

TABLE III  
WAVE LENGTHS CHOSEN FOR PAIRING OF OPTICAL DENSITIES

Amines determined	Wave length pairs, m $\mu$
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 pH 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 pH 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.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

## Cyclic Dienes. IX. Synthesis of 1,2-Dimethylene-4-cyclohexene<sup>1,2</sup>

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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<sup>5</sup> used this method to synthesize *t*-butylethylene without rearrangement. Marvel and Williams<sup>6</sup> 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.<sup>7</sup> 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.<sup>8</sup> 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.<sup>9</sup>

However, there have also been reported several syntheses in which the olefin obtained was not pure, indicating that some rearrangement or dehydrogenation had taken place.<sup>10</sup>

Liquid-phase pyrolysis often results in extensive rearrangement. Thus, Manjunath and Plant<sup>11</sup> pyrolyzed 9-acetyl-10-acetoxy-11-hydroxy-6-methylhexahydrocarbazole to obtain 6-acetyl-9-methyl-4-indoxylspiro-pentane 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.

- (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).

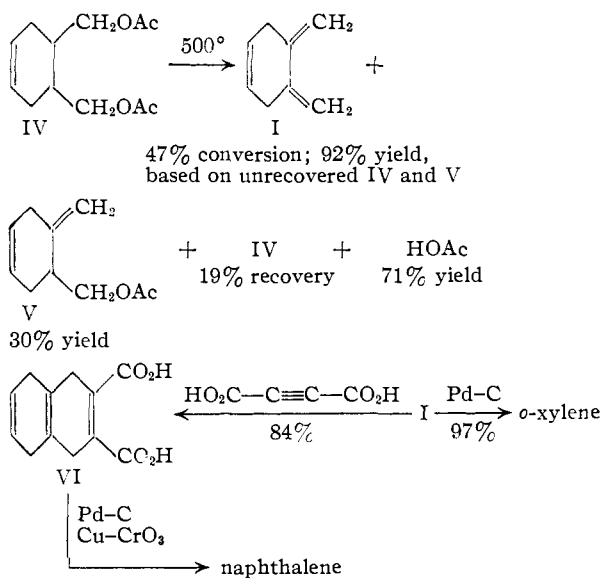
(11) B. L. Manjunath and S. G. P. Plant, *J. Chem. Soc.*, 2260 (1926).

In the synthesis of the strained cyclic dienes,<sup>7,9</sup> for example, it was shown that the optimum yield (based on unrecovered starting material) was obtained when only 60 to 70% of the theoretical acetic acid was cracked out and substantially no carbonization occurred. When a higher percentage of acetic acid was cracked out, carbonization which occurred in the column was accompanied by isomerization and aromatization plus the formation of gaseous products. It is probable that this carbon deposit is responsible for the low yields and impure products reported for the pyrolysis of esters. In order to test this hypothesis, an attempt was made to synthesize a compound that would have a very great tendency to rearrange. The highly strained 1,2-dimethylene-4-cyclohexene (I) appeared to be such a compound. This triene, which is an isomer of *o*-xylene, would have a large driving force to undergo rearrangement to form a stable aromatic ring. Thus, the synthesis of this triene in high yields would prove that in the pyrolysis of esters, in spite of the very high temperatures, the absence of any acidic catalyst produces relatively mild conditions and that if proper experimental conditions are employed the pyrolysis can be made to follow only a stereospecific cyclic transition state to produce unrearranged olefins.

*cis*- $\Delta^4$ -Tetrahydrophthalic anhydride (II) was reduced with lithium aluminum hydride to produce the glycol III in an 80% yield. III, in turn, was converted to *cis*- $\Delta^4$ -tetrahydrophthalyl diacetate (IV) in a 93% yield. The diacetate IV was dropped through a vertical tube packed with glass helices and externally heated at 500°. The rate of addition, flow of nitrogen, and the temperature of the column were controlled so that only 71% of the theoretical acetic acid was cracked out. Under these conditions no carbonization took place, and 1,2-dimethylene-4-cyclohexene (I) was obtained in a 47% conversion or a 92% yield (based on unrecovered starting material and the monoacetate V). If more vigorous conditions were used, a lower yield of material containing isomeric aromatics was obtained.

The structure of this highly unsaturated compound was proved by isomerization to *o*-xylene, conversion to naphthalene through an intermediate Diels-Alder adduct, and ultraviolet absorption. The ultraviolet absorption spectrum of the triene I, which showed no maximum or minimum above 220  $m\mu$  but appeared to reach a maximum just below 220  $m\mu$ , indicated the presence of conjugated double bonds, but the complete absence of any *o*-xylene. Treatment of 1,2-dimethylene-4-cyclohexene (I) with hydrochloric acid in acetic acid resulted in a low yield of *o*-xylene plus a polymer. However, the triene was recovered unchanged from a refluxing solution of anhydrous acetic acid. A high yield of *o*-xylene was obtained by heating the triene with palladium-on-charcoal. Dry Ice plus a trace of boron trifluoride converted the triene I to a soluble high molecular weight polymer. The properties of this polymer will be discussed in a subsequent paper. The triene I undergoes a Diels-Alder reaction with acetylenedicarboxylic acid to produce 1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic acid (VI). Simultaneous dehydrogenation and decarboxylation of this adduct produced naphthalene.

