After the hydrogen absorption ceased, the reaction mixture was cooled to room temperature and filtered to remove the catalyst. The solid residue obtained by concentration of the alcohol solution at reduced pressure was treated with dilute hydrochloric acid to separate the amine as its water-soluble hydrochloride, and the water-insoluble hydroxy derivative was extracted by ethyl ether. After washing the ether extract with equal volumes of water and 5% sodium bicarbonate solution and drying over anhydrous magnesium sulfate, the solution was concentrated to yield 3.6 g. of white solid. Recrystallization of this product from methanol afforded a white solid, m.p. 277.0–278.0° (lit.,[6] m.p. 282°). Sublimation of this material gave colorless needles with no change in melting point.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.82; H, 10.54.

The hydrolysis of 1-bromoadamantane by refluxing with dilute aqueous silver nitrate solution afforded a hydroxyadamantane with the same melting point as that obtained from the air oxidate derivative. A mixed melting point of these two compounds gave no depression.

2-Aminoadamantane hydrochloride. The aqueous hydrochloride acid solution from which hydroxyadamantane was separated (see above) was neutralized in 10% sodium hydroxide solution. The free amine which separated was extracted by ethyl ether and the solution was dried over anhydrous magnesium sulfate. Concentration of the solution yielded 0.6 g. of the amine, which on sublimation (75° and 15–20 mm.) afforded pure 2-aminoadamantane, m.p. 230.5–236°. (Due to the rapid absorption of water and carbon dioxide from the atmosphere, an analytically pure sample of the free amine was not obtained.)

The sublimed 2-aminoadamantane was dissolved in ethyl ether plus a small amount of ethyl alcohol, and the hydrochloride derivative was precipitated by passing dry hydrogen chloride into the solution. Recrystallization of the amine hydrochloride from isopropyl alcohol yielded colorless needles of 2-aminoadamantane hydrochloride which, on heating in a capillary, gradually decomposed over the range 300–325°.

Anal. Calcd. for $C_{10}H_{18}NCl$: C, 63.99: H, 9.67; N, 7.46. Found: C, 64.35; H, 9.59; N, 7.43.

Acknowledgment. The authors wish to express their appreciation to Mr. L. J. Lohr for the interpretation of the infrared spectra and the vapor-phase chromatographic work.

GIBBSTOWN, N. J.

[CONTRIBUTION FROM THE EVANS CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Condensed Cyclobutane Aromatic Compounds. XIV. Naphtho[*b*]cyclobutene: Reactions of the Aromatic Nucleus

M. P. CAVA AND R. L. SHIRLEY

Received December 21, 1960

Peracetic acid oxidation of naphtho[*b*]cyclobutene (I) gave the quinone 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (II). The butadiene adduct (III) of this quinone was reduced to diol IV, which was dehydrated with rearrangement to 9,10-ethanoanthracene. The 3-nitro and 3-amino derivatives of naphtho[*b*]cyclobutene are described, and the effect of the cyclobutene ring upon the chromophores of these compounds is discussed.

The synthesis of the hydrocarbon naphtho[*b*]-cyclobutene (I) was described in a previous paper of this series.[1] Some transformations of I are now described which involve attack upon the naphthalene nucleus of this molecule.

The direct oxidation of naphtho[b]cyclobutene with peracetic acid occurred readily to give, in 22% yield, a single bright yellow neutral compound $C_{12}H_8O_2$. This substance was assigned the structure 1,2-dihydrocyclobuta[b]naphthalene-3,8-dione (II) on the basis of the analogous oxidation of 2,3-dimethylnaphthalene to 2,3-dimethyl-1,4-naphthoquinone.[2] This assignment was verified by an interesting series of transformations leading to 9,10-ethanoanthracene.

I II

The new quinone II reacted with butadiene at 90–100° to give, after ninety minutes, a colorless adduct (III), m.p. 92–93°, in 93% yield. In contrast to this behavior, 2,3-dimethyl-1,4-naphthoquinone was recovered unchanged after five days under the same conditions. The greatly enhanced reactivity of quinone II as a dienophile must be attributed to the decrease in strain which results by conversion of the cyclobutene ring of II to the cyclobutane system of the adduct.

