Anal. Calcd. for $C_{11}H_{20}O_3$: C, 66.0; H, 10.0; carbonyl value, 0.50 eq./100 g. Found: C, 65.7; H, 10.0; carbonyl value, 0.50 eq./100 g.

Reaction of VI with Hexachlorocyclopentadiene. A mixture of 30 g. (0.1 mole) of hexachlorocyclopentadiene (Hooker Electrochemical Co.) and 16 g. (0.1 mole) of VI was heated to 180°, whereupon an exothermic reaction set in. Distillation of the partly charred product gave 12 g. of recovered diene, b.p. 57–60° (1 mm.), followed by 29 g. (60%) of viscous yellow products, b.p. 160–168° (0.5 mm.). Redistillation gave 21 g. of a product, analyses of which indicate that it may contain 2,3,4,5,7,7-hexachloro-1,2,5,6-tetrahydro-2,5-methanobenzaldehyde, 2-methyl-2,4-pentanediol acetal, b.p. 157–160° (0.5 mm.).

Anal. Calcd. for $C_{14}H_{26}Cl_6O_2$: C, 39.2; H, 3.8; Cl, 49.5. Found: C, 40.3; H, 3.8; Cl, 49.9.

Reaction of VI with Cyclopentadiene. Twenty-one grams (0.32 mole) of freshly distilled cyclopentadiene and 18 g. (0.12 mole) of VI were heated for 4 hr. at 180° in a stainless steel vessel. Distillation and redistillation through a 2-foot helices-packed column gave 12 g. of recovered VI, b.p. 60–70° (3 mm.), and 19 g. (50% conversion, 70% yield based on VI of 1,2,5,6-tetrahydro-2,5-methanobenzaldehyde, 2-methyl-2,4-pentanediol acetal, b.p. 93–4° (3 mm.), n_D^{20} 1.4747.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.8; H, 10.0. Found: C, 75.7; H, 10.0.

3,9-Bis(2-chloroethyl)-2,4,8,10-tetroxaspiro[5.5]undecane. Dry hydrogen chloride was passed into a stirred solution of 278 g. (1.3 mole) of I in 350 ml. of chloroform at −15° to −10°. When hydrogen chloride was no longer absorbed the solution was stirred for 1 hr. with solid sodium carbonate. After filtration and removal of solvent, the residue was distilled from a flask equipped with a Claisen head. The first cut, b.p. 113–144° (0.6 mm.), 31 g., was redistilled, b.p. 118–122° (1 mm.) and gave analyses in agreement with 3(2-chloroethyl)-9-vinyl-2,4,8,10-tetroxaspiro[5.5]undecane.

Anal. Calcd. for $C_{11}H_{17}ClO_4$: C, 53.2; H, 6.9; Cl, 14.3. Found: C, 53.3; H, 7.2; Cl 14.1.

Analyses indicate that the main cut, b.p. 140–150°

(0.2 mm.), contains 3,9-bis(2-chloroethyl)-2,4,8,10-tetroxaspiro[5.5]undecane, XVIIa, apparently contaminated with the mono-chloro derivative.

Anal. Calcd. for $C_{11}H_{18}Cl_2O_4$: C, 46.5; H, 6.3; Cl, 24.8. Found: C, 47.3; H, 6.5; Cl, 24.0.

3,9-Bis(2-cyanoethyl)-2,4,8,10-tetroxaspiro[5.5]undecane. This was prepared from 0.5 mole of crude XVIIa in the manner described above. Simple distillation of the product gave a large (62 g.) unidentified forecut, b.p. 46–178° (0.14 mm.) and 65 g. (49%) of dinitrile, b.p. 187–199° (0.14 mm.). Redistillation gave a product, b.p. 180–181° (0.2 mm.), with analyses in agreement with 3,9-bis(2-cyanoethyl)-2,4,8,10-tetroxaspiro[5.5]undecane.

Anal. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.2; H, 6.8; N, 10.1. Found: C, 58.5; H, 7.0; N, 10.1.

