reported[2] m.p. 97°, and γ-phenyltropolone (VI), m.p. 125.5–127°, reported[2] m.p. 125–126°, were isolated in 9 and 5% yields respectively. Infrared analysis of the crude mixture shows it to consist of approximately 61% β-phenyltropolone (IV) and 39% γ-phenyltropolone (VI). The infrared bands used for the analysis follow: β-isomer: 1387 cm.$^{-1}$ (d = 0.22) and 828 cm.$^{-1}$ (d = 0.20); γ-isomer: 1364 cm.$^{-1}$ (d = 0.32) and 862 cm.$^{-1}$ (d = 0.43) at 0.2 molar concentration in chloroform in a 0.104-mm. cell.

4-Hydroxycyclohexanone. Hydroquinone was catalytically reduced to cyclohexanediol-1,4[27] which was then converted to 4-hydroxycyclohexanone according to the method of Jones and Sondheimer.[28]

4-Hydroxycycloheptanone (1-hydroxy-8-oxabicyclo[3.2.1]-octane) (VII). In a 200-ml., three necked, round bottom flask equipped with a mercury-sealed stirrer, an equilibrating addition funnel and a calcium chloride tube were placed 11.4 g. of 4-hydroxycyclohexanone, 100 ml. of absolute methanol and 2 g. of anhydrous powdered potassium carbonate. Ethyl *N*-nitroso-*N*-methylcarbamate (14.5 g.) was added dropwise over a period of 1.5 hr. at 0°. The mixture was stirred for 0.5 hr. and allowed to stand at room temperature overnight. Filtration and distillation left a residue which was distilled *in vacuo*. The fraction distilling at 94° (2 mm.; bath temperature 145–152°) weighed 11.6 g. (90%).

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 65.6; H, 9.7.

The 2,4-dinitrophenylhydrazone derivative melted at 154–155° after crystallization from 95% ethanol; the melting point of a mixture with the 2,4-dinitrophenylhydrazone of the starting material (m.p. 155–156°) was depressed, m.p. 130–150°.

Anal. Calcd. for $C_{13}H_{16}N_4O_5$: C, 50.6; H, 5.2; N, 18.2. Found: C, 50.9; H, 5.5; N, 18.2.

1,4-Cycloheptanedione. To 2.6 g. of VII in 10 ml. of glacial acetic acid, a solution of 2 g. of chromic anhydride in 2 ml. of water and 8 ml. of glacial acetic acid, was added in portions with ice-cooling over a period of 5 min. The resulting solution was allowed to stand in an ice bath for 1 hr. and at room temperature overnight and was then poured over ice and extracted thoroughly with chloroform. The chloroform extracts were washed with aqueous sodium bicarbonate, dried and concentrated by distillation through a Vigreux column. The residue was evaporatively distilled at 90° (0.8 mm.); 1.3 g. (50%); n_D^{21} 1.4842. The bis-2,4-dinitrophenylhydrazone melted at 237° dec.; reported[22] m.p. 242° dec.

x-Bromo-4-hydroxycyclohepta-2,4,6-trienone. To 1 g. of 1,4-cycloheptanedione in 1 ml. of glacial acetic acid, a solution of 2.56 g. of bromine in 1 ml. of acetic acid was added with cooling and swirling over a period of 20 min. The solution was allowed to stand in an ice bath for 0.5 hr. and then at room temperature overnight. The reaction mixture was steam distilled and the residue extracted thoroughly with ether. On partial distillation of the ether, a powdery yellow solid precipitated, which was crystallized from absolute ethanol; 155 mg., m.p. 195–196°.

Anal. Calcd. for $C_7H_5BrO_2$: C, 41.8; H, 2.6; Br, 39.7; O, 15.9. Found: C, 42.0; H, 2.8; Br, 40.1; O, 15.9.

The yield of material was not reproducible, 0.10 g. being obtained in one instance and as little as 0.02 g. in others. It was insoluble in chloroform, carbon tetrachloride, carbon disulfide, and soluble in sodium bicarbonate solution. The bromoisotropolone reacted with ethereal diazomethane to give a liquid methyl ether.

