

and the contents were dissolved in 200 ml. of boiling ethanol. The ethanol solution was poured into 500 ml. of water, cooled and the oily solid that separated was collected. This material (dry) was mixed with 100 ml. of ether to produce crystals; the mixture was cooled to -10° , filtered and the product was recrystallized from ethanol to give 10.7 g. (75%) of X melting at $114-114.5^{\circ}$.

N-Ethyl-2,4-dinitroaniline (XI).—This compound was prepared by a method previously described,²³ m.p. $114-115^{\circ}$ after two recrystallizations from ethanol-water.

Infrared Absorption Spectra.—The infrared spectra of compounds (–)-D,D-VIII and (–)-D,L-VIII were examined

(23) P. van Romburgh, *Rec. trav. chim.*, **R2**, 104 (1883), reports a m.p. of $113-114^{\circ}$.

at wave lengths between 2 and 4μ in 5 and 6% carbon tetrachloride solutions, respectively, using a 0.3-mm. rock salt cell and a NaCl prism. Model compounds IX, X and XI were similarly examined in 3% solutions in a 1-mm. rock salt cell. A Beckman (model IR2T) spectrophotometer was used in all cases. The H–N stretching frequencies (symmetrical peaks) were found to occur as follows: (–)-D,D-VIII, at 2.93μ ; (–)-D,L-VIII at 2.93μ ; IX, at 2.81μ and 2.92μ ; X at 2.94μ ; and XI at 2.93μ .

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LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

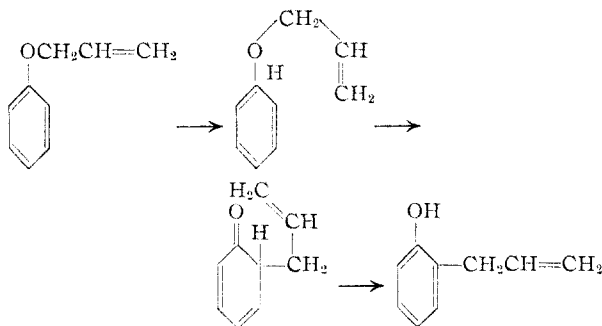
The Claisen Rearrangement of Phenyl Allyl Ethers, Labeled with Carbon-14

BY J. P. RYAN¹ AND P. R. O'CONNOR

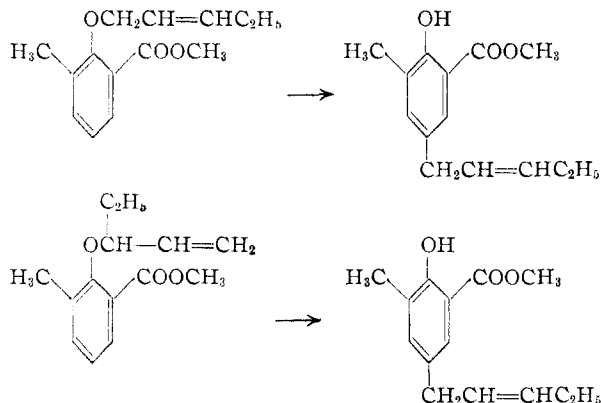
RECEIVED APRIL 26, 1952

The Claisen rearrangement of 3-phenoxy-1-propene-1- C^{14} and 3-(2,6-dimethylphenoxy)-1-propene-1- C^{14} has been investigated. The ortho rearrangement proceeds with inversion of the allyl group; the para rearrangement proceeds with no inversion of the allyl group. Possible mechanisms are discussed. It is shown that a four-membered oxygen ring is not an intermediate in a displacement reaction that is part of the synthetic route.

