water. After the aqueous mixture was extracted four times with 100 ml. of ethyl ether, the ether extract was washed with 5% sodium bicarbonate solution and water. The ether was removed and the residue purified by chromatography on 75 g. of alumina. A yellow solid (430 mg.) was eluted with 40% benzene in petroleum ether (30–60°). Recrystallization of the crude material from petroleum ether (60–68°) gave 2-nitro-3,5-diphenylthiophene (360 mg., 40%, m.p. 110–111°). A mixture melting point with III obtained by the nitration of 2,4-diphenylthiophene was not depressed.

Nitration of 2,4-Diphenylthiophene.—2,4-Diphenylthiophene[9] (608 mg., 2.60 mmoles) was dissolved in acetic anhydride (50 ml.) and to this solution was added the nitrating mixture (0.25 ml., 2.5 mmoles) described in the first experiment. The reaction mixture turned yellow and was kept at room temperature for ten minutes. The solution was poured into ice-water and after the acetic anhydride was hydrolyzed, the yellow solid that formed was filtered, washed well with water, dried and chromatographed on 65 g. of alumina. The eluant with 20% benzene in petroleum ether (30–60°) contained unchanged starting material (395 mg., 65%, m.p. 119.5–121°). This material did not depress the melting point of 2,4-diphenylthiophene.

With 30% benzene in petroleum ether (30–60°), a pale yellow solid (21 mg., 3%, m.p. 105–107) was first eluted. Recrystallization of this crude material from petroleum ether (60–68°) gave 2,4-diphenyl-3-nitrothiophene, m.p. 113–115°.

After the 2,4-diphenyl-3-nitrothiophene, a bright yellow solid (180 mg.) was eluted with 30% benzene in petroleum ether (30–60°). Recrystallization of this solid from petroleum ether (60–68°) gave 2-nitro-3,5-diphenylthiophene (135 mg., 18%, m.p. 108–109°). A pure sample melted at 110–111° and the infrared and ultraviolet spectra of this sample were identical to those of III. Also a mixture of the two samples melted at 110–111°.

MINNEAPOLIS, MINNESOTA

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[9] E. Campaigne, THIS JOURNAL, **66**, 684 (1944).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

Orientation in Aromatic Substitution by the Benzenesulfonimido Radical[1]

BY O. C. DERMER AND M. T. EDMISON[2]

RECEIVED JUNE 5, 1954

The thermal decomposition of benzenesulfonyl azide in solution yields radicals capable of initiating vinyl polymerization. The action of these radicals on various monofunctional derivatives of benzene and hydrolysis of the resulting substituted benzenesulfonanilides gives a mixture of isomeric substituted anilines. Spectrophotometric determination of these anilines showed that groups *ortho–para* directing in ordinary electrophilic substitution produce *ortho–meta–para* orientation of the benzenesulfonimido group in a ratio roughly approaching **4**:1:2.

The orientation in substitution of radicals on aromatic nuclei already bearing other groups is of value in the elucidation of mechanism of radical reactions. The reaction described by Curtius and co-workers,[3] in which the thermal decomposition of arenesulfonyl azides in aromatic liquids gave simple and N-substituted arenesulfonamides, appears to have involved radicals, as he thought, although it is not discussed by Waters.[4] Curtius' finding that *p*-toluenesulfonyl azide and dimethylaniline thus yield *p*-toluenesulfonamidodimethylanilines in the isomeric ratio of 2 *ortho* to 1 *para* is particularly interesting in view of recently published results of phenylation and hydroxylation experiments.

Methyl acrylate and especially acrylonitrile were found to polymerize at 110° in the presence of small amounts of decomposing benzenesulfonyl azide; this is taken as good evidence[5] of the presence of radicals. Furthermore, such polymerization of acrylonitrile was inhibited by the presence of traces of hydroquinone or *p*-benzoquinone.