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KATONAH, N. Y.

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(27) L. N. Owen and P. A. Robins, *J. Chem. Soc.*, 320 (1949).

(28) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF INDUSTRIAL CHEMISTRY, FACULTY OF ENGINEERING, KYÔTO UNIVERSITY]

The Friedel-Crafts Reaction of *o*-Xylylene Bromide

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The Friedel-Crafts reaction of *o*-xylylene bromide with benzene in the presence of aluminum chloride was found to afford a mixture of anthracene and diphenylmethane. Similar reaction with toluene gave a eutectic mixture of 2,6- and 2,7-dimethylanthracenes besides 3,4′-dimethyldiphenylmethane, while *o*-xylene afforded 3,4-dimethyl- and 3,3′,4,4′-tetramethyldiphenylmethanes. No anthracene derivative was isolated in the last mentioned reaction. The condensation of *o*-xylylene bromide with benzene by means of titanium tetrachloride resulted in the formation of *o*-dibenzylbenzene, neither anthracene nor diphenylmethane being isolated. The use of ferric chloride catalyst gave a mixture of *o*-dibenzylbenzene and diphenylmethane, while the latter hydrocarbon was a sole product in the reaction with stannic chloride. Boron trifluoride was found to be inactive in this reaction.

There are many examples which indicate the Friedel-Crafts reaction of dihaloalkanes with benzenoid compounds affords cycli-alkylated products whenever possible.[1] The condensation of *o*-xylylene bromide with benzene would therefore, be expected to give 9,10-dihydroanthracene (I) which should then readily be dehydrogenated to anthracene (II) in the presence of aluminum chloride.[2] Such an expectation could be realized to only a limited extent. When a solution of *o*-xylylene bromide in benzene was treated with anhydrous

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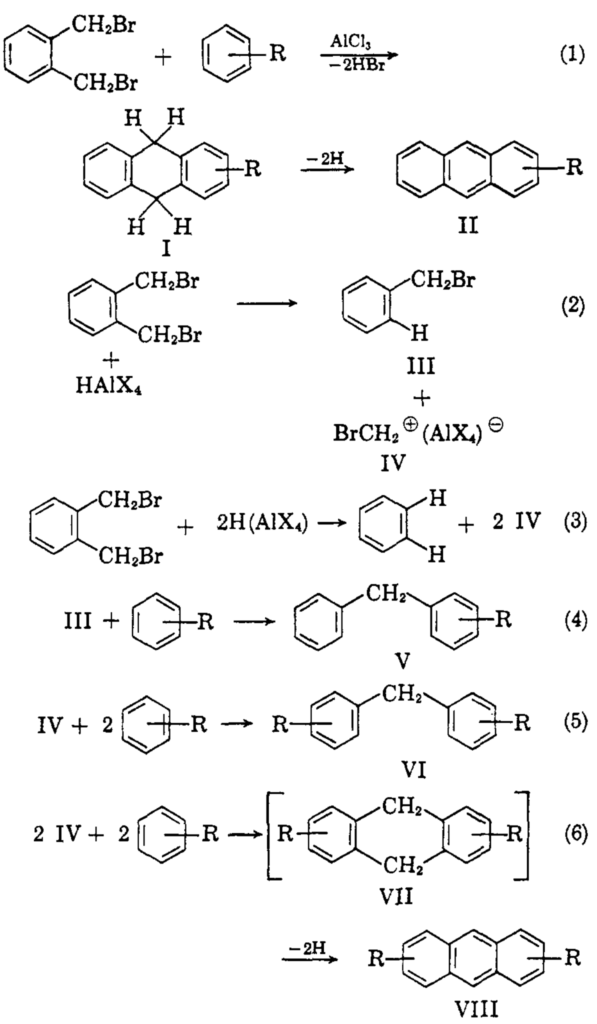
(1) (a) S. Yura and R. Oda, *J. Soc. Chem. Ind. Japan*, **46**, 531 (1943). (b) K. Sisido and H. Nozaki, *J. Soc. Chem. Ind. Japan*, **47**, 516 (1944). (c) W. Reppe, *Ann.*, **596**, 80 (1955). (d) K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **69**, 861 (1947). (e) K. Sisido and H. Nozaki, *J. Am. Chem. Soc.*, **70**, 1288, 1609 (1948). (f) H. A. Bruson and J. W. Kroeger, *J. Am. Chem. Soc.*, **62**, 36 (1940). (g) P. C. Myhre and W. M. Schubert, *J. Org. Chem.*, **25**, 708 (1960).