The thermal rearrangement of phenyl allyl ethers to allyl phenols has been the subject of many investigations.² In most cases the allyl group migrates to the ortho position of the benzene ring, when one of these is available, or to the para position when both ortho positions are substituted. Migration to the meta position has apparently not been observed. The rate of rearrangement obeys a first-order kinetic equation and evidence³ points strongly to an intramolecular mechanism for the ortho rearrangement. This information is incorporated in the following reactions for the mechanism of the ortho rearrangement.⁴



The argument for the mechanism of the para rearrangement is less clear. Although a first-order kinetic equation is followed, the para rearrangement has not been shown to be exclusively intramolecular in character.⁵ Moreover, only one example has been examined in which the α - and γ -isomers of a



substituted ether have been employed.^{6,7} This would indicate that, in the course of the rearrangement, the migrating allyl group is free enough to resonate so that only one product results, the one of lower energy. At the present time the two mechanisms that are given most consideration are the two-cycle mechanism advanced by Hurd and Pollack⁸ and the π -complex mechanism of Dewar.⁹

In the two-cycle mechanism the migration of the allyl group to an ortho position with inversion is proposed, to form an unstable compound which rapidly stabilizes by migration of the allyl group to the para position, again with inversion. Such a reaction path incorporating two intermediate quasi six-membered rings seems possible when molecular models are constructed.

In the π -complex mechanism the interaction of the allyl group with the π -electron cloud of the benzene ring is proposed, with migration of the allyl

(1) From the Ph.D. Thesis of J. P. Ryan, 1952.

(2) D. S. Tarbell, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1.

(3) C. D. Hurd and L. Schmerling, *THIS JOURNAL*, **59**, 107 (1937).

(4) Cf. W. M. Lauer and W. F. Filbert, *ibid.*, **58**, 1388 (1936), for examples of the abnormal rearrangement involving the β -carbon of the allyl group.

(5) See, however, E. R. Alexander and R. W. Kluiber, *ibid.*, **73**, 4304 (1951).

(6) O. Mumm and J. Diedericksen, *Ber.*, **72**, 1523 (1939).

(7) O. Mumm, H. Homhardt and J. Diedericksen, *ibid.*, **72**, 102 (1939).

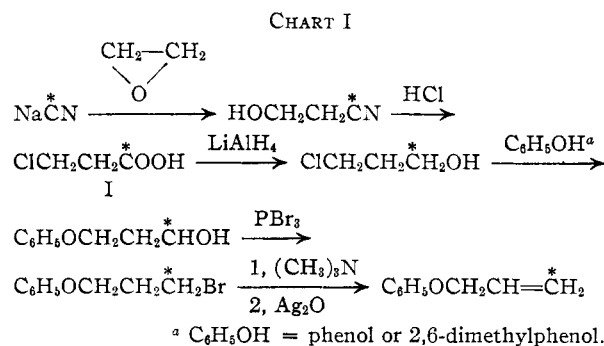
(8) C. D. Hurd and M. A. Pollack, *J. Org. Chem.*, **3**, 550 (1939).

(9) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 230.

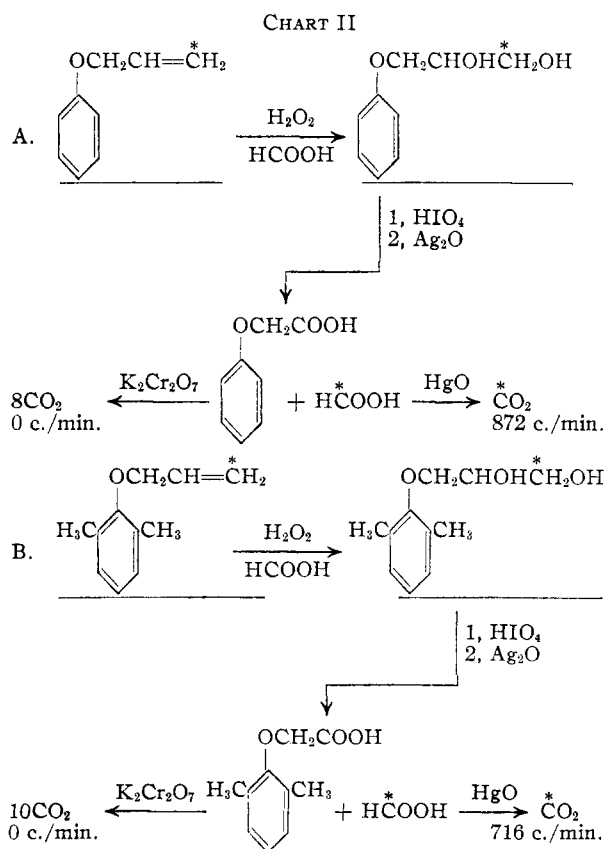
group from the oxygen atom down the ring to the para position. It might be possible then for the migrating allyl group to undergo resonance with only one product formed from isomeric ethers.