According to the method of Curtius,[3] benzenesulfonyl azide was decomposed at 105–120° in various monosubstituted benzenes to yield nitrogen, benzenesulfonamide, and isomeric benzenesulfonanilides. The solid sulfonamide–sulfonanilide mixture was isolated and hydrolyzed in 25% hydrochloric acid and the substituted anilines were extracted, usually after steam distillation from alkaline solution. The extract was analyzed spectrophotometrically for the *ortho*, *meta* and *para* isomeric forms of the substituted anilines by the method of Vaughn and Stearn.[6]

The quantitative results are shown in Table I.

TABLE I

ISOMER RATIOS IN SUBSTITUTED ANILINES

Aromatic substrate	Ratio of isomeric anilines, % *ortho*	 *meta*	 *para*
Toluene	60,61	12,11	28,28
Chlorobenzene	54,57	18,13	28,30
Bromobenzene	54,61	14,6	32,33
Anisole	48,60	26,17	26,33
Phenol	58	20	22

Experiments with benzoyl chloride, benzonitrile and methyl benzoate as substrates all yielded mixed aminobenzoic acids as final products, but these could not be isolated for spectrophotometric analysis without disturbing the isomer ratio in the mixture, as shown by knowns. Unfortunately chromatographic separation was not tested. The results were sufficient only to indicate that *ortho* substitution was predominant in the reaction of these derivatives of benzoic acid. The reaction of benzenesulfonyl azide with nitrobenzene gave an intractable tar, as reported by Curtius, and nitric oxide, evidently by an unexpected reaction with the nitro group. The preferential attack on a nitro

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[1] Abstracted from the Ph.D. dissertation of M. T. Edmison, May, 1952. Presented in part at the 7th Southwest Regional Meeting of the American Chemical Society, December, 1951.

[2] University of Arkansas, Fayetteville, Arkansas.

[3] T. Curtius, *J. prakt. Chem.*, **125**, 303 (1930).

[4] W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, New York, N. Y., 1946.

[5] K. Ziegler, W. Deparade and H. Kuhlhorn, *Ann.*, **567**, 151 (1950); K. Ziegler, W. Deparade and W. Meye, *ibid.*, **567**, 141 (1950).

[6] R. T. Vaughn and A. E. Stearn, *Anal. Chem.*, **21**, 1361 (1949).

group by radicals has been noted by Hammond and co-workers.[7]

Whether the mechanism of nuclear attack involves a true "free" geminal biradical or a "krypto-radical" intermediate[8] is pure speculation. It is possible that the benzenesulfonimido radical adds to an aromatic nucleus, as the substituted methylene radical from ethyl diazoacetate does,[9] with later rupture of one bond coincident with or subsequent to migration of a hydrogen atom from carbon to nitrogen. However, an induced mechanism modeled after that suggested by DeTar and Sagmanli[10] better accounts for the formation of benzenesulfonamide.

$$C_6H_5SO_2N_3 \longrightarrow C_6H_5SO_2N\colon + N_2 \tag{1}$$

$$C_6H_5SO_2N\colon + ArH \longrightarrow C_6H_5SO_2NH\cdot + Ar\cdot \tag{2}$$

$$Ar\cdot + C_6H_5SO_2N_3 \longrightarrow C_6H_5SO_2\underset{\cdot}{N}Ar + N_2 \tag{3}$$

$$C_6H_5SO_2\underset{\cdot}{N}Ar + ArH \longrightarrow C_6H_5SO_2NHAr + Ar\cdot \tag{4}$$

$$C_6H_5SO_2NH\cdot + ArH \longrightarrow C_6H_5SO_2NH_2 + Ar\cdot \tag{5}$$

The obvious unanswered question here is why the Franck–Rabinowitsch proximity of the two radicals generated in equation 2 does not invariably cause their combination. Whether biphenyl derivatives are formed by the interaction of Ar· and ArH remains unknown; the analytical procedure used would not tell.

Table I shows that *ortho* substitution products considerably predominate, as they do in the majority of substitutions in aromatic nuclei by radicals. The fact that the over-all isomer ratios approach the statistical 2:1 for *ortho–para* substitution may be coincidental but appears worthy of remark, the more so since it confirms Curtius' more limited observation.