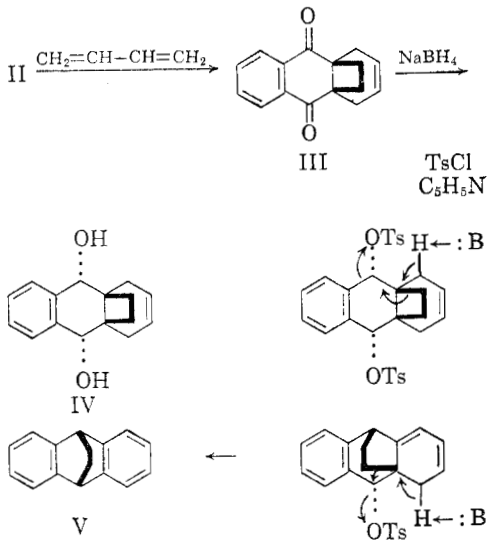
The diketone III was reduced smoothly by sodium borohydride to a single diol IV, m.p. 205.5–206°, in 79% yield. The configuration assigned to the diol, on mechanistic grounds, is that in which the hydroxyl groups are *cis* to each other as well as to the cyclohexene ring. This stereochemistry would result from attack of borohydride ion on the carbonyls of III from the less hindered cyclobutane side of the molecule.

Diol IV reacted with two equivalents of *p*-toluenesulfonyl chloride in pyridine to give directly, in 60% yield, 9,10-ethanoanthracene (V).[3] This

(1) M. P. Cava and R. L. Shirley, *J. Am. Chem. Soc.*, 82, 654 (1960).

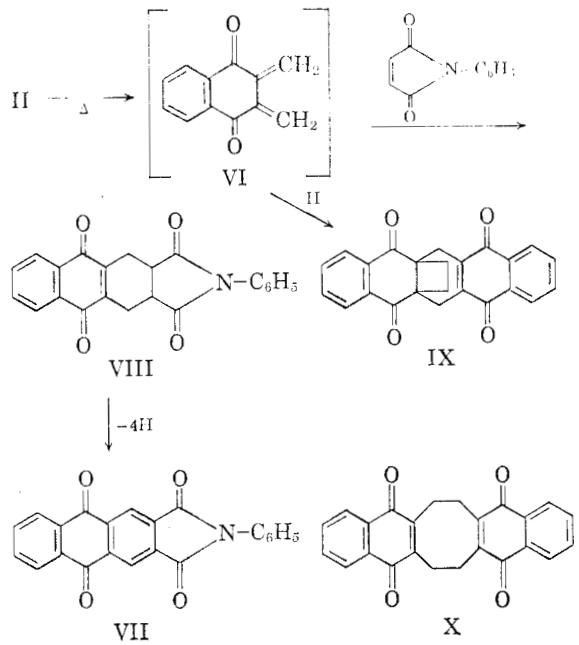
(2) R. T. Arnold and R. Larson, *J. Org. Chem.*, 5, 250 (1940).

rearrangement reaction can be explained most simply as proceeding via the ditosylate of diol IV, by a series of two solvolytic carbonium ion shifts, probably concerted in nature as shown below. Both the relief of strain resulting from expansion of the cyclobutane ring and the aromatization of the cyclohexene system provide driving forces for the process.



Although quinone II reacts normally as a dienophile in the Diels-Alder reaction, it may also react as a diene at elevated temperatures, probably by thermal rupture of the cyclobutene ring to generate a transient true diene intermediate VI. Thus II reacted with *N*-phenylmaleimide at 200–220° to give *N*-phenyl-9,10-anthraquinone-2,3-dicarboximide (VII) in 14% yield. This anthraquinone derivative was identical with a sample prepared by the chromic acid oxidation of *N*-phenylanthracene-2,3-dicarboximide.[1] The expected initial adduct (VIII) was not found: probably it was dehydrogenated directly to VII by quinone II, a hypothesis consistent with the low yield of VII obtained in the reaction.