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Thus, it has been shown that 1,2-dimethylene-4-cyclohexene (I) has been synthesized in a high yield and in a high degree of purity by choosing pyrolysis conditions such that no carbonization takes place in the column. Therefore it seems likely that, if a triene with such an unstable structure can be synthesized by the pyrolysis of an ester, this same procedure can be used to produce almost any simple unsaturated compound without rearrangement. Research designed to determine the scope of this interesting reaction is now in progress in this Laboratory.

### Experimental<sup>12</sup>

*cis*- $\Delta^4$ -Tetrahydrophthalyl Alcohol (III).—To a suspension of 46 g. (1.21 moles) of lithium aluminum hydride in 250 ml. of dry ether, contained in a 5-liter, three-necked flask, equipped with a stirrer, a condenser and a dropping funnel, was added, with stirring, an ether suspension of 125 g. (0.822 mole) of *cis*- $\Delta^4$ -tetrahydrophthalic anhydride (II). After the mixture had been stirred for 18 hours, 3 liters of 5% hydrochloric acid was added, and the water layer was exhaustively extracted with ether for 24 hours. The ether extracts were combined with the original ether layer and the solvent was removed by distillation. Fractionation of the residue through a 45 × 1.6 cm. Vigreux column yielded 103.7 g. (89%) of *cis*- $\Delta^4$ -tetrahydrophthalyl alcohol (III), b.p. 130–137° (1.0–1.5 mm.),  $n_D^{25}$  1.0980.

*Anal.* Calcd. for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>: C, 65.57; H, 9.92. Found: C, 65.72; H, 10.14.

*cis*- $\Delta^4$ -Tetrahydrophthalyl Diacetate (IV).—A mixture of 630 g. (4.44 moles) of *cis*- $\Delta^4$ -tetrahydrophthalyl alcohol (III) and 300 g. of glacial acetic acid was added dropwise to 3000 g. (29.4 moles) of acetic anhydride refluxing in a 5-liter, three-necked flask, equipped with a stirrer, a condenser and a dropping funnel. The mixture was heated under reflux for an additional 48 hours and was then fractionated through a 45 × 1.6 cm. Vigreux column to yield 938.0 g. (93%) of *cis*- $\Delta^4$ -tetrahydrophthalyl diacetate (IV), b.p. 121–128° (1.0 mm.),  $n_D^{25}$  1.1009.

*Anal.* Calcd. for C<sub>12</sub>H<sub>18</sub>O<sub>4</sub>: C, 63.70; H, 8.02. Found: C, 63.96; H, 8.22.

1,2-Dimethylene-4-cyclohexene (I).—At the rate of 1.5 g. per minute, 300 g. (1.33 moles) of *cis*- $\Delta^4$ -tetrahydrophthalyl diacetate (IV) was dropped through a vertical, 20

(12) All melting points are corrected. The authors are indebted to Vivian Kapuscinski, Robert Keen and James French for the analyses.

× 300 mm. borosilicate glass combustion tube that was packed with 1/16-inch helices. The tube was continuously swept out with dry, oxygen-free nitrogen and externally heated at 500° with a 12-inch Hoskins furnace.<sup>7</sup> The pyrolysate was condensed in a 6-inch spiral condenser and then collected in a receiver immersed in a Dry Ice-acetone-bath. The pyrolysate was washed with water and dried over anhydrous potassium carbonate. Titration of aliquots of the washings indicated that 71% of the total theoretical acetic acid had been liberated. The pyrolysate was fractionated through a 16 × 1.7 cm. column, packed with 1/8-inch helices, to yield 68.1 g. (47%) of 1,2-dimethylene-4-cyclohexene (I), b.p. 90° (100 mm.),  $n_D^{25}$  1.4968,  $d_4^{25}$  0.8692; 66.0 g. (30%) of 2-methylene- $\Delta^4$ -tetrahydrobenzyl acetate (V); and 56.4 g. (19%) of recovered diacetate IV. The total yield of 1,2-dimethylene-4-cyclohexene (I), based on unrecovered diacetate IV and olefin acetate V was 92%. The recovered IV and V could be pyrolyzed separately to produce additional I.

*Anal.* Calcd. for C<sub>8</sub>H<sub>10</sub>: C, 90.50; H, 9.50. Found: C, 90.68; H, 9.68.