Experimental

Benzenesulfonyl Azide.—To 22 g. (0.34 mole) of recrystallized sodium azide dissolved in 50 ml. of warm water was added a 90-ml. portion of 95% alcohol and the mixture was cooled in an ice–salt-bath. Forty-five grams (0.25 mole) of benzenesulfonyl chloride, diluted with twice its volume of 95% alcohol, was added slowly to the mechanically stirred cold sodium azide solution. The mixture turned orange and then red in color. Stirring was continued for 30 minutes in the cold and for another 30 minutes at room temperature. At the end of this time the red color had disappeared. The mixture was transferred to a one-liter separatory funnel and diluted with 100 ml. of water. Upon standing, the mixture deposited a clear colorless oil at the bottom of the funnel; 48 g. of such crude product was removed. The water layer was extracted with two 25-ml. portions of the ethyl ether and the ether extract was added to the oil in a small separatory funnel. The ether solution was then washed four times with 30-ml. portions of water and dried over sodium sulfate. Removal of the ether by warming on a water-bath at 50° under vacuum gave 39 g. of benzenesulfonyl azide (84% based on benzenesulfonyl chloride). Pure benzenesulfonyl azide decomposed rapidly but quietly upon being warmed to approximately 105°, but the crude product obtained prior to final thorough washing of the ether solution detonated violently upon heating. A small amount of the crude product was sufficient to cause a shattering explosion.

Preparation of Substitution Products.—Substitution reactions with various monofunctional derivatives of benzene were accomplished by adding benzenesulfonyl azide to the aromatic liquid in sufficient quantity to make a solution of 5–10% concentration. This solution was then heated at 105–120° in a flask carrying a reflux condenser equipped with a calcium chloride drying tube. Evolution of nitrogen was no longer apparent after approximately 10 hr., but heating was continued without interruption in each case for a total of 48 hours.

At the end of the 48-hour period the excess aromatic liquid was removed from the reaction mixture by vacuum distillation followed by steam distillation. Steam distillation sometimes caused hydrolysis of part of the aromatic liquid to difficultly distillable products, but these were eliminated by subsequent extractive procedures.

The tarry non-volatile residue was extracted with much 5% aqueous sodium hydroxide solution in order to dissolve all benzenesulfonamide and benzenesulfonanilides. The basic extract, which was very dark in color, was treated with a small amount of decolorizing charcoal, filtered, and made acid with dilute hydrochloric acid. The liquid, now containing suspended precipitate, was thoroughly extracted with ether and the ether was then evaporated in order to obtain a crystalline mixture of benzenesulfonamide and isomeric benzenesulfonanilides. The various runs thus made are summarized in Table II.

TABLE II

PREPARATION OF SUBSTITUTION PRODUCTS

Aromatic liquid Name	Moles	Benzenesulfonyl azide, moles × 10^2	Crystalline product, moles × 10^{2a}
Toluene	1.09	5.5	2.2
Toluene	1.85	8.2	3.2
Chlorobenzene	1.43	8.7	5.8
Chlorobenzene	1.79	8.2	4.3
Bromobenzene	1.91	9.8	2.6
Bromobenzene	1.91	11.5	1.8
Anisole	1.85	8.2	1.3
Anisole	1.85	8.2	1.9
Phenol	2.13	8.2	3.4
Nitrobenzene	1.63	5.5	None
Benzonitrile	1.94	5.5	0.97
Benzonitrile	1.55	6.0	1.2
Methyl benzoate	1.47	8.2	17[b]
Methyl benzoate	1.10	5.5	12[b]
Benzoyl chloride	1.43	8.2	19[b]
Benzoyl chloride	1.43	8.2	14[b]

[a] Calculated as sulfonanilides. [b] Evidently much benzoic acid remained at this stage.