Epoxidation of (I).[14] A mixture of 53 g. (0.25 mole) of the bisacetal, 150 ml. of chloroform, and 92 g. (0.56 mole) of freshly prepared peracetic acid was stirred gently at room temperature. Titration after 16 hr. showed 57% consumption of active oxygen, and after 40 hr., 90% consumption. The solution was stirred with sodium bicarbonate solution, dried over magnesium sulfate, filtered, and relieved of solvent.

The 55 g. of residue was distilled and redistilled from a Claisen still, giving 10 g. of recovered acetal, b.p. 102–110° (2 mm.), and 10 g. of a fraction containing mainly the mono epoxide, b.p. 138° (1 mm.).

Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.9; H, 7.1; epoxide value, 0.44 eq./100 g. Found: C, 58.0; H, 7.1; epoxide value, 0.37 eq./100 g.

A third fraction contained the bisacetal of glycidaldehyde, b.p. 176° (1 mm.) 11 g.

Anal. Calcd. for $C_{11}H_{16}O_6$: C, 54.2; H, 6.6; epoxide value 0.82 eq./100 g. Found: C, 55.1; H, 6.7; epoxide value, 0.67 eq./100 g.

EMERYVILLE, CALIF.

(14) Fischer, R. F., U. S. Patent 2,895,962 (1959) to Shell Development Co.

[CONTRIBUTION NO. 1051 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Reaction of Benzyne With An Allylic Olefin

EDWARD M. ARNETT

An attempted Diels-Alder condensation of benzyne with 2,5-dimethyl-2,4-hexadiene produced 2,5-dimethyl-3-phenyl-1,4-hexadiene (II), the first example, to our knowledge, of alkylation by an olefin through the benzyne intermediate. It is suggested that the reaction follows the mechanism that has been well established for the addition of allylic olefins to other dienophiles at high temperatures. At this point the reaction we have observed appears to offer little promise of having general synthetic value.

In the past several years considerable interest[1–4] has developed in the synthesis of the unknown hydrocarbon *o*-di-*t*-butylbenzene and varying estimates have been made of its strain energy. An attractive path to its synthesis that would avoid the difficult step of forcing two bulky groups into *ortho-* positions through substitution on the benzene nucleus would be through the Diels-Alder condensation of the benzyne intermediate[5] with 2,5-dimethyl-2,4-hexadiene to give the unknown 1,1,4,4-tetramethylnaphthalene (I) which could then be oxidized to *o*-phenylenebis(α-isobutyric acid)[6] and hence by suitable reduction to the desired hydrocarbon.

(1) H. C. Brown, D. Gintis, and L. Domash, *J. Am. Chem. Soc.*, **78**, 5390 (1956).

(2) R. B. Turner, D. E. Nettleton, Jr., and M. Perelman, *J. Am. Chem. Soc.*, **80**, 1430 (1958).

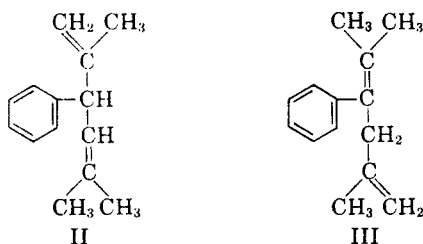(3) M. S. Newman and G. R. Kahle, *J. Org. Chem.*, **23**, 666 (1958).

(4) W. H. Puterbaugh and M. S. Newman, *J. Am. Chem. Soc.*, **81**, 1611 (1959).

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

This reaction was attempted using carefully purified 2,5-dimethyl-2,4-hexadiene and o-fluorobromobenzene with magnesium in tetrahydrofuran as a source of benzyne, following Wittig's work. The only isolable product gave an analysis consistent with the formula for I, decolorized bromine in carbon tetrachloride, gave a positive test for unsaturation with tetranitromethane, and showed an infrared spectrum generally permissive of this formula except for a strong band at 895 cm.$^{-1}$

The NMR spectrum[7] did not show the expected ratio of 2:4:12 for the ethylenic:aromatic:aliphatic protons but gave instead 3:5:10 with one aliphatic hydrogen slightly removed from the others. This suggested that we were dealing with an isomer of I in which a side chain had become attached to the benzene ring at only one point leaving five aromatic hydrogens on the ring. Although some difficulty was encountered in oxidizing the product cleanly, the use of potassium permanganate in acetone with pyridine at room temperature gave a high yield of benzoic acid, supporting the belief that only monosubstitution of the benzene ring had occurred.