The present investigation was undertaken to examine the various mechanisms proposed for the Claisen rearrangement. Phenyl allyl ether and 2,6-dimethylphenyl allyl ether have been synthesized with the γ -carbon of the allyl group tagged with radioactive carbon-14 and the path of carbon-14 through the rearrangement has been determined.

The two ethers were prepared from NaC¹⁴N¹⁰ by the following route.

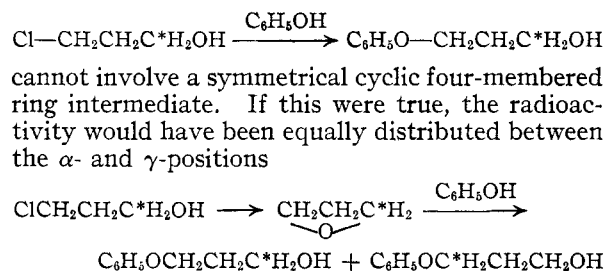


It was necessary to establish unequivocally the location of radioactive carbon in these ethers before proceeding to the rearrangement. Chart II indicates the degradative scheme employed and the counting rates obtained for various fractions.



(10) Radioactive NaCN obtained from Tracerlab, Inc., Boston, Mass., with authorization from the Isotopes Division, Atomic Energy Commission.

Compounds that were isolated and characterized chemically are represented by underlined formulas in the following charts. Since the amount of radioactive sodium cyanide was different in the synthesis of the two ethers, counting rates in the ortho rearrangement series should not be compared with the values for the para rearrangement. It is apparent that the synthesis was specific in labeling only the γ -carbon of the allyl group with carbon-14. An important result is the fact that no change of the carbon skeleton took place in the synthesis. This means that the reaction



This is in marked contrast with the accepted mechanism for the two carbon analog where the intermediate three-membered oxygen ring is usually postulated.¹¹

The rearrangements were carried out by heating the ethers in sealed tubes at 190–200° for five hours. The phenols that were formed were converted to the corresponding methoxy compounds for ease of handling in the subsequent oxidation steps. Chart III is a flow sheet of the degradative procedure.

Table I summarizes the radioactive counting data for the various carbon atoms of the allyl group in the ethers and phenols.