Preparation of Samples for Analysis.—The mixture of amides and isomeric anilides from each experiment was hydrolyzed by refluxing for 48 hours in approximately 10 ml. of 25% hydrochloric acid per gram of crystalline mixture. In every case where the isomeric substituted anilines produced by hydrolysis were steam-distillable, superheated steam was passed into the reaction flask after the solution had been made distinctly alkaline with sodium hydroxide solution. Steam distillation was continued in each case until the distillate no longer gave a positive 2-naphthol coupling test for aromatic amine. The steam distillate was collected in brown bottles to minimize discoloration of the distillate prior to extraction of the amine from the aqueous mixture. As a control a mixture of the synthetic benzenesulfonyl derivatives in known ratio (for the toluidines) or a similarly known mixture of the three isomeric amines (for the other substituted anilines) was refluxed in 25% hydrochloric acid and treated in every way just like the unknown mixture throughout the remaining procedures.

Repeated extraction of the bases was carried out, in some instances with the solvent which was to be used in the spectrophotometric procedure. In others, ether was used for the extraction and evaporated off afterward. Since steam distillation from the hydrolyzed mixture was not feasible in the case of aminophenols and aminobenzoic acids, they were isolated by extraction only.

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(7) G. S. Hammond and P. D. Bartlett, *J. Polymer Sci.*, **5**, 617 (1951); G. S. Hammond and A. Ravve, THIS JOURNAL, **73**, 1891 (1951); G. S. Hammond, J. T. Rudesill and F. J. Modic, *ibid.*, **73**, 3929 (1951).

(8) R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).

(9) *Cf.* the similar but erroneous structure suggested by T. Curtius and Schmidt, *Ber.*, **55**, 1571 (1922); Schmidt, *ibid.*, **55**, 1581 (1922).

(10) D. F. De Tar and S. V. Sagmanli, Jr., THIS JOURNAL, **72**, 965 (1950).

The acid hydrolyzate that contained hydrochlorides of the aminophenols was first freed of any steam-volatile material by passing superheated steam through it for three hours. The solution was then transferred to a brown bottle, cooled in an ice-bath, neutralized with 20% sodium carbonate solution, and quickly extracted with ether. The ether solution was dried over anhydrous sodium sulfate in a dark cupboard. It was necessary to accomplish these steps rapidly and with minimum access of air in order to avoid rapid discoloration of the solution of aminophenols.

The acid hydrolyzate containing the hydrochlorides of aminobenzoic acids was likewise freed of steam-volatile material by the use of superheated steam. The solution was then made strongly alkaline by addition of sodium hydroxide solution and superheated steam was again passed through it for a two-hour period. The mixture was then adjusted to the arbitrarily chosen *p*H of 5 and the isomeric aminobenzoic acids, which partly precipitated, were removed by repeated extraction with ether. The combined ether solutions were then dried over anhydrous sodium sulfate.

Determination of Isomer Ratios.—All analyses of mixtures of isomeric substituted anilines were done by the method of Vaughn and Stearn[6] using the Beckman quartz spectrophotometer, model DU, with hydrogen lamp and 1-cm. quartz cells. Standard solutions of each of the three isomers involved in any one experiment were carefully prepared from amines especially purified or in two cases synthesized (*m*-anisidine and *m*-aminobenzoic acid) for the purpose. All three solutions were of the same concentration (approximately 0.001 *M*). The optical density of each solution was then determined at wave lengths 1 mμ apart in the range 240 to 320 mμ. The numerical values for the optical density were then plotted as a function of the wave length. The curves thus produced, which corresponded closely to those found in the literature,[11] were used in choice of wave lengths, pairing of optical densities, and graphical evaluation of the composition of the mixtures—first for the known, next for the unknown, and then for a verifying known matching the behavior of the unknown.

The concentrations of solutions of the mixed isomeric substituted anilines had to be established in order to permit dilution to the same molar concentration as the standard solutions and finally to match each solution empirically by mixing standard solutions of pure isomers. Titrations for this purpose were carried out in glacial acetic acid with perchloric acid in the same solvent using methyl violet as the indicator.[12] Verification of the accuracy of dilution was obtained in each case by the fact that the values obtained for optical density agreed with those of the matching mixture of standard solutions.