Careful observation of the melting point behavior of quinone II revealed that, upon rapid heating, it melted at about 185–190° but immediately resolidified to a sparingly soluble yellow dimer (IX), melting at 255–260° with decomposition. A compound of structure IX would be formed by the thermal cleavage of II to diene VI, followed by a rapid Diels-Alder addition of VI to unchanged quinone II. In support of structure IX, the ultraviolet spectrum of the dimer was essentially identical to that of an equimolar solution of the butadiene adduct III and 2,3-dimethyl-1,4-naphthoquinone. The spectral evidence eliminated from serious consideration the alternate dimer formulation X, which should show ultraviolet



absorption quite similar to that of 2,3-dimethyl-1,4-naphthoquinone alone.

Nitration of naphtho[*b*]cyclobutene with 70% nitric acid gave 3-nitronaphtho[b]cyclobutene (XI). The ultraviolet spectrum of XI exhibited a chromophore very different from that of 2,3-dimethyl-1-nitronaphthalene. Comparison of these spectra with the ultraviolet spectrum of 1-nitronaphthalene[4] showed the 2,3-dimethylnaphthalene derivative to be the anomalous member of this series. Its spectrum shows a simple naphthalene type chromophore, whereas the other two nitro compounds possess characteristic spectra similar to each other. This apparent anomaly may be explained by steric considerations. In 1-nitronaphthalene the nitro group can rotate freely and thus can resonate with the aromatic naphthalene system. The same is true for 3-nitronaphtho[*b*]cyclobutene, the methylene groups being tied back sufficiently so as not to interfere with the free rotation of the nitro group. In 2,3-dimethyl-1-nitronaphthalene, however, the adjacent methyl group prevents the nitro group from becoming coplanar with the naphthalene ring system and resonance is effectively inhibited. Thus, 2,3-dimethyl-1-nitronaphthalene exhibits a naphthalene type chromophore rather than a nitronaphthalene type chromophore.

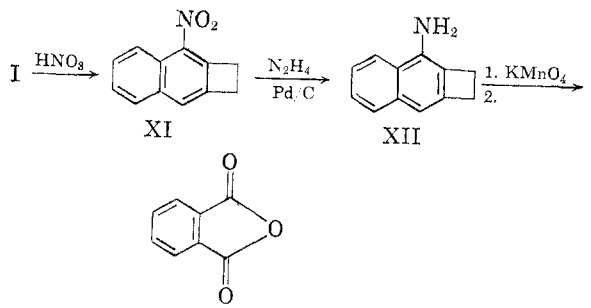
3-Nitronaphtho[*b*]cyclobutene was reduced catalytically with palladium on carbon and hydrazine[5] to 3-aminonaphtho[b]cyclobutene (XII). The ultraviolet spectrum of XII is similar to that of 1-amino-2,3-dimethylnaphthalene except for small differences in the position of the maxima beyond 300 mμ. These minor changes are attributed to the

(3) An authentic comparison sample of this hydrocarbon was prepared by hydrogenation of 9,10-ethenoanthracene, kindly provided by Prof. C. A. Grob.

(4) H. Mohler, *Helv. Chem. Acta*, **26**, 121 (1943); ultraviolet data were approximated from a spectrum given therein.

(5) S. Pietro, *Ann. Chim.* (*Rome*), **45**, 850 (1955).

strain provided by the cyclobutene ring in XII rather than to any steric rotation effects in the two compounds.



Permanganate oxidation of amine XII gave phthalic acid which was isolated as the anhydride. This result confirmed the assumption that naphtho[*b*]cyclobutene was nitrated in the *alpha* position adjacent to the four-membered ring.

EXPERIMENTAL[6]

1,2-Dihydrocyclobuta[b]naphthalene-3,8-dione (II). To a solution of naphtho-[*b*] cyclobutene (2.0 g.) in glacial acetic acid (30 ml.) at 50°, was added 30% hydrogen peroxide (6 ml.). The temperature was raised to 80–85° for 5 hr., then one half the acetic acid was evaporated *in vacuo*, water added, and the mixture cooled to give orange crystals which were filtered, washed well with water and aqueous sodium bicarbonate (10%), then again with water, and dried. Trituration with petroleum ether (b.p. 30–60°) afforded starting material (0.29 g.) upon evaporation of the petroleum ether. The orange needles, crystallized from acetic acid, gave 0.45 g. (22%) of the quinone, m.p. 200–210° dec. (see discussion). A benzene solution of the quinone was passed through a column of Woelm alumina (neutral, activity I) and the solvent evaporated to give the analytical sample as bright yellow needles, m.p. 185–190° (rapid heating). Upon very slow heating, a thermal transformation product was obtained at the melting point. This product melted at 255–260° with decomposition.