TABLE I
DISTRIBUTION OF RADIOACTIVITY

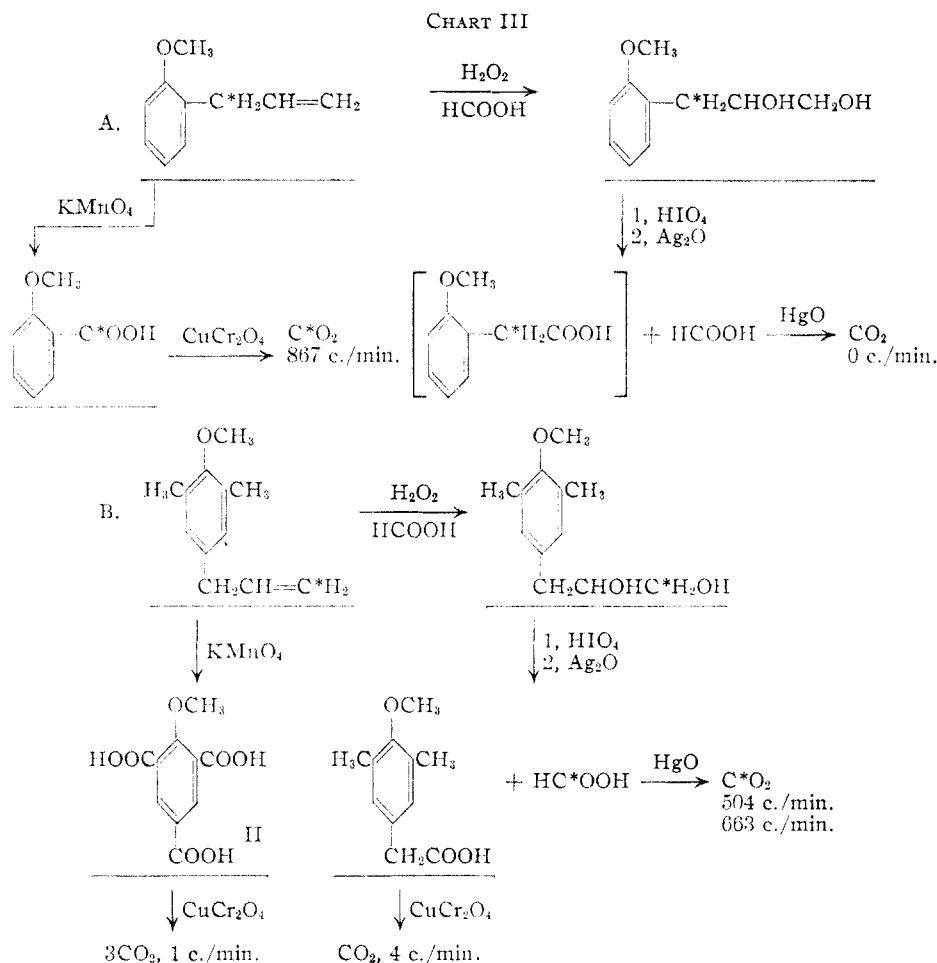
Compound	Carbon position	Counting rates, c./min.
Phenyl allyl ether	γ -Carbon of allyl	872 \pm 13 ¹²
	All except γ -carbon of allyl	0 \pm 5
<i>o</i> -Allylphenol	α -Carbon of allyl	867 \pm 13
	γ -Carbon of allyl	5 \pm 4
2,6-Dimethylphenyl allyl ether	γ -Carbon of allyl	723 \pm 12
	γ -Carbon of allyl	708 \pm 12
	All except γ -carbon of allyl	0 \pm 5
4-Allyl-2,6-dimethylphenol	γ -Carbon of allyl	504 \pm 10 ¹³
	γ -Carbon of allyl	663 \pm 10
	β -Carbon of allyl	4 \pm 4
	α -Carbon of allyl	3 \pm 4

The results of the ortho rearrangement show that migration with inversion of the allyl group is the

(11) E.g., C. E. Wilson and H. J. Lucas, *THIS JOURNAL*, **58**, 2396 (1936).

(12) All measurements were carried out with a Q-gas counter, a windowless, gas flow Geiger-Muller counter. The counting rates were determined for "infinitely" thick uniform layers of barium carbonate. These values are proportional to the specific activity of the specific carbon position and can be compared directly. The counting error is the standard deviation error for sample and background counting rates.

(13) The low radioactivity balance for the para rearrangement may be due to the lack of specificity of periodic acid in cleaving the glycol. A small amount of oxidation of the β -carbon would lower the counting rate for the γ -carbon.



only reaction that occurs. The radioactive balance is excellent and the picture of an intramolecular cyclic mechanism is corroborated by this study.

The results for the para rearrangement indicate clearly that migration with no inversion of the allyl group is the only reaction that occurs. In the rearrangement the allyl group is never free enough to undergo resonance. This is in accord with Hurd's double-cycle mechanism or with a π -complex mechanism in which the allyl group does not undergo resonance.