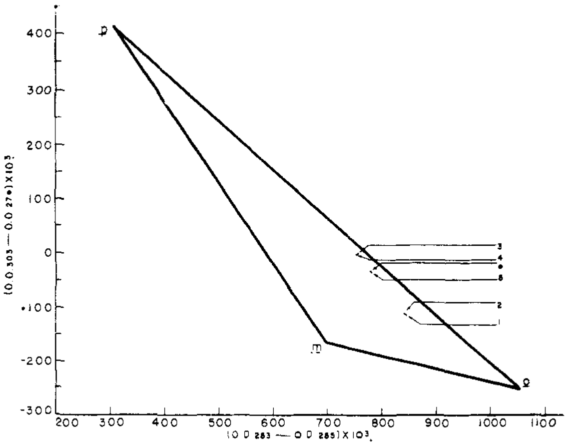

Fig. 1.—Differences in optical density at selected wave lengths, chloroanilines: 1, control mixture; 2, matching solution for control; 3, experiment 3; 4, matching solution for experiment 3; 5, experiment 4; 6, matching solution for experiment 4.

The detailed procedure is illustrated by the following typical experiment. Sixteen grams of benzenesulfonyl azide was added to 160 g. of dry pure chlorobenzene in a 300-ml. three-neck flask equipped with a reflux condenser carrying a calcium chloride drying tube. The temperature was maintained at 105–120° for 48 hours, during which time the mixture changed from yellow to light brown and then to a very dark brown. Evolution of gas was apparent almost as soon as the temperature reached 105° but was no longer noticeable after six hours. At the end of the 48-hour period the excess chlorobenzene was removed by vacuum distillation followed by steam distillation; a total of three liters of aqueous distillate was collected. The dark residue remaining in the flask was extracted with 200 ml. of 5% sodium hydroxide solution in four portions. All the material in the flask apparently dissolved. To the solution was added 5 g. of decolorizing carbon which was then filtered out by suction and washed with water. The combined filtrate was extracted with 200 ml. of ether which was discarded. The basic aqueous solution was then made distinctly acid by addition of 25% hydrochloric acid and the acid mixture was extracted with three 100-ml. portions of ethyl ether. The ether solution was then dried for 12 hours over anhydrous sodium sulfate.

The sodium sulfate was removed from the ether solution by careful decanting and filtering, after which the ether was removed by evaporation. The yield was 16.25 g. of light brown crystalline material.

Most (15.50 g.) of the mixture of benzenesulfonamide and isomeric chloroanilides of benzenesulfonic acid was placed in a 300-ml. round-bottom flask and 150 ml. of 25% hydrochloric acid was added. The mixture was refluxed for 48 hours. A control mixture of 3.000 g. of *o*-chloroaniline, 1.500 g. of *m*-chloroaniline and 1.000 g. of *p*-chloroaniline (54.5, 27.3 and 18.2%, respectively) was refluxed in 25 ml. of 25% hydrochloric acid for the same length of time.

While the above mixtures were being refluxed in hydrochloric acid, standard solutions of *o*-chloroaniline, *m*-chloroaniline and *p*-chloroaniline, each 0.0006 *M*, were prepared in spectrographic-grade isoöctane. From the optical densities of these solutions, it was determined that wave lengths 265, 274, 285 and 305 mμ were suitable for establishing the necessary triangle. The optical densities at these wave lengths were paired and differences taken (optical density$_{285}$ − optical density$_{265}$ and optical density$_{305}$ − optical density$_{274}$). The values were plotted and the points connected to determine the triangle shown in Fig. 1.

The acid mixture from the control, which had been refluxed for 48 hours, was cooled, treated with 3 g. of decolorizing charcoal, filtered and rendered distinctly alkaline by the addition of 25% sodium hydroxide solution. It was then steam-distilled in an all-glass system, with no stopcock grease on any of the joints, until the distillate being collected failed to give a 2-naphthol coupling test for aromatic amine. Approximately 2 liters of distillate was collected. This was extracted with 200 ml. of isoöctane in three portions. The isoöctane solution was then dried over anhydrous sodium sulfate in a dark cupboard for three hours, after which the solution was titrated as described previously and diluted to the same concentration as the standard solutions (0.0006 *M*). The values obtained were plotted in Fig. 1 and the approximate ratio was determined graphically from the position of the point on lines drawn in turn from each apex through the point to the opposite side of the triangle. The actual value was then determined by preparation of a matching solution from pure standards as is indicated also in Fig. 1.