Structure II suggested by the NMR study[7] explained all of the facts so far observed including the infrared band at 895 cm.$^{-1}$ which is typical of a terminal methylene group.[8] This was confirmed further by catalytic hydrogenation and ozonization. Using palladium on charcoal as catalyst, the product absorbed two moles of hydrogen; the first rapidly, presumably saturating the terminal ethylene group; and the second mole much more slowly as it added to the more sterically hindered double bond. Exactly two moles of ozone were absorbed and formaldehyde and acetone were isolated from the products. Although it is possible to write another structure III for the product which will fit most of the evidence, we reject it as being in

compatible with the NMR results (it would show a 2:5:11 ratio), because no conjugation is apparent from the infrared or ultraviolet spectra and because we can see no convenient mechanistic path for the formation of III whereas an easily available one with good precedent can be proposed for the formation of II.

We are somewhat puzzled as to why II is not isomerized to 2,5-dimethyl-3-phenyl-2,4-hexadiene during the reaction. It may be that the magnesium fluorobromide which could catalyze isomerization also catalyzes polymerization of the 2,4-diene much more easily than the 1,4-diene isolated. If this were so, any isomerization would result in products that we would not isolate by distillation.

DISCUSSION

We have observed the reaction of an allylic olefin with a dienophile to give a product in which the multiplicity of the reactive bond in the dienophile is reduced by one and in which the double bond in the olefin has migrated to a new position allylic to the point of attack by the dienophile. Ample precedent for this type of reaction may be found in the work of Alder,[9-11] Arnold,[12,13] Rondestvedt,[14,15] and others[16] on the high temperature reaction of strong dienophiles with allylic olefins. Several elegant experiments by Arnold's group[12,13] give clear evidence that the reaction proceeds through a concerted ionic mechanism involving a six-membered ring transition state and this suggestion is supported by Rondestvedt's[14,15] results. It is proposed that the reaction described above follows the same course.
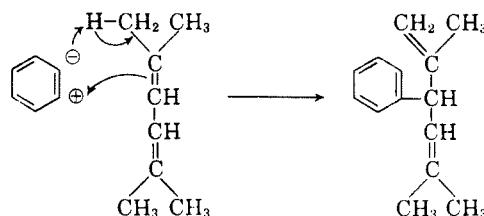
Although abundant examples of the high temperature reaction are to be found in the references above, to our knowledge none of them presents a case where the high temperature addition takes

II   III

(6) While we were attempting to prepare the diacid by the unsuccessful method described here, its synthesis by a different route was described by H. A. Bruson, F. W. Grant, and E. Bobko, J. Am. Chem. Soc., 80, 3633 (1958). To our knowledge this is the first o-di-t-butylbenzene derivative to be described in the literature.

(7) This spectrum was determined and interpreted by Dr. Aksel Bothner-By of Mellon Institute who suggested the correct structure on the basis of this result. We wish to express our gratitude to him for this experimental work and for his many helpful suggestions in the course of this study.

(8) L. J. Bellamy, The Infrared Spectra of Complex Molecules, 2nd ed., John Wiley and Sons, New York, N. Y., 1958, p. 51.

(9) K. Alder, F. Pascher, and A. Schmitz, Ber., 76, 27 (1943).

(10) K. Alder and T. Noble, Ber., 76, 54 (1943).

(11) K. Alder and C. Schmidt, Ber., 76, 183 (1943).

(12) R. T. Arnold and J. F. Dowdall, J. Am. Chem. Soc., 70, 2590 (1948).

(13) R. T. Arnold and J. S. Showell, J. Am. Chem. Soc., 79, 419 (1957).

(14) C. Rondestvedt and B. Wark, J. Org. Chem., 20, 368 (1955).

(15) C. Rondestvedt and A. Filbey, J. Org. Chem., 19, 548 (1954).

