

bond is facilitated by the presence of a side methyl group in the 2-position. This is illustrated by the comparable results in experiments I > III > II.

Experiment number: I, III and II
% Rearrangement: 39, 58 and 81

It is also noteworthy that the rearrangement of dimethylallyl occurred more easily than that of diallyl for all different sets of experimental conditions which were used.

The same observation concerning the effect of a side chain methyl group was made in the cases of 1-octene and 2-methyl-1-heptene, both prepared by magnesium condensations of allylic chlorides and reported in a previous paper.^{1c} No isomerization of 1-octene occurred under the reaction conditions used, whereas the 2-methyl-1-heptene rearranged to 2-methyl-2-heptene whenever magnesium chloride was present and the temperature was allowed to rise.

(c) For symmetrical carbon skeletons, the direction of the shift is mainly toward the center of the molecule; only a small amount of diene with its conjugated system at one end of the molecule was found in the case of 1,3-hexadiene obtained from 1,5-hexadiene.

(d) In the cases where the tendencies of shifting toward the center and of shifting past a methyl group would conflict, the tendency to

shift past the side chain predominates; *e. g.*,
 $C=C-C(C)-C-C=C-C \rightarrow C-C-C(C)=C-C=C-C$
 $C-C=C-C$ and $C=C-C(C)-C-C=C \rightarrow C-C-C(C)=C-C=C$.

(e) Some pyrolysis or shift in the carbon structure is observed in all the cases of hot alumina treatment, and small amounts of low boiling hydrocarbons are obtained. In the case of 1,5-heptadiene, a carbon skeleton rearrangement product was isolated, namely, 3-methyl-1,5-hexadiene.

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Summary

The displacement of the double bonds in diolefins has been investigated. The diolefins dimethylallyl and diallyl were first studied to determine various sets of conditions which would promote isomerization, and to establish a standard procedure for use with other hydrocarbons. After this a series of 1,5-diolefins was subjected to catalytic alumina treatment, and the products were separated, studied and identified. The characteristics of the isomerization reaction have been discussed.

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Diazonium Borofluorides. III. Their Use in the Bart Reaction

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Of the various methods for preparing aromatic arsonic acids, that developed by Bart¹ has been most widely used. Solutions of diazonium chlorides or sulfates are added to sodium arsenite in alkaline or neutral solution in the presence of various metals or their salts. Subsequent investigators have introduced various modifications and improvements² so that now in many instances good yields are possible. However, Bart's original procedure and all subsequent modifications are handicapped by the use of unstable diazonium intermediates.

The use of the stable diazonium borofluorides

in these Laboratories for the preparation of aromatic mercurials³ and of aromatic nitro compounds⁴ suggested their use also in the Bart reaction. Results justified the expectations.

The diazonium borofluorides of aromatic amines may be readily prepared in excellent yields by allowing the amine to react with fluoboric acid and sodium nitrite. Because of their increased stability they were observed to have less tendency to decompose or to form by-products when allowed to react with sodium arsenite; furthermore, the reactions could be carried out at room temperature.

This modification was introduced into the Bart

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(1) Bart, German Patents 250,264, 254,092, and 268,172.

(2) (a) Mouneyrat, British Patent 142,947; (b) Schmidt, *Ann.*, **421**, 159 (1920); (c) Doak, *THIS JOURNAL*, **62**, 167 (1940).

(3) Dunker, Starkey and Jenkins, *ibid.*, **58**, 2308 (1936); Dunker and Starkey, *ibid.*, **61**, 3005 (1939).

(4) Starkey, *ibid.*, **59**, 1479 (1937).

reaction as applied to aniline and various nuclear substituted anilines in order to determine the effect of the different substituents on the course of the reaction. A comparison of the results given below indicates that the yields of arsonic acid are best from the *p*-substituted compound and least from the *m*-derivatives.

Experimental

The conditions described below are optimum, and appreciable deviation from them leads to adverse results.

Diazonium Borofluorides.—Aromatic amines of technical quality were diazotized according to the procedure already described.⁵ The yields of diazonium borofluoride were well above 90% (approached theory except for manipulative losses) from aniline; *o*-, *m*- and *p*-nitroanilines; *o*-, *m*- and *p*-toluidines; *o*- and *p*-chloroanilines; ethyl *p*-aminobenzoate; and *p*-aminoacetophenone. Other yields are: from *p*-phenetidine, 87%; from *p*-aminobenzoic acid, 84%; and from *o*-aminobenzoic acid, 46%.