Since the results obtained from the control mixture indicated only very slight disturbance of the isomer ratio during steam distillation and subsequent manipulations, the unknown mixtures obtained from a duplicate experiment with chlorobenzene were treated in exactly the same manner with results also as shown in Fig. 1.

Since the selection of wave lengths in the several analyses is quite critical, those used are shown in Table III.

Great care was exercised in each step of the anlytical procedure to avoid alterations of the isomer ratios. The products obtained from the decomposition of benzenesulfonyl azide were isolated by extraction of the reaction mixtures with sodium hydroxide. This procedure isolated the desired alkali-soluble compounds, after volatile components

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[11] C. Forster and J. Wagner, *Z. physik. Chem.*, **35**, 343 (1937); P. Grammaticakis, *Bull. soc. chim., France*, **18**, 220 (1951); R. A. Morton and A. McGookin, *J. Chem. Soc.*, 901 (1934); R. A. Morton and A. L. Stubbs, *ibid.*, 1347 (1940); M. Pestemer and H. Flaschka, *Monatsh.*, **71**, 325 (1938).

[12] E. Wilson, *J. Soc. Chem. Ind.*, **67**, 237 (1948); P. C. Markunas and J. A. Riddick, *Anal. Chem.*, **23**, 337 (1951).

TABLE III

WAVE LENGTHS CHOSEN FOR PAIRING OF OPTICAL DENSITIES

Amines determined	Wave length pairs, mμ
Toluidines	285–260, 296–256
Chloroanilines	285–265, 305–274
Bromoanilines	296–269, 305–273
Anisidines	302–269, 286–263
Aminophenols	286–258, 299–264
Aminobenzoic acids	255–310, 244–325

had first been removed by distillation. No attempt was made to separate benzenesulfonamide from the N-substituted sulfonamides since such a separation would have been prejudicial to the maintenance of original isomer ratios.

The procedure subsequent to hydrolysis effected a second purification. Steam was first passed through the *acid* reaction mixture to remove any volatile material which might still have been present, and steam distillation after the solution had been made *alkaline* effected a further separation from any possible non-volatile components still present. Ammonia from hydrolysis of the sulfonamide would still be present but not appreciably extracted from the dilute aqueous solutions by the organic solvents used. Moreover, ammonia does not absorb in the spectral region used for analysis.

The results reported for the reaction with phenol are based upon one experiment only, and isolation of the mixed aminophenols was accomplished by extraction rather than by steam distillation. Nevertheless, comparison of the results with those of the control procedure with the aminophenols leads to the conclusion that the results are substantially correct.

The *p*H chosen for precipitation of the aminobenzoic acids did not allow them to be isolated in the ratio of isomers which existed in the reaction products. Thus a known mixture of 50% *o*-, 30% *m*- and 20% *p*-aminobenzoic acids appeared after processing to consist of 53% *o*-, 47% *m*- and no *p*-. It is extremely doubtful whether any suitable single *p*H value could be found for this precipitation.

When benzenesulfonyl azide was heated in nitrobenzene as indicated in Table II, a considerable evolution of a brown gas was noticed. This gas instantly liberated iodine from aqueous potassium iodide solution, and on this basis and that of color was tentatively identified as nitrogen dioxide. However, when the reaction occurred in a nitrogen atmosphere, the gas evolved failed to liberate iodine from oxygen-free potassium iodide solution. After passing through a 5% sodium hydroxide solution into an air-mixing chamber, the gas did liberate iodine from a second portion of the potassium iodide solution. It is evident that nitric oxide was produced and that it subsequently reacted with oxygen to produce nitrogen dioxide. There was no evidence of production of oxides of nitrogen from nitrobenzene alone and none when benzenesulfonyl azide was decomposed in toluene as a control experiment. The liquid reaction mixture from the reaction with nitrobenzene yielded only useless tars.