Anal. Calcd. for $C_{12}H_8O_2$: C, 78.25; H, 4.38; mol. wt., 184. Found: C, 78.38, 78.47; H, 4.56, 4.33; mol. wt. (isothermal distillation in methylene chloride), 191.

Ultraviolet spectrum (ethanol): λ_{max} 232 (log ϵ 4.16), 240 (4.12), 245, 250 (4.14), 265 (4.08), 338 (3.26), shoulder at 312 mμ.

The *ultraviolet spectrum of 2,3-dimethyl-1,4-naphthoquinone* (in ethanol) was grossly similar to that of II but showed less fine structure: λ_{max} 244 (log ϵ 4.26), 249 (4.27), 264 (4.21), 270 (4.25), 330 (3.44).

Thermal treatment of quinone II. A solution of quinone II (0.02 g.) in 1,2-bis(2-methoxy)ethane (1 ml.) was heated to 185–190° in an oil bath overnight (*ca.* 10 hr.) Upon cooling the solution, yellow needles (0.02 g., 100%), m.p. 255–260° dec. precipitated. The material was insoluble in benzene, but could be crystallized from chloroform. It was unreactive toward bromine and *N*-phenylmaleimide.

Anal. Calcd. for $C_{24}H_{16}O_4$: C, 78.25; H, 4.38; mol. wt., 368. Found: H, 4.75, 4.60; C, 78.59, 78.37; 4.75, 4.60; mol. wt. (Rast in camphor), 440.

The high value found for the molecular weight probably resulted from the limited solubility of the dimer in camphor.

(6) Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Melting points are uncorrected unless stated otherwise.

Ultraviolet spectrum (ethanol): λ_{max} 226 (log ϵ 4.54), 246 (4.42), 308 (3.44), 333 (3.44).

1,4-Dihydro-4a,9a-ethanoanthracene-9,10-dione (III). Quinone II (0.10 g.), benzene (2 ml.), and excess butadiene (*ca.* 1.5 ml.) were sealed in a Pyrex tube (*ca.* 10 ml.) and heated on a steam bath for 1.5 hr. Within 1 hr., the solution had become almost colorless. The excess butadiene was evaporated, and the remaining solution was passed through a column of alumina, which was eluted with benzene. The eluate was evaporated to dryness to give slightly yellow crystals of dione III (0.12 g., 93%), m.p. 92–93°. Sublimation at 110° (1 mm.) gave the analytical sample as white needles, m.p. 93.0–93.5° (corr.).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.47; H, 6.11.

Ultraviolet spectrum (ethanol): λ_{max} 226 (log ϵ 4.53), 251 (3.94), 299 (3.14).

1,4,9,10-Tetrahydro-4a,9a-ethanoanthracene-9,10-diol (IV). To a solution of sodium borohydride (0.08 g.) in water (1 ml.) and methanol (1 ml.) was added slowly, at room temperature, a solution of dione III (0.20 g.) in methanol (2 ml.). Small white plates precipitated out almost immediately. The mixture was heated on the steam bath for 10 min., then water was added until the solution became cloudy, and the mixture was cooled to give diol IV (0.16 g., 79%) as white plates, m.p. 205.5–206.0°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.18; H, 7.52.

9-10-Ethanoanthracene (V). *A. Rearrangement of diol IV.* Diol IV (0.10 g.), *p*-toluenesulfonyl chloride (0.30 g.), and pyridine (0.7 ml.) were stirred at 5° for 2 hr. Stirring was continued for a total of 5.5 hr. while the temperature was slowly increased to 50°. The mixture was diluted with hydrochloric acid (sp. gr. 1.19) and poured over ice. The precipitated gum was extracted with benzene and chromatographed on alumina (neutral Woelm, activity I). A fluorescent band containing the product was easily followed by means of an ultraviolet lamp. The eluate was evaporated to dryness to give a slightly yellow residue, m.p. 100–140°. Three crystallizations from ethanol gave large white needles (0.05 g., 60%), m.p. 142–143°, giving no depression upon admixture with authentic ethanoanthracene (see B below). The infrared spectrum of the rearranged product was identical to that of the authentic sample.