Experimental

3-Phenoxy-1-propene-1-C¹⁴ and 3-(2,6-Dimethylphenoxy)-1-propene-1-C¹⁴.—Chart I indicates the synthetic route used to prepare two phenyl allyl ethers containing radioactive carbon. Standard synthetic procedures were used throughout. From preliminary experiments with non-radioactive compounds, it was known that the LiAlH₄ reduction of the acid (I) was the step with lowest yield (25–35%). This reaction was carried out according to the procedure of Nystrom and Brown¹⁴ at ice temperature to minimize reduction of the chloro group. A typical preparation was made from 6.2 g. of NaCN containing approximately 300 microcuries of C¹⁴; yield¹⁵ 9.3 g. of 3-phenoxy-1-propene-1-C¹⁴, b.p. 88–90° (22 mm.), n_D^{20} 1.5200 (lit. b.p. 91–91.5° (19 mm.), n_D^{20} 1.5231¹⁶); 8.5 g. of 3-(2,6-dimethyl-

phenoxy)-1-propene-1-C¹⁴, b.p. 90–94° (13 mm.); n_D^{20} 1.5053 (lit. b.p. 67–68° (2 mm.), n_D^{20} 1.5048¹⁷).

The following new compounds in this synthetic scheme were analyzed¹⁸: 3-(2,6-dimethylphenoxy)-propanol, b.p. 144–146° (13 mm.), colorless liquid, n_D^{20} 1.5170.

Anal. Calcd. for C₁₁H₁₆O₂: C, 73.3; H, 8.90. Found: C, 73.1; H, 9.23.

3-(2,6-Dimethylphenoxy)-propyl bromide, colorless liquid, b.p. 140–142° (12 mm.), n_D^{20} 1.5290.

Anal. Calcd. for C₁₁H₁₆OB: C, 54.3; H, 6.17. Found: C, 54.4; H, 6.17.

Degradation of the Ethers.—Chart II indicates the degradative procedure used to determine the distribution of radioactive carbon in the ethers.

A. Hydroxylation Reaction.—The method described by Swern, Billen and Scanlan¹⁹ was used: 1,2-dihydroxy-3-phenoxypropane-1-C¹⁴, m.p. 62–64° (lit. m.p. 48–53°, can be raised to 70° by repeated recrystallizations from anhydrous ether).²⁰ 1,2-Dihydroxy-3-(2,6-dimethylphenoxy)-propane-1-C¹⁴, white needles, m.p. 48–49°.

Anal. Calcd. for C₁₁H₁₆O₃: C, 67.3; H, 8.18. Found: C, 67.3; H, 8.11.

B.—These glycols were cleaved with periodic acid, the resulting aldehydes were oxidized with silver oxide, and formic acid was steam distilled from the mixture. The formic acid fraction was oxidized with HgO according to the procedure of Wood, Osburn and Werkman.²¹ The carbon dioxide evolved was absorbed in NaOH and precipitated as BaCO₃. A sample for radioactivity measurements was prepared by filtration.²²

The residual phenoxyacetic acids were purified and totally combusted using the Van Slyke-Folch wet oxidation method.²³ Samples for radioactivity measurements were made from this fraction: 1, 3-phenoxy-1-propene-1-C¹⁴: HCOOH, 872 ± 13 c./min.; phenoxyacetic acid (m.p. 96–96.5°), 0 ± 5 c./min.; 2,3-(2,6-dimethylphenoxy)-1-propene-1-C¹⁴: HCOOH, 732 ± 12 c./min., 708 ± 12 c./min.; 2,6-dimethylphenoxyacetic acid (m.p. 138–138.5°), 0 ± 5 c./min.

Rearrangement of the Ethers.—The rearrangement reactions were carried out by heating the ethers in sealed glass tubes for 5 hours at 190–200°. The products were dissolved in 20% NaOH and extracted with pet. ether (b.p. 68°) to remove any unrearranged material. The methoxy derivatives were prepared using dimethyl sulfate and purified.

1-(2-Methoxyphenyl)-2-propene-1-C¹⁴, b.p. 87–89.5° (13 mm.), n_D^{20} 1.5218 (lit. b.p. 86–87° (12 mm.), n_D^{20} 1.526).²⁴

(17) D. S. Tarbell and J. F. Kincaid, *THIS JOURNAL*, **62**, 728 (1940).

(18) The analyses were carried out by Mr. R. E. Kelly, E. L. Wheeler and R. K. Davis.

