and 6.8 g. of material, m.p. 83–85°, was obtained. Upon recrystallization from methanol the sample had a m.p. 85.5–86.5°.

Anal. Calcd. for $C_{16}H_{11}S_2Br$: C, 55.34; H, 3.19; S, 18.46. Found: C, 54.81; H, 3.18; S, 18.4.

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(7) We also have observed an apparent complex formation between II and *m*-terphenyl but not *p*-terphenyl. Unfortunately the complex with *m*-terphenyl has, so far, resisted attempts to obtain it in an analytically pure state.

(8) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 717.

(9) W. E. Parham and V. J. Traynelis, THIS JOURNAL, **76**, 4960 (1954); **77**, 68 (1955).

(10) (Added October 14, 1955). We are now able to oxidize II to a white solid, m.p. 114–115° (decomposition to red material), which contains the sulfoxide function (strong infrared band at 1040 cm.$^{-1}$), and which readily undergoes decomposition to give I. Since this solid gives I in the absence of II, we are led to believe that the elimination of sulfur dioxide takes place during a disproportionation reaction involving two sulfoxide molecules.

(11) All melting points are uncorrected. Microanalyses by Drs. Strauss and Weiler, Oxford, England.

(12) M. T. Bogert and P. P. Herrera, THIS JOURNAL, **45**, 238 (1923).

(13) R. C. Fuson, C. L. Fleming and R. Johnson, *ibid.*, **60**, 1984 (1938).

(14) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954, pp. 295, 297.

(B) Dibromo Derivative of II.—A solution of 4.5 g. of II, 6.0 g. of N-bromosuccinimide and 60 cc. of carbon tetrachloride was placed in a desiccator containing sodium hydroxide pellets, and the desiccator was partially evacuated. After five days at room temperature the mixture was filtered, and the filtrate was concentrated *in vacuo*. The resulting solid was crystallized from a mixture of ethanol and benzene and 4 g. of solid, m.p. 164–165°, was obtained.

Anal. Calcd. for $C_{16}H_{10}Br_2S_2$: C, 45.09; H, 2.36. Found: C, 45.17; H, 2.38.

The identical material was obtained in 63% yield by the treatment of the above mentioned monobromo compound with an excess of N-bromosuccinimide in the presence of catalytic amounts of benzoyl peroxide using carbon tetrachloride as the solvent and room temperature conditions.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BROOKLYN COLLEGE]

The Pyrolysis of Amides

BY DAVID DAVIDSON AND MARVIN KARTEN

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In its early stages the thermal conversion of an amide to the corresponding nitrile is characterized by the evolution of ammonia, the appearance of the secondary amide (imide) and the accumulation of the corresponding carboxylic acid. These facts may be accounted for by assuming that the primary step in the pyrolysis is the bimolecular deammonation of the amide to the isoimide, RC(=NH)OCOR. In part, the isoimide may then decompose to nitrile and carboxylic acid and, in part, rearrange reversibly to the imide. The carboxylic acid, in turn, may react with the ammonia being formed to regenerate one molecule of amide and yield water. It is only under conditions favorable for this last reaction that the thermal conversion of amides to nitriles becomes a dehydration reaction. The exchange reaction, $CH_3CONH_2 + PhCOOH \rightarrow CH_3COOH + PhCONH_2$, appears to involve a partial decomposition of the acetamide according to the scheme given above; *i.e.*, $2CH_3CONH_2 \rightarrow CH_3CN + CH_3COOH + NH_3$, coupled with the reaction of benzoic acid with the ammonia formed to yield benzamide and water. Once water is formed the reaction may take the course, $CH_3CONH_2 + H_2O \rightarrow CH_3COOH + NH_3$ and $PhCOOH + NH_3 \rightarrow PhCONH_2 + H_2O$, the water thus serving a catalytic function in the exchange. It is also possible that the amide and acid react to form the isoimide and water; after rearrangement to the imide, the product would be capable of hydrolyzing to regenerate the original amide and acid or the exchanged pair. The previously observed reactivity of partially pyrolyzed amides toward aniline is probably due to catalysis by the carboxylic acids present.