(16) For further references to the work of these and other authors in this field, see a recent review by R. D. Gilliom in M.I.T. Seminar Reports, 1956–57, 456.

place with a diene in preference to a Diels-Alder condensation as we have observed. The reason for this unusual behavior of 2,5-dimethyl-2,4-hexadiene is apparent from a model of the molecule which shows that it cannot be forced into the conformation required for ring closure but that the two isobutylene groups assume a position *trans* to each other and one of them is in the proper position for the addition to the dipolar bond in benzyne. The fact that the reaction occurs at room temperature attests to the reactivity of benzyne.

The discovery of this reaction for 2,5-dimethyl-2,4-hexadiene at once suggested that a general synthetic alkylation procedure using other allylic olefins might be developed. We are currently investigating this possibility but must report that at present the results are not at all promising; so far we have not found another case. (Using isobutylene as olefin we have obtained a 2% yield of an oil with the correct boiling point, infrared and NMR for 2-methyl-3-phenyl-propene-1 but with very poor analysis and refractive index.) Although allylbenzene gives particularly high yields in the thermal reaction with maleic anhydride, we have been unable to isolate 1,3-diphenylpropene from its reaction with benzyne under our conditions. Also reaction of cyclohexene with benzyne formed either from o-fluorobromobenzene and magnesium or from the reaction of bromobenzene and sodium amide in liquid ammonia failed to produce 3-phenylcyclohexene. Perhaps the reason that we cannot isolate simple adducts in these cases involving relatively favorable olefins but can find a simple product in the apparently less favorable case of 2,5-dimethyl-2,4-hexadiene is that the product of such a reaction is always another allylic olefin which if sufficiently reactive can continue to add to more benzyne molecules. If these following reactions are rapid enough in the cases of allylbenzene and cyclohexene, the main products will remain in the pot with the polymer that is always formed in the reaction and may not be separated by distillation.

EXPERIMENTAL

o-Fluorobromobenzene was prepared through pyrolysis of o-bromobenzenediazonium fluoroborate following directions of Bartlett and Giddings[17] based on a method of Schieman and Winkelmüller.[18] *2,5-Dimethyl-2,4-hexadiene* was purchased from Matheson, Coleman, and Bell. Since distillation failed to give adequate purification, the material was repeatedly frozen and the liquid phase decanted. This gave a product melting at 14.5° in agreement with the highest literature melting point[19] but with n_D^{20} = 1.4769 instead of 1.4796. Further purification failed to improve this value.

(17) P. D. Bartlett and W. Giddings, private communication.

(18) G. Schiemann and W. Winkelmüller, *Org. Syntheses*, Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 299.

(19) Heilbron, *Dictionary of Organic Compounds*, Vol. II, Oxford University Press, New York, N. Y., 1953, p. 311.

The well known[20] proclivity of this diene to polymerize explains the difficulty in purifying it.

Other reagents and solvents were commercially available and were purified until physical constants agreed with literature values.

Preparation of 2,5-dimethyl-3-phenyl-1,4-hexadiene (II). In a flame dried 100-ml. three necked flask with stirrer, condenser and addition funnel were placed 5.0 g. (0.207 mol.) of Grignard-grade magnesium turnings covered with 12 ml. of dry tetrahydrofuran. In the addition funnel was placed a solution of 20 ml. (0.200 mol.) of o fluorobromobenzene and 28.3 ml. (0.200 mol.) of 2,5-dimethyl-2,4-hexadiene in 93 ml. of dry tetrahydrofuran. In cases where the reaction did not begin spontaneously within 5 min. after the addition of 5-10 ml. of solution from the funnel, it could be initiated easily by scratching the magnesium, addition of a crystal of iodine or local heating with a match. The reaction was maintained at reflux by the addition of reactants, which required about an hour. Further refluxing with stirring on the steam bath consumed most of the remaining magnesium and produced a clear brown, viscous solution. After stripping off the solvent with water pump and steam bath, the residue was hydrolyzed with saturated ammonium chloride and 5% hydrochloric acid was added until two clear layers formed. The system was extracted with three successive portions of ether. After treatment with 5% sodium carbonate solution until no more carbon dioxide was evolved, the ether layer was washed with three portions of distilled water and the ether stripped off.