It appeared on the basis of structure that chloramine-T might decompose and react like benzenesulfonyl azide. Accordingly an approximately 7% solution of chloramine-T in nitrobenzene was heated. At 140° there was evolution of a brown gas, as from the azide solution, but no nitroanilides of *p*-toluenesulfonic acid could be isolated from the liquid reaction mixture. Owing to the comparatively high temperature needed to decompose chloramine-T, the reaction was not attempted in other aromatic liquids.

STILLWATER, OKLAHOMA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

Cyclic Dienes. IX. Synthesis of 1,2-Dimethylene-4-cyclohexene[1,2]

BY WILLIAM J. BAILEY[3] AND JOSEPH ROSENBERG[4]

RECEIVED MARCH 3, 1954

Proof that the pyrolysis of esters is an excellent synthetic procedure, if carried out so that carbonization is completely avoided, was obtained by the preparation of 1,2-dimethylene-4-cyclohexene in a 92% yield without the formation of any of the isomeric *o*-xylene. The structure of this triene was proved by isomerization to *o*-xylene, ultraviolet absorption and conversion to a known derivative through an intermediate Diels–Alder adduct.

The pyrolysis of esters has been used in many syntheses of olefins to avoid rearrangement. Thus, Whitmore and Rothrock[5] used this method to synthesize *t*-butylethylene without rearrangement. Marvel and Williams[6] pyrolyzed esters to synthesize 2-alkylbutadienes that could not be prepared in a pure state by dehydration of the alcohols. Pyrolysis of hexahydrophthalyl diacetate produced the strained diene, 1,2-dimethylenecyclohexane, in an 89% yield.[7] Even though the double bonds exocyclic to the six-membered ring have a strong tendency to rearrange to an internal position, the cyclic diene was pure enough to produce a high molecular weight polymer by emulsion polymerization.[8] In a similar manner, 4-methyl-1,2-dimethylenecyclohexane was produced in a 94% yield and 4,5-dimethyl-1,2-dimethylenecyclohexane in a 97% yield.[9]

However, there have also been reported several syntheses in which the olefin obtained was not pure, indicating that some rearrangment or dehydrogenation had taken place.[10]

Liquid-phase pyrolysis often results in extensive rearrangement. Thus, Manjunath and Plant[11] pyrolyzed 9-acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole to obtain 6-acetyl-9-methyl-4-indoxylspiropentane by a pinacol rearrangement.

It seemed likely that the side reactions that formed the impurities were due to drastic conditions and not inherent in the pyrolysis reaction.

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(1) Previous paper in this series, THIS JOURNAL, **76**, 5421 (1954).

(2) Presented before the Organic Division at the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(3) Department of Chemistry, University of Maryland, College Park, Maryland.

(4) Office of Naval Research Fellow, 1950–1951.

(5) F. C. Whitmore and H. S. Rothrock, THIS JOURNAL, **55**, 1106 (1933).

(6) C. S. Marvel and J. L. R. Williams, *ibid.*, **70**, 3842 (1948).

(7) W. J. Bailey and H. R. Golden, *ibid.*, **75**, 4780 (1953).

(8) W. J. Bailey and H. R. Golden, *ibid.*, **76**, 5418 (1954).

(9) W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **76**, 2251 (1954).

(10) (a) J. P. W. Houtman, J. Van Steenis and P. M. Heertjes, *Rec. trav. chim.*, **65**, 781 (1946); (b) R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin and P. V. Smith, *Ind. Eng. Chem.*, **39**, 887 (1947); (c) E. R. Alexander and A. Mudrak, THIS JOURNAL, **72**, 1810, 3194 (1950); (d) C. G. Overberger, A. Fischman, C. W. Roberts, L. A. Arond and J. Lab, *ibid.*, **73**, 2540 (1951).

(11) B. L. Manjunath and S. G. P. Plant, *J. Chem. Soc.*, 2260 (1926).