B. Catalytic hydrogenation of 9,10-ethenoanthracene. 9,10-Ethenoanthracene[8] (0.10 g.) absorbed the theoretical amount of hydrogen in 1.5 min. using 10% palladium on carbon as catalyst and ethanol as solvent. The mixture was filtered and the filtrate concentrated and cooled to give large white needles (0.09 g., 94%), m.p. 142–143° (reported:[7] 142–143°).

N-Phenyl-9,10-anthraquinone-2,3-dicarboximide (VII). *Method A.* A mixture of quinone II (0 18 g.), *N*-phenylmaleimide (0.20 g.), and 1,2-bis(2-methoxy-ethoxy)ethane (3 ml.) was heated to 200–220° for 1 hr. and then cooled. The small orange needles were filtered and washed with water and dried. Crystallization from acetic acid gave the anthraquinone derivative VII (0.05 g., 14%,) m.p. 347–350°, identical in melting point, infrared, and ultraviolet spectra to that prepared in *B* below.

Anal. Calcd. for $C_{22}H_{11}O_4N$: C, 74.78; H, 3.14; N, 3.96. Found: C, 74.90; H, 3.23; N, 4.02.

Ultraviolet spectrum (ethanol): λ_{max} 230 (log ϵ 4.57) 258 (4.66), 332 (3.62).

Method B. To a refluxing solution of *N*-phenyl-2,3-anthracenedicarboximide[1] (0.07 g.) in acetic acid (*ca.* 90 ml.) was added 1 drop of a solution of chromic anhydride (0.18 g.) in a few drops of water. Almost instantaneously the reaction solution turned from orange-red to green. The remaining chromic acid solution was added and the refluxing was continued for 20 min. Some acetic acid (*ca.* 30 ml.) was removed by distillation; then the solution was cooled in the refrigera-

(7) C. L. Thomas (Universal Oil Products Co.), U. S. Patent **2,406,645**; August 27, 1946.

tor and yellow amorphous material precipitated which was filtered and recrystallized from acetic acid to give anthraquinone VII (0.065 g., 85%) m.p. 347–350°, identical in all respects to that prepared in *A* above.

3-Nitronaphtho[b]cyclobutene (XI). Naphtho[*b*]cyclobutene (1.54 g.) was added slowly with stirring to 70% nitric acid (1.53 g.) cooled by an ice bath to 0°. The reaction mixture became dark and viscous, but became lighter as the yellow crystalline nitro derivative appeared. After 1 hr., the ice bath was removed and the reaction allowed to run its course at room temperature for an additional 3 hr. As the reaction progressed, stirring became very difficult and more nitric acid (*ca.* 2 ml.) was added. The mixture was nearly a solid mass at the end of the reaction. Water was added and the crystalline material filtered, washed with 5% aqueous sodium bicarbonate, then water, and dried. Three crystallizations from ethanol gave yellow-orange needles (0.80 g., 40%), m.p. 129.0–130.5°. A fourth recrystallization gave the analytical sample, m.p. 131.0–131.5° (corr.).

Anal. Calcd. for $C_{12}H_9O_2N$: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.24; H, 4.71; N, 6.94.

Ultraviolet spectrum (ethanol): λ_{max} 244 (log ϵ 3.85) 342 (3.77).

3-Aminonaphtho[b]cyclobutene (XII). A mixture of 3-nitronaphtho[b]cyclobutene (0.20 g.), 10%, palladium on carbon (0.01 g.), excess hydrazine hydrate[6] (0.5 ml.), and 95% ethanol (20 ml.) was refluxed for 1 hr. and filtered hot. Water (*ca.* 20 ml.) was added to the filtrate until it became cloudy, and the mixture cooled in the refrigerator. The small white needles (0.12 g.) m.p. 91.0–91.5°, were filtered and dried. Concentration of the filtrate yielded an additional 0.02 g. of amine XII (total yield: 82%), which was recrystallized from petroleum ether (b.p. 30–60°).