aluminum chloride, there was obtained pure anthracene in a 36 mole % yield.[3] A most serious side reaction was found to involve the formation of diphenylmethane which was isolated in a 60 mole % yield. It is of interest to note that the reaction of *m*-xylylene bromide with benzene in the presence of aluminum chloride has been recorded to yield a mixture of diphenylmethane and a small amount of *p*-dibenzylbenzene and anthracene.[4]

The character of the present condensation was disclosed by further extension to other benzene derivatives. It was surprising to find that toluene reacted with *o*-xylylene bromide to afford the eutectic mixture of 2,6- and 2,7-dimethylanthracenes in a 40 mole % yield in addition to 3,4′-dimethyldiphenylmethane in a 41 mole % yield. Any isomeric diphenylmethane derivatives could not be detected. The reaction of toluene with methylene chloride in the presence of aluminum chloride has long been known to afford quite similar products.[5]

The reaction of *o*-xylene with *o*-xylylene bromide has been found to furnish a mixture of 3,3′,4,4′-tetramethyldiphenylmethane and 3,4-dimethyldiphenylmethane in 90 and 36 mole % yields, respectively. These diphenylmethanes were characterized by mixed melting point and comparison of the infrared spectra with those of authentic samples prepared in following unambiguous ways. 3,3′,4,4′-Tetramethyldiphenylmethane was synthesized by the condensation of *o*-xylene and formaldehyde in the presence of sulfuric acid and 3,4-dimethyldiphenylmethane was obtained by the reduction of 3,4-dimethylbenzophenone.

In view of these findings, it is apparent that the reaction proceeds to a very minor extent, if any, according to Equation 1 as initially supposed. Instead, the main reaction consists in the cleavage of carbon to carbon bond of *o*-xylylene bromide according to Equation 2. The formation of diphenylmethane (V) with an unsubstituted phenyl group such as 3,4-dimethyldiphenylmethane in the reaction of *o*-xylene is explained by Equation 4. The bromomethyl aluminum complex (IV) produced by Equation 2 is supposedly an active source of the methylene group of the diphenylmethane substituted on both benzene rings (VI) as well as of the *meso*-carbon atoms of the anthracene compounds (VIII) (Equations 5 and 6). However, the rather high yields of dimethyldiphenylmethane and dimethylanthracenes in the reaction of toluene, *i.e.*, 41 and 40 mole % yields, respectively, makes it untenable to believe that the product of Equation 2 is the sole source responsible for the methylene carbon in VI and for the *meso*-carbons in VIII. It might be supposed that there is a removal of both bromomethyl groups of *o*-xylylene bromide to produce benzene and two moles of IV (Equation 3).



An investigation of the action of some Lewis acids other than aluminum chloride was also carried out. Previous research in our laboratory on the Friedel-Crafts reaction of α-halo ketones in the presence of various catalysts has shown that the course of the reaction strongly depends on the nature of the metallic halides used as a condensation agent.[6] Profft and others[7] have reported the formation of 1,2,4,5-tetrabenzylbenzene as a main product in

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(2) (a) K. Sisido and T. Isida, *J. Am. Chem. Soc.*, **70**, 1289 (1948). (b) K. Sisido, *J. Soc. Chem. Ind. Japan*, **45**, 432 (1942).

(3) Every yield throughout this paper is given in mole % based on one mole of *o*-xylylene bromide, because of the uncertainty of the reaction mechanism.

(4) (a) F. Reindel and F. Siegel, *Ber.*, **56**, 1550 (1923). (b) R. Sholl and C. Seer, *Ber.*, **55**, 330 (1922). For the formation of anthracene in the Friedel-Crafts reaction see K. Sisido and S. Andô, *J. Soc. Chem. Ind. Japan*, **44**, 829 (1941); see also literature cited throughout in the monograph: C. A. Thomas, *Anhydrous Aluminum Chloride in Organic Chemistry*, Reinhold Publishing Corp., New York, 1941.