Replacement of the Diazonium by the Arsonic Acid Group.—To 600 ml. of water at room temperature was added 52 g. (0.4 mole) sodium meta-arsenite (NaAsO₂) and 6 g. of cuprous chloride. To this mixture was added, with vigorous stirring and over the period of about an hour, the diazonium borofluoride from a quarter mole of amine suspended in 300 ml. of cold water. The foaming which accompanied the evolution of free nitrogen was controlled by the addition of ether. As the reaction proceeded an additional 100 ml. of sodium hydroxide solution (0.25 mole) was added to maintain the proper alkalinity. Stirring was continued for another hour and the mixture then allowed to stand overnight. The next morning it was warmed at 65° for about thirty minutes and then filtered with suction through a Büchner funnel. Hydrochloric acid was added to the filtrate until acid to litmus; any tar separating out at this point was removed by filtration; activated charcoal was added and the solution was concentrated over a flame to approximately 200 ml.; the charcoal was removed by filtration and the liquid made acid to congo red with hydrochloric acid. The solution was now chilled and the arylarsonic acid which crystallized was filtered off. Further concentration of the mother liquors yielded a second crop of product.

(5) Starkey, *Org. Syntheses*, **19**, 40 (1939).

The arsonic acids were purified by dissolving in ammonium hydroxide solution and reprecipitating with hydrochloric acid and then washing with cold water. Characteristic crystals of the various compounds may, however, be obtained by crystallization from hot water.

The yields of a number of arylarsonic acids prepared by this procedure follow:⁶ phenyl, m. p. 156°, 58% (55);⁷ *o*-nitrophenyl, m. p. 232–4° dec., 67% (93);⁷ *m*-nitrophenyl, m. p. 182°, 47% (28)⁷ (54);²⁰ *p*-nitrophenyl, m. p. 300° dec., 79% (45);⁷ *o*-tolyl, m. p. 159–160°, 63% (50);⁷ *m*-tolyl, m. p. 150°, 54% (46);⁷ *p*-tolyl, m. p. 300° dec., 73% (50–65);⁸ *o*-chlorophenyl, m. p. 182°, 52% (60–75);⁸ *p*-chlorophenyl, m. p. above 300°, 63% (60–85);⁸ *p*-ethoxyphenyl, m. p. 185°, 73% (100);⁷ *o*-carboxyphenyl, m. p. above 300°, 65% (50–60);⁹ *p*-carboxyphenyl, m. p. 232° dec., 67% (50–60);¹⁰ *p*-carbethoxyphenyl, m. p. 260°, 60%; *p*-acetophenyl, m. p. 175°, 70% (66).¹¹

p-Carbethoxyphenylarsonic acid has been previously described¹² but it is believed that this is its first synthesis from the readily available ethyl *p*-aminobenzoate.

The compounds were all analyzed for arsenic by the method developed by Cislak and Hamilton,¹³ and in each instance the arsenic content agreed with that required for the arsonic acid in question.

Summary

A study has been made of the Bart reaction, using the more stable diazonium borofluorides as intermediates. In some cases the yield of arsonic acid was lower than that reported by the usual Bart procedure, but in more instances it was as good or even better. When using the diazonium borofluorides less tar and other by-products were obtained, and the reaction was carried out at room temperatures.

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(6) The figures in parentheses are yields reported by other workers using other procedures; they are included here for purposes of comparison.

(7) Bart, *Ann.*, **429**, 55 (1922).

(8) Palmer and Adams, *THIS JOURNAL*, **44**, 1392 (1922).

(9) Lewis and Cheetham, *ibid.*, **45**, 510 (1923).

(10) Lewis and Hamilton, *ibid.*, **45**, 757 (1923).

(11) Gibson and Levin, *J. Chem. Soc.*, 2388 (1931).

(12) Fournéau and Oechslin, *Bull. soc. chim.*, [4] **11**, 911 (1912).

(13) Cislak and Hamilton, *THIS JOURNAL*, **52**, 638 (1930).