Anal. Calcd. for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.32; H, 6.68; N, 8.30.

Ultraviolet spectrum (ethanol): λ_{max} 241 (log ϵ 4.42) 311 (3.66).

Permanganate oxidation of 3-aminonaphtho[b] cyclobutene. Two per cent aqueous potassium permanganate solution was added drop by drop to a suspension of amine XIII (32 mg.) in water (5 ml.) until the reaction solution remained pink. The excess permanganate was decomposed by formaldehyde and the manganese dioxide removed by filtration. The slightly yellow solution was passed through a column of hydrochloric acid–washed Amberlite IR 120 (washed with distilled water until chloride ion test was negative). The acid fraction (eluate was tested with Alkacid paper) was collected and the water evaporated *in vacuo* to give a light brown paste which was sublimed at atmospheric pressure to give white needles (10 mg.), identified as phthalic anhydride by infrared analysis. The infrared spectrum showed no trace of pyromellitic or succinic anhydrides.

2,3-Dimethyl-1-nitronaphthalene was prepared by the procedure of Willstaedt.[8] After several crystallizations from ethanol it melted at 111° (reported[8] m.p. 111°).

Ultraviolet spectrum (ethanol): λ_{max} 269 (log ϵ 358), 307 (3.02), 321 (3.02).

2,3-Dimethyl-1-aminonaphthalene. To a solution of 2,3-dimethyl-1-nitronaphthalene (2.0 g.) in 95% ethanol (35 ml.) was added hydrazine hydrate (8 ml.) and 10% palladium on carbon (0.15 g.). The mixture was refluxed for 2 hr., filtered, and diluted with water until cloudy. Slow evaporation of the alcohol at room temperature resulted in the precipitation of pink leaflets (1.62 g., 95%), m.p. 48–50° (reported,[8] m.p. 42°). Neither sublimation, distillation (177° at 14 min.) nor crystallization from petroleum ether changed the melting point. Because of the discrepancy with the reported melting point, elemental analyses were carried out.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 84.33; H, 7.80; N, 8.38.

Ultraviolet spectrum (ethanol): λ_{max} 244 (log ϵ 4.47) 320 (3.63), shoulder at 328 mμ.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation and by a Fellowship from the Nitrogen Division, Allied Chemical Corp. This aid is gratefully acknowledged.

COLUMBUS 10, OHIO

(8) H. Willstaedt, *Svensk. Kem. Tid.*, **54**, 223 (1942).

[CONTRIBUTION FROM THE CHEMISCHES INSTITUT]

Synthesis of Some Methyl-Substituted Anthracenes

ENNO WOLTHUIS[1,2]

Received October 17, 1960

A new route to the synthesis of a variety of methyl-substituted anthracenes is described. *o*-Dibromobenzene, or its homolog, is metallated with butyllithium to give benzyne, or its homolog, which is treated with furan or methyl-substituted furans to give 1,4-epoxy-1,4-dihydronaphthalenes. The latter, as dienophiles, are condensed with methyl-substituted butadienes, and the products dehydrated, and then dehydrogenated to produce the methylated anthracenes. These products have been used to study the bathochromic effect of the methyl group on the ultraviolet spectrum maxima of anthracene.

When fluorobenzene is treated with phenyllithium the fluorine atom becomes unusually active and is easily replaced by a phenyl group to give, after hydrolysis, biphenyl. Wittig[3] first suggested that this reaction probably proceeds *via* the intermediate, benzyne, or dehydrobenzene. Since that time many other reactions involving metallation of halogenated benzenes have been explained in terms of such an intermediate.[4–6]

One of the best indications that benzyne is actually formed, though short-lived, is the fact, discovered by Wittig,[7] that the product is a dieno-

(1) Present address: Calvin College, Grand Rapids, Mich.

(2) This work was done at the University of Heidelberg under a National Science Foundation Faculty Fellowship, 1959–60.

(3) G. Wittig, *Naturwissenschaften*, **30**, 696 (1942).

(4) G. Wittig, *Angew. Chem.*, **69**, 245 (1957).

(5) R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960).

(6) J. D. Roberts, *Chem. Soc. Symposia*, Bristol, 1958, Special Publication No. 12, p. 115.

(7) G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).