(5) J. Lavaux, *Ann. chim. phys.*, **20**, 433 (1909); **21**, 131 (1910).

(6) K. Sisido, K. Okano, M. Sindô, and H. Nozaki, *J. Am. Chem. Soc.*, **79**, 3591 (1957).

(7) K. Profft, G. Drechsler, and H. Oberender, Abstracts of Papers presented at *Chemie-Dozenten-Tagung in der DDR*, June 24–26, 1959. See *Angew. Chem.*, **71**, 577 (1959).

the condensation of 1,2,4,5-tetrakis(chloromethyl)benzene with benzene in the presence of ferric chloride.

Upon treatment of the benzene solution of *o*-xylylene bromide with titanium tetrachloride *o*-dibenzylbenzene was isolated in a yield of 29.5 mole %. Higher boiling products were obtained in quantity, but were not investigated.

The reaction in the presence of anhydrous ferric chloride under similar conditions afforded *o*-dibenzylbenzene in a 30 mole % yield, besides a diphenylmethane in a 79 mole % yield. The formation of anthracene was not observed.

The use of stannic chloride as a Lewis acid gave an 18 mole % yield of diphenylmethane, a considerable amount of the bromide being recovered unchanged.

The condensation appeared not to proceed to any appreciable extent in the presence of boron trifluoride–etherate, the only substances isolated were unchanged starting materials.

These results indicate that the expected Friedel-Crafts reaction of *o*-xylylene bromide proceeds most cleanly in the presence of titanium tetrachloride, the reaction affording a product in which each halogen atom is replaced by a phenyl group. On the other hand the use of anhydrous aluminum chloride as a condensation agent results in the cleavage of the carbon to carbon bond of the dibromide. Similar properties have been observed in the cases of ferric and stannic chlorides.

EXPERIMENTAL[8]

The reaction of o-xylylene bromide with benzene in the presence of aluminum chloride. To a stirred suspension of 2.5 g. (0.019 mole) of powdered, anhydrous aluminum chloride in 50 ml. of benzene a solution of 6.6 g. (0.025 mole) of *o*-xylylene bromide in 40 ml. of benzene was added dropwise during 90 min., the reaction temperature being kept at 10–15°. After an additional 4 hr. of stirring at 20–21°, the reaction mixture was treated with ice cold hydrochloric acid and the whole was subjected to steam distillation. Recrystallizations of the distillate afforded 0.42 g. of anthracene, m.p. and mixed m.p. 214.5° (recorded 216°). Fractional distillation of the mother liquor gave 2.5 g. (60 mole %) of diphenylmethane, m.p. 25°, whose infrared spectrum was completely superimposable with that of an authentic sample. From the residual gum in the steam distillation flask an additional 1.2 g. (total yield being 1.62 g. or 36 mole %) of anthracene, m.p. and mixed m.p. 214.5°, was isolated.

The reaction of o-xylylene bromide with toluene in the presence of aluminum chloride. The condensation was carried out as above using 5.0 g. (0.038 mole) of anhydrous aluminum chloride and 13.2 g. (0.05 mole) of *o*-xylylene bromide in 170 ml. of toluene. From the steam-volatile part there were obtained 1 g. of benzene identified as dinitrobenzene, 0.5 g. of the eutectic mixture of 2,6- and 2,7-dimethylanthracenes, m.p. and mixed m.p. 224–225° (recorded m.p. 226°),[9] and 5.7 g. (41 mole %) of oily product, b.p. 140–156° (18 mm.), which was characterized as 3,4′-dimethyldiphenylmethane[5] as follows. Analyses for carbon and hydrogen agreed with the formula $C_{15}H_{16}$. Comparison of the infrared spectrum with authentic 3,4′-dimethyldiphenylmethane, which was prepared by the Huang-Minlon reduction of 3,4′-dimethylbenzophenone,[10] showed small differences, but oxidation of the oily product with chromic anhydride in acetic acid, followed by chromatography on silica-gel, afforded a single dimethylbenzophenone, m.p. 72°. Mixed melting point with authentic 3,4′-dimethylbenzophenone (m.p. 72°, recorded 72°[10a] or 75°[10b]) showed no depression. Any isomeric dimethylbenzophenones could not be isolated in the chromatography.