Distillation at 0.2 mm. began at 45° and between 65-67° a clear main fraction was obtained. Raising the temperature did not remove any other well defined fractions, the major portion of the product remaining in the pot as an intractible polymer. The 65-67° cut was not homogeneous but contained crystals that had apparently sublimed with the liquid phase. These were precipitated by adding ligroin and after recrystallization from carbon tetrachloride melted at 198°. This material was identified as triphenylene, a common by-product when benzyne is generated from o-fluorobromobenzene[6]; the melting point was undepressed by mixture with authentic triphenylene purchased from K and K Laboratories.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.69; H, 5.31. Found: C, 94.06; H, 5.51 (Schwarzkopf).

After removal of the ligroin, 4.29 g. (11.9% yield) of clear oil remained. This distilled completely at 83-86°, 0.45 mm., but very serious foaming, which could not be suppressed, interfered with all attempts to purify the product by distillation. The product decolorized bromine in carbon tetrachloride instantly, and showed unsaturation with tetranitromethane and potassium permanganate. The ultraviolet curve (using Beckman DU and 95% ethanol) showed gradual loss of optical density from 220-300 mµ and no aromatic fine structure. This may be attributed to masking by end absorption from the double bonds. The infrared spectrum was obtained with a Perkin-Elmer Model 21 Spectrophotometer (purchased on a grant from the National Science Foundation) with carbon tetrachloride as solvent.

Anal. Calcd. for $C_{14}H_{18}$: C, 90.26; H, 9.73. Found: C, 89.83; H, 9.96 (Microanalytical Laboratory of Mellon Institute).

Oxidation of the product. The product (0.637 g.) was dissolved in 100 ml. of acetone containing 5 ml. of pyridine and 4.0 g. of potassium permanganate. It was stirred rapidly at room temperature for 72 hr., rendered slightly acid with dilute sulfuric acid, and then treated with sodium bisulfite until the manganese dioxide disappeared. The solution was extracted with three 100-ml. portions of chloroform and the combined chloroform solutions dried over sodium sulfate and then Drierite. Evaporation of the chloroform left light green crystals corresponding in weight to a quantitative yield (0.424 g.) of benzoic acid. Recrystallization from water

(20) M. C. Kloetzel, *Org. Reactions*, 4, 13 (1948).

gave white crystals melting at 121° (undepressed upon admixture with authentic benzoic acid).

Hydrogenation. Hydrogenation of 0.195 g. (1.05 mmol.) of product was performed in ethyl alcohol using palladium on charcoal in the usual way[21] at room temperature. The first molar equivalent of hydrogen was absorbed within 15 min. while 24 hr. was required for the second mole.

Ozonization. To a 0.8409-g. sample dissolved in 100 ml. of anhydrous methanol as participating solvent was added ozone at −40° from a Welsbach T 23 ozonizer at a flow rate of 17 l. per hr. and an ozone concentration of 66.5 mg. per l.; oxygen pressure was eight p.s.i. and potential was 90.[22] It was estimated that at this rate 23.2 min. would be required for complete ozonization of two double bonds. After 20 min. the first traces of ozone broke through to the ozone meter and the reaction was stopped at 23 min. Now 2 g. of zinc dust was added and after warming to room temperature, 10 ml. of 5% sulfuric acid was added to destroy remaining peroxides. The solution was steam distilled until the distillate tested negative with 2,4-dinitrophenylhydrazine, the volume at this point being nearly 3 l. The first 1500-ml. portion of distillate was made just acid and 3 g. of dimedone in 50 ml. of 50% aqueous ethanol added.[23] A fluffy precipitate formed slowly which when dried gave the proper melting point for the formaldehyde-dimedone adduct, 196° (hot stage), and was not lowered by mixing with authentic adduct.

The filtrate from the dimedone reaction was steam distilled and 2,4-dinitrophenylhydrazine added. The mixed

(21) K. G. Stone, *Determination of Organic Compounds,* McGraw-Hill, New York, N. Y., 1956, p. 21.