Amides have been found to pyrolyze in two ways: (a) to nitrile and water[1,2]; (b) to nitrile, carboxylic acid and ammonia.[3] The second of these has been said to result from the direct dehydration of one molecule of amide followed by the hydrolysis of a second molecule. A third mode of pyrolysis has been hypothesized,[4] *i.e.*, scission to ketene and ammonia. While partially pyrolyzed amides were found to be much more reactive toward aniline than the original amides, this behavior was not restricted to amides in which the formation of ketenes was structurally possible but was also shown by benzamide. Suffice it to say that the evolution of ammonia has been generally recognized to accompany the pyrolysis of amides.

The observation[5] that monocarboxylic acids yield anhydrides when heated above 250° suggested that the evolution of ammonia from amides might be due to the analogous deammonation to imides. Isoimides are possible intermediates in this reaction. N-Substituted isoimides rearrange readily to N-substituted imides.[6,7]

The formation of cyclic imides by heating certain diamides such as phthalamide is well known[8] and the formation of acyclic imides from monoamides has been shown to occur in the presence of hydrogen chloride.[9] Furthermore, acyclic imides undergo facile pyrolysis to nitriles and acids,[10] presumably reverting to isoimides in the process.[11] In sum, the reactions involving the formation and pyrolysis of the imide equal the result given above as mode (b) for the pyrolysis of amides. Since carboxylic acids react with ammonia to form amides and water,[12] it follows that the thermal dehydration

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[1] R. S. Boehner and C. E. Andrews, THIS JOURNAL, **38**, 2503 (1916), refluxed amides with massive amounts of contact agents such as alumina, pumice, glass, sand and graphite.

[2] R. S. Boehner and A. L. Ward, *ibid.*, **38**, 2505 (1916), passed the vapors of amides over the same contact agents at 425°.

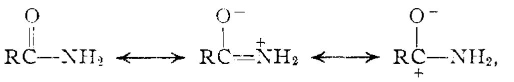
[3] A. W. Ralston, H. J. Harwood and W. O. Pool, *ibid.*, **59**, 986 (1937), distilled stearamide at atmospheric pressure.

[4] C. D. Hurd, M. F. Dull and K. E. Martin, *ibid.*, **54**, 1974 (1932).

[5] D. Davidson and P. Newman, *ibid.*, **74**, 1515 (1952).

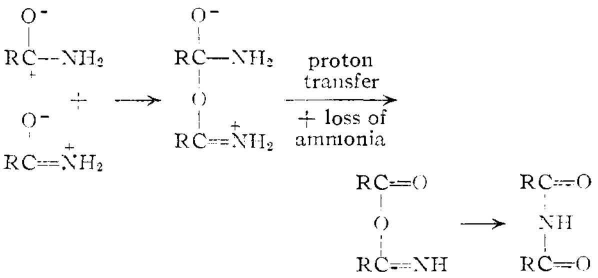
[6] M. L. Sherrill, F. L. Schaeffer and E. P. Shoyer, *ibid.*, **50**, 474 (1928).

[7] Amides are resonance hybrids,



$$RC(=O)-NH_2 \longleftrightarrow RC(-O^-)=\overset{+}{N}H_2 \longleftrightarrow R\overset{+}{C}(-O^-)-NH_2,$$

in which the oxygen atom appears to be the more basic center. It is, therefore, possible that the addition of one molecule of amide to the carbonyl carbon atom of another will take place as



$$RC(O^-)-NH_2 + RC(O^-)=\overset{+}{N}H_2 \longrightarrow RC(O^-)(NH_2)-O-RC=\overset{+}{N}H_2 \xrightarrow[\text{+ loss of ammonia}]{\text{proton transfer}} RC(=O)-O-RC=NH \longrightarrow RC(=O)-NH-RC=O$$

The process may also be looked upon as the addition of one molecule of amide in the enol form to a second in either enol or keto form. The finding of Q. E. Thompson, THIS JOURNAL, **73**, 5841 (1951), that tribenzamide is formed more rapidly from benzamide than from dibenzamide is readily explained by the assumption that the isoimide is the primary product in the benzoylation of benzamide.

[8] F. W. Stacey, J. G. Lindsay and A. N. Bourns, *Can. J. Chem.*, **30**, 135 (1952).

[9] J. B. Polya and T. M. Spotswood, *Rec. trav. chim.*, **67**, 927 (1948).

[10] C. D. Hurd and M. F. Dull, THIS JOURNAL, **54**, 2432 (1932).

[11] H. Meyer and A. Hofmann, *Monatsh.*, **38**, 343 (1917).

[12] J. A. Mitchell and E. E. Reid, THIS JOURNAL, **53**, 321, 187 (1931).