Recrystallizations of the residual solid obtained upon steam distillation gave further 3.6 g. (total amount 4.1 g. or 40 mole %) of the eutectic mixture of 2,6- and 2,7-dimethylanthracenes, m.p. and mixed m.p. 224–225°.

The reaction of o-xylylene bromide with o-xylene in the presence of aluminum chloride. The reaction was effected as above using 5.0 g. (0.036 mole) of aluminum chloride, 13.2 g. (0.05 mole) of *o*-xylylene bromide and 200 ml. of *o*-xylene. The steam-distillable product was redistilled *in vacuo* to afford 3.5 g. (or 36 mole %) of an oil, b.p. 136–138° (14 mm.), which solidified upon cooling, m.p. 27–29°. This was identified as 3,4-dimethyldiphenylmethane by mixed melting point and comparison of the infrared spectrum with an authentic sample prepared as shown below.

Anal. Calcd. for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 91.61; H, 8.61.

Fractional distillation of the residue in the steam distillation flask gave 11.2 g. (90 mole %) of 3,3′,4,4′-tetramethyldiphenylmethane, b.p. 153° (5 mm.), m.p. 34–35°, which was identified by a mixed melting point and by comparison of the infrared spectrum with an authentic sample prepared as follows.

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 91.01; H, 9.00.

3,4-Dimethyldiphenylmethane. A solution of 2.1 g. of 3,4-dimethylbenzophenone[11] in 20 ml. of anhydrous ethanol was treated with 1.0 g. of metallic sodium at the boiling point. The reduction product was purified by distillation *in vacuo*, b.p. 137–138° (14 mm.). Recrystallization from ethanol gave a pure sample melting at 27–29°.

3,3′,4,4′-Tetramethyldiphenylmethane. A solution of 3.0 g. (0.1 mole) of methylal in 8.4 g. (0.08 mole) of *o*-xylene was treated with 30 g. of 74% sulfuric acid, which was added dropwise in the course of 20 min. at 10–15° under stirring. The reaction mixture was stirred for an additional 3 hr. at room temperature and the product was isolated in the usual way. Distillation gave an oily fraction, b.p. 160° (6 mm.), which solidified and melted after recrystallization from petroleum ether (b.p. 40–60°)–ethanol at 35–36°.

The reaction of o-xylylene bromide with benzene in the presence of titanium tetrachloride. To a solution of 13.2 g. (0.05 mole) of *o*-xylylene bromide in 80 ml. of benzene 19.0 g. (0.1 mole) of titanium tetrachloride was added dropwise during an hour under stirring at −2°. Stirring was continued for an additional 5 hr. at room temperature and the mixture was allowed to stand overnight. Upon treatment of the reaction mixture, 3.8 g. (30 mole %) of *o*-dibenzylbenzene, b.p. 204–208° (5 mm.), was obtained, which melted after recrystallizations from ethanol at 75–76° (recorded[12] 78–79°) and gave correct analyses for carbon and hydrogen.

Considerable amounts of higher boiling products were obtained, but further investigations were not carried out.

The reaction of o-xylylene bromide with benzene in the

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[8] All melting and boiling points are uncorrected. Analyses by Miss Kenko Ogawa.

[9] G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2203 (1929); D. H. Hey, *J. Chem. Soc.*, 72 (1935).

[10] (a) K. Ishimura, *Bull. Chem. Soc. Japan*, **16**, 196, 252 (1941); *Chem. Abstr.*, **36**, 4487 (1942). (b) P. L. Pickard and D. J. Vaughan, *J. Am. Chem. Soc.*, **72**, 5017 (1950).

[11] C. F. H. Allen, A. C. Bell, A. Bell, and J. V. Allan, *J. Am. Chem. Soc.*, **62**, 656 (1940).