(22) These conditions were chosen by Dr. R. H. Callighan of Mellon Institute who performed the ozonization for us. We are grateful for this help from him.

(23) R. P. Linstead, J. A. Elvidge, and M. Whalley, *A Course in Modern Techniques of Organic Chemistry,* Butterworths, London, 1955, Chapter 20.

derivatives were collected by filtration, dried, dissolved in chloroform and chromatographed first on Fisher alumina and then on Woelm alumina using chloroform as eluent in both cases. The wide range of melting points for acetone-2,4-dinitrophenylhydrazone that may be found in the literature attests to the difficulty in its purification. Several recrystallizations of the twice chromatographed product failed to raise the melting point from 123° to the desired 126°.[24] However, chromatography on Florosil with benzene eluent raised the melting point to the desired temperature and the identification was completed by mixed melting point and comparison of the infrared spectrum (Nujol mull)[25] with an authentic sample.

NMR spectrum.[7] This was obtained using a Varian Dual-Purpose 60-mc. NMR Spectrometer coupled to a Varian 60-mc. magnet with flux stabilizer. In addition to the gross features of the spectrum described above it was noticed that the hydrogens in the olefinic region consisted of a nonequivalence quartet and one sharp peak of intensity two. The quartet implies the presence of two lone hydrogens on adjacent carbons and the single spike the presence of two equivalent hydrogens on a carbon adjacent to another carbon bearing no hydrogens (*i.e.,* the methylene hydrogen on carbon-1). The lower of the nonequivalent lone hydrogens is that on carbon-4 of the 1,4-hexadiene chain and the higher one is presumably on carbon-3 and is shifted to its low position by its proximity to two trigonal carbons.

Acknowledgment. The writer is glad to express his appreciation to Professor Robert Levine of this Department and Dr. Bothner-By of Mellon Institute for critical readings of this manuscript.

PITTSBURGH 13, PA.

(24) Shriner, Fuson, and Curtin, *The Systematic Identification of Organic Compounds,* 4th ed., John Wiley and Sons, New York, N. Y., 1956, p. 316.

(25) J. H. Ross, *Anal. Chem.,* **25,** 1288 (1953).

Bridged Polycyclic Compounds. XI.
Epoxidation of Norbornene and of *exo*-Dihydrodicyclopentadiene[1]

S. B. SOLOWAY AND STANLEY J. CRISTOL

Epoxidation of norbornene has been shown to give 2,3-epoxynorbornane and epoxidation of *exo*-dihydrodicyclopentadiene (*exo*-5,6-cyclopentano-2-norbornene) has been shown to give *exo*-2,3-epoxy-*exo*-5,6-cyclopentanonorbornane. Thus both epoxidations occur without rearrangement and by *exo* addition to the bicycloheptene ring.

The epoxidations of norbornene (bicyclo(2,2,1)-heptene-2) with monoperoxyacetic acid[2] and monoperoxyphthalic acid[3] have been reported. The structure of the oxide was formulated as *exo*-2,3-epoxynorbornane (I) in view of its reduction by lithium aluminum hydride to *exo*-2-norborneol[2] and its ring opening to a 2,7-dihydroxynorborn-

I   II
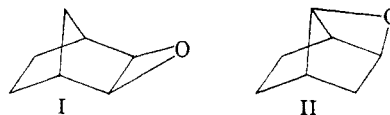
ane.[2,3] This formulation of the epoxide as the 2,3-isomer suggests that Wagner-Meerwein rearrangement has occurred in the ring-opening step, but the facts available in the literature are also consistent with the formulation of the epoxide as the 2,7- isomer, if the assumption is made that reduction by lithium aluminum hydride involves attack at the bridge carbon atom. We had pre-

(1) Previous paper in series: S. J. Cristol, W. K. Seifert, and S. B. Soloway, *J. Am. Chem. Soc.,* in press (1960).

(2) H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.,* **76,** 5396 (1954).

(3) H. Kwart and W. B. Vosburgh, *J. Am. Chem. Soc.,* **76,** 5400 (1954).