**Catalytic Isomerization of 1,2-Dimethylene-4-cyclohexene (I).**—A mixture of 3.0 g. (0.028 mole) of 1,2-dimethylene-4-cyclohexene (I) and 0.5 g. of palladium-on-charcoal was heated under reflux for 48 hours. The mixture was filtered to give 2.9 g. (97%) of *o*-xylene,  $n_D^{25}$  1.5066. One gram (0.0094 mole) of this filtrate was oxidized with alkaline potassium permanganate, according to the directions of Shriner and Fuson,<sup>13</sup> to yield 1.48 g. (94%) of phthalic acid, m.p. 208°, which showed no depression in its melting point when it was mixed with authentic phthalic acid.

(13) R. L. Shriner and R. C. Fuson, "Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 198.

**Acid Isomerization of 1,2-Dimethylene-4-cyclohexene (I).**—In order to test the stability of the 1,2-dimethylene-4-cyclohexene (I) to acetic acid, which is formed in the pyrolysis, 5 g. of the triene I was refluxed with 100 ml. of anhydrous glacial acetic acid for 2 hours and was recovered unchanged. However, if a drop of concentrated hydrochloric acid was added to the mixture, an immediate reaction took place. Distillation of the reaction mixture produced 1.1 g. of *o*-xylene, with no recovered triene I; a polymeric substance remained as the residue in the flask.

**1,4,5,8-Tetrahydronaphthalene-2,3-dicarboxylic Acid (VI).**—A solution of 5.7 g. (0.05 mole) of acetylenedicarboxylic acid in 50 ml. of benzene was heated under reflux in a 100-ml., three-necked flask, equipped with a stirrer, a dropping funnel, and a condenser. After 5.3 g. (0.05 mole) of 1,2-dimethylene-4-cyclohexene (I) was added dropwise with stirring, the mixture was allowed to stand for 24 hours. The precipitate was filtered off and the filtrate was concentrated. The concentrate was diluted with petroleum ether to produce an additional quantity of material. Recrystallization of the adduct from acetic acid gave 9.2 g. (84%) of 1,4,5,8-tetrahydronaphthalene-2,3-dicarboxylic acid (VI), m.p. 200–201°.

*Anal.* Calcd. for C<sub>12</sub>H<sub>12</sub>O<sub>4</sub>: C, 65.45; H, 5.45. Found: C, 65.28; H, 5.32.

An intimate mixture of 0.2 g. of the adduct VI, 0.1 g. of 5% palladium-on-charcoal, and 0.05 g. of copper chromite was placed in a dehydrogenation apparatus. The system was flushed with carbon dioxide, the mixture was heated at 270°, and 43.0 ml. (90%) of hydrogen was collected. The solid (0.1 g.) that sublimed to the cold finger melted at 80° and no depression of its melting point was observed when it was mixed with an authentic sample of naphthalene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

## Pyrolysis of Esters. I. Selectivity in the Direction of Elimination by Pyrolysis<sup>1</sup>

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RECEIVED MARCH 26, 1954

When unsymmetrical secondary esters were pyrolyzed under mild conditions, it was found that the dehydroacetoxylation proceeded in a highly selective manner to give only a single olefin following the Hofmann rule. Many uses of this new synthetic tool are outlined.

Because olefins are widely used as monomers for polymerization and reactive chemical intermediates, their syntheses through elimination reactions have been studied thoroughly. One particular problem that has attracted interest has been the direction of the elimination when two olefins are possible.<sup>4</sup> The Hofmann rule states that in the decomposition of a quaternary ammonium hydroxide the major product will be that olefin having the smallest number of attached alkyl groups. The Saytzeff rule states that when an alkyl halide is converted to an olefin the major product will be the most highly branched olefin. Ingold<sup>5</sup> found, however, that with ammonium and sulfonium ions the Hofmann rule was followed only if the reaction

involved second-order kinetics. In all other elimination reactions which he studied, including the dehydration of alcohols, the Saytzeff rule predominated. His work further emphasized that a mixture of products was obtained in each elimination reaction.

Brown and Moritani<sup>6</sup> have recently shown that with base-catalyzed dehydrohalogenation the Saytzeff rule is followed only in the very simple cases, and the product of the reaction is governed by the steric requirements of the base. With the 2-bromo-3-methylbutane they were able to change the amount of 3-methyl-1-butene from 29% using sodium ethoxide to 66% using potassium *t*-butoxide. Thus it appears that, except for highly strained molecules, first-order elimination reactions tend to follow the Saytzeff rule but bimolecular elimination reactions may follow either rule, depending on the steric nature of the groups or reagent.

The pyrolysis of esters is an excellent method for the introduction of unsaturation. It was shown in this Laboratory that the highly strained 1,2-dimethylene-4-cyclohexene, which is an isomer of *o*-

(1) Presented before the Division of Organic Chemistry at the 120th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

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(4) E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 113.

(5) E. D. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

(6) H. C. Brown and I. Moritani, *THIS JOURNAL*, **75**, 4112 (1953).