[12] Z. Földi, *Ber.*, **61**, 1609 (1928).

presence of ferric chloride. A mixture of 13.2 g. (0.05 mole) of *o*-xylylene bromide and 170 ml. of benzene was treated with 6.0 g. (0.037 mole) of ferric chloride in the same manner as above. The products isolated were as follows: 6.6 g. (79 mole %) of diphenylmethane, b.p. 133–135° (13 mm.), and 3.8 g. (30 mole %) of *o*-dibenzylbenzene.

The reaction of o-xylylene bromide with benzene in the presence of stannic chloride. Similar treatment of 13.2 g. (0.05 mole) of *o*-xylylene bromide and 80 ml. of benzene with 11.9 g. (0.1 mole) of stannic chloride gave 1.5 g. (18 mole %) of diphenylmethane, besides 5.2 g. of *o*-xylylene bromide which was recovered unchanged.

KYÔTO, JAPAN

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

Ring Opening in Benzocyclobutene Derivatives. I. The Reaction of *trans*-1,2-Diiodobenzocyclobutene with Dimethylamine[1]

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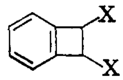
Treatment of *trans*-1,2-diiodobenzocyclobutene with dimethylamine leads to the formation of α,α,α'-trisdimethylamino-*o*-xylene and a small amount of α-dimethylamino-*o*-tolualdehyde. The formation of these products is rationalized by postulating an opening of the four-membered ring initiated by nucleophilic attack of dimethylamine.

Benzocyclobutene and its derivatives have lately become of interest for two reasons: First, these compounds are highly strained due to the presence of a fused benzene and four-membered ring system; second, benzocyclobutene derivatives are possible precursors of benzocyclobutadiene, a compound of great theoretical interest for which some molecular orbital calculations predict a substantial delocalization energy.[3]



I. X = Br
II. X = I

Due to the strain inherent in the benzocyclobutene nucleus, the prediction has been made that compounds containing this structural feature might not be capable of existence, or at best be highly reactive.[4] However, a whole series of benzocyclobutene derivatives, including benzocyclobutene itself, have been prepared and have been found to be quite stable.[5–8] Among these stable benzocyclobutene derivatives were the dihalobenzocyclobutenes, 1,2-dibromobenzocyclobutene (I) and 1,2-diiodobenzocyclobutene (II). These dihalides were stable towards boiling alcohol, alcoholic potassium acetate, and maleic anhydride.[5] Catalytic reduction did not rupture the four-membered ring but, instead, produced benzocyclobutene.[7] It was only when dibromide I was heated with bromine at 150° for twelve hours that ring opening occurred to give α,α,α',α'-tetrabromo-*o*-xylene.[5,9]

It has recently been found in this laboratory, however, that dihalides I and II undergo a facile ring opening when treated with secondary amines. This reaction was first observed when a mixture of dibromide I and diiodide II was treated with piperidine. Upon heating to 50° a mixture of piperidinium bromide and iodide precipitated and an undistillable red oil was obtained. In the subsequent investigation of this reaction, pure *trans*-diiodide II was used to eliminate the possibility of different reactions from different stereoisomers and to make possible the determination of the amount of amine salt formed. Dimethylamine was employed as the amine in order to make the products readily distillable.

When *trans*-diiodide II was treated with an excess of dimethylamine in an Adkins bomb at 60° for six hours, a mixture of two liquid products was formed along with two equivalents of dimethylammonium iodide. The lower boiling product, formed in 10% yield, was shown to be α-dimethylamino-*o*-tolualdehyde (III); evidence for the structure of this compound is presented below. The major product, formed in 64% yield, was a highly re-

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[1] This paper is based on portions of a thesis submitted by M. W. Hanna to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[3] J. D. Roberts, A. Streitweiser, Jr., and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952).

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[5] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 1701 (1957).

[6] M. P. Cava, R. L. Little, and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2257 (1958).

[7] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **80**, 2255 (1958).

[8] M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **79**, 3606 (1957).

[9] Some other examples of ring opening in benzocyclobutene derivatives have recently been reported. See M. P. Cava and K. Muth, *J. Am. Chem. Soc.*, **82**, 652 (1960).