(19) D. Swern, G. N. Billen and J. T. Scanlan, *THIS JOURNAL*, **68**, 1506 (1946).

(20) T. S. Wheeler and F. G. Wilken, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 297.

(21) H. G. Wood, O. L. Osburn and C. H. Werkman, *Ind. Eng. Chem., Anal. Ed.*, **5**, 247 (1935).

(22) F. C. Henriques, Jr., G. B. Kistiakowsky, C. Margnetti and W. G. Schneider, *ibid.*, **18**, 349 (1946).

(23) D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **163**, 509 (1940).

(24) R. Adams and R. E. Rindfusz, *THIS JOURNAL*, **41**, 659 (1919).

(14) R. F. Nystrom and W. G. Brown, *THIS JOURNAL*, **70**, 3738 (1948).

(15) Non-radioactive compounds were added at various stages of the synthesis to prevent holdup. Consequently it is not possible to give an over-all yield.

(16) R. M. Leekley, Ph.D. Thesis, Univ. of Minnesota, 1938.

3-(3,5-Dimethyl-4-methoxyphenyl)-1-propene-1-C¹⁴, colorless liquid, b.p. 113–114° (11 mm.), n_D^{20} 1.5182.

Anal. Calcd. for C₁₂H₁₆O: C, 81.8; H, 9.10. Found: C, 81.8; H, 9.18.

Degradation of Rearrangement Products.—Chart III indicates the degradative route used to determine the distribution of radioactive carbon-14 after the rearrangement.

A. Hydroxylation Reaction.—The method described by Swern, Billen and Scanlan was used.¹⁹ The oily products were dissolved in sufficient anhydrous ether to give a viscous, but not solid, mass at –80°. Crystallization was induced by scratching the walls of the container as the material was warmed slowly to room temperature. As soon as crystals formed, the solvent was removed at reduced pressure to prevent the solid from redissolving.

2,3-Dihydroxy-1-(2-methoxyphenyl)-propane-1-C¹⁴, white needles, m.p. 62–63°.

Anal. Calcd. for C₁₀H₁₄O₃: C, 66.0; H, 7.70. Found: C, 66.2; H, 8.21.

1,2-Dihydroxy-3-(3,5-dimethyl-4-methoxyphenyl)-propane-1-C¹⁴, white needles, m.p. 81–82°.

Anal. Calcd. for C₁₂H₁₈O₃: C, 68.6; H, 8.58. Found: C, 69.0; H, 8.79.

B. Periodic Acid Cleavage of the Glycols.—1-(2-Methoxyphenyl)-2-propene-1-C¹⁴, HCOOH fraction, 5 ± 4 c./min. The corresponding methoxyphenylacetic acid was not isolated. KMnO₄ oxidation of 1-(2-methoxyphenyl)-2-propene-1-C¹⁴ yielded 2-methoxybenzoic-carboxy-C¹⁴ acid which was decarboxylated with copper chromite catalyst²⁵; 3-(3,5-dimethyl-4-methoxyphenyl)-1-propene-1-C¹⁴; HCOOH fraction, 504 ± 10 c./min.; 663 ± 10 c./min.; 3,5-dimethyl-4-methoxyphenylacetic acid, white needles, m.p. (sealed tube) 191–192°.

Anal. Calcd. for C₁₁H₁₄O₃: C, 68.0; H, 7.23. Found: C, 67.8; H, 7.14.

Decarboxylation of this acid with copper chromite gave the following counting rate: 4 ± 4 c./min.

KMnO₄ oxidation yielded methoxytrimesic acid (II); white powder, m.p. 235–250° dec. (lit. m.p. 248° dec.).²⁶ This compound was further characterized by preparation of its trimethyl ester using diazomethane; m.p. 85–86° (lit. m.p. 86°).²⁶ Decarboxylation of II with copper chromite gave: 1 ± 4 c./min.

(25) W. A. Lazier and H. R. Arnold, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 142.

(26) F. Ullmann and K. Brittner, *Ber.*, **42**, 2543 (1909).

MINNEAPOLIS 14, MINNESOTA

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

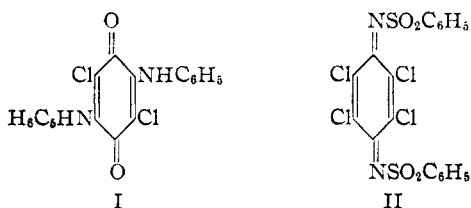
Quinone Imides. XXII. The Reaction of Primary Aromatic Amines with 2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide¹

BY ROGER ADAMS AND B. H. BRAUN²

RECEIVED JULY 10, 1952

2,3,5,6-Tetrachloro-*p*-quinonedibenzenesulfonimide (II) gives equimolar addition products with aniline, *o*-toluidine, *m*-toluidine and 2,6-dimethylaniline; it is reduced to the corresponding diamide by *p*-toluidine, 2,4-dimethylaniline and mesidine; no reaction occurs with 2,4,6-trichloroaniline. The addition products contain primary amino groups, as exemplified by reactions of the anilino compound; benzenesulfonation, diazotization and coupling to a dye with β -naphthol, replacement of the amino group with hydrogen. Confirmation that the *para* hydrogen to the amino group has taken part in the addition was obtained by the fact that dimethylaniline also added. The adducts appear to be *p,p'*-diaminodiphenylamine derivatives (III, IV) formed by 1,6-addition of the amines to the N,N conjugated system.

Chloranil reacts readily with aniline³; the chief product is 2,5-dianilino-3,6-dichloro-*p*-quinone (I). Other primary aromatic amines react similarly.^{3,4}



2,3,5,6-Tetrachloro-*p*-phenylenedibenzenesulfonamide has been synthesized by successive oxidations and additions of hydrogen chloride to *p*-phenylenedibenzenesulfonamide⁵ or more conveniently by chlorination of *p*-phenylenedibenzenesulfonamide in

dimethylformamide.⁶ By oxidation, the dibenzenesulfonimide analog of chloranil, 2,3,5,6-tetrachloro-*p*-quinonedibenzenesulfonimide (II), is formed.

The reaction of II with aniline and other amines has been investigated. The results were unexpected; the course of the reaction is completely different from that of chloranil with the same amines.

When II and either one mole equivalent or excess of aniline were mixed in chloroform solution, a reaction occurred and a colorless addition product separated in good yield. It was an adduct of one molecule of aniline and one molecule of II, with chloroform of solvation. Acetone and acetic acid solvates were also prepared. The solvation did not interfere with the subsequent reactions of the compound. The product contained a primary amino group as revealed by diazotization and coupling with β -naphthol to form a dye, by benzenesulfonation, and by diazotization and replacement of the amino group by hydrogen. The infrared spectrum indicated the presence of three N–H groupings. The molecule, on the basis of these facts, was postulated as being a diphenylamine derivative of structure III. A 1,6 addition to the N,N conjugated system of II had occurred with a proton

(1) For paper XXI, see R. Adams and W. Moje, *THIS JOURNAL*, **74**, 5562 (1952).

(2) An abstract of a portion of a thesis submitted by B. H. Braun to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) O. Hesse, *Ann.*, **114**, 292 (1860); H. von Knapp and G. Schultz, *ibid.*, **210**, (1881); M. Niemeyer, *ibid.*, **228**, 322 (1885); M. Andresen, *J. prakt. Chem.*, **136**, 422 (1883); A. W. Hofmann, *Jahresb.*, 416 (1863).

(4) H. Imbert and J. Pages, *Bull. soc. chim. France*, [3] **19**, 575 (1893); M. Martynoff and G. Tsatsas, *ibid.*, [5] **14**, 52 (1947); Swiss Patent 225,370, May 17, 1943 [*C. A.*, **43**, 5964 (1949)].

(5) R. Adams, E. F. Elslager and K. F. Heumann, *THIS JOURNAL*, **74**, 2608 (1952).

(6) R. Adams and B. H. Braun, *ibid.*, **74**, 3171 (1952).