spectral data the dye was about 33% pure. Ignition gave a residue of silver and analysis showed the presence of 6.05% of silver which corresponds to 7.5% of silver cyanide.

Tricyanovinylations with tricyanovinyl chloride and tetracyanoethylene–silver nitrate offer advantages when working with materials that may be adversely affected by dimethylformamide or for preparation of tricyanovinyl compounds that are decomposed because of the basicity of normally useful solvents. A case in point is the preparation of 4-tricyanovinyl-1-p-tolylamino-7-p-tolylimino-1,3,5-cycloheptatriene.[12]

Other salts that promoted tetracyanoethylene condensations included ferric nitrate, zinc nitrate, zinc acetate, cobalt acetate, nickel acetate, nickel nitrate, cobalt nitrate and chromium acetate. These were less effective than silver nitrate and required heating. Blank experiments showed that no condensation occurred between benzaldehyde phenylhydrazone and tetracyanoethylene in acetonitrile even when boiled to dryness.

(12) Contribution No. 591, "N,N-Disubstituted 1-Amino-7-imino-1,3,5-cycloheptatrienes," by W. R. Brasen, H. E. Holmquist and R. E. Benson, in publication.

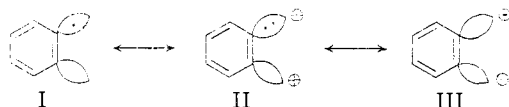# A Cycloaddition Reaction of Benzyne

BY HOWARD E. SIMMONS

The strained bicyclic hydrocarbons bicyclo[2.2.1]heptadiene and bicyclo[2.2.1]heptene reacted cleanly with benzyne to give cyclobutane derivatives, exo-3,4-benzotricyclo[4.2.1.0^{2,5}]nona-3,7-diene and exo-3,4-benzotricyclo[4.2.1.0^{2,5}]non-3-ene, respectively. Benzyne reacted with simple olefins to give complex mixtures of products that result from hydrogen abstraction. Some implications of these results are discussed.

Introduction.—The electrically neutral intermediate benzyne $(C_6H_4)^1$ is highly reactive when prepared under a variety of conditions.[2] The kinds of reactions undergone by benzyne that have been distinguished thus far include facile attack by nucleophiles,[1-4] dimerization and trimerization,[5] and Diels–Alder addition.[5,6] The observed products and the conditions under which many of these reactions occur indicate that benzyne is one of the most highly reactive hydrocarbon species known. Because of this high chemical reactivity, benzyne has never been isolated and little is known of its electronic structure. Most workers have interpreted the reactions undergone by benzyne in terms of the polar structures II and III, although it is generally recognized that benzyne is probably best represented as a resonance hybrid of structures I–III.

I II III

Cycloaddition Reactions.—When benzyne was generated by the reaction of o-fluorobromobenzene with magnesium in tetrahydrofuran[6a] in the presence of bicyclo[2.2.1]heptadiene, there was obtained in 15–21% yields a liquid hydrocarbon adduct IV. Vapor phase chromatography (v.p.c.) of the reaction mixture showed the presence of another product that was formed in such low yield

(1) J. D. Roberts, H. E. Simmons, L. A. Carlsmith and C. W. Vaughan, J. Am. Chem. Soc., **75**, 3290 (1953).

(2) For an excellent review of benzyne chemistry, see R. Huisgen and J. Sauer, Angew. Chem., **72**, 91 (1960).

(3) J. D. Roberts, D. A. Semenow, H. E. Simmons and L. A. Carlsmith, J. Am. Chem. Soc., **78**, 601 (1956), and earlier references cited therein.

(4) H. E. Simmons, J. Org. Chem., **25**, 691 (1960).

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

(6) (a) G. Wittig and R. Ludwig, Angew. Chem., **68**, 40 (1956); (b) G. Wittig and E. Knauss, Ber., **91**, 895 (1958); (c) G. Wittig and W. Behnisch, ibid., **91**, 2358 (1958); (d) G. Wittig and Niethammer, ibid., **93**, 944 (1960); (e) other examples have been cited by Professor Wittig in a private communication.

that isolation and characterization were not feasible. The n.m.r. spectrum of the minor product showed the absence of ethylenic protons. The major product was isolated in a pure state by preparative v.p.c. and analysis showed it to be a 1:1 adduct, $C_{13}H_{12}$. The adduct was unsaturated as determined by the rapid decolorization of bromine and potassium permanganate solutions.

The infrared spectrum of the adduct confirmed the presence of the aromatic ring, and olefinic unsaturation of the bicyclo[2.2.1]heptene type was indicated by a band at 6.39 μ. The spectrum was in agreement with the suggestion that the adduct resulted from a cycloaddition reaction and was a benzocyclobutene derivative. Proton nuclear magnetic resonance studies showed this indeed to be the case and further proved that no skeletal rearrangement had occurred. The spectral studies are discussed in detail below.

Bicyclo[2.2.1]heptadiene has frequently been reported to give 1:1 adducts with dienophiles by addition across the 2,6-positions.[7] In the reaction of benzyne with bicyclo[2.2.1]heptadiene it was anticipated that an analogous 2,6-adduct might be a reaction product.[8] Since epoxidation[9] of and addition of iodomethylzinc iodide[10] to the bicycloheptene type of double bond occur with

(7) Such additions to give nortricyclene derivatives have been reported with maleic anhydride (E. F. Ullman, Chemistry & Industry, 1173 (1958)) and with tetracyanoethylene (A. T. Blomquist and Y. C. Meinwald, J. Am. Chem. Soc., **81**, 667 (1959)). Tetrafluoroethylene gave a single adduct with this diene (W. R. Brasen, U. S. Patent 2,928,865 (1960)), and unpublished work in this Laboratory has shown conclusively that the adduct is the cyclobutane derivative i of exo configuration (R. E. Putnam).

(8) No saturated hydrocarbon products were detected in the crude reaction mixture with certainty, although a minor product that appeared saturated in the n.m.r. was isolated and partially purified by v.p.c. (see Experimental). This product may be the anticipated 2,6-adduct.

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

(10) H. E. Simmons and R. D. Smith, ibid., **81**, 4256 (1959).
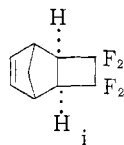
predominant or exclusive formation of *exo*-adducts, it seemed reasonable that the approach of the bulky benzyne molecule would lead to the isomer of *exo* geometry as indicated in structure IV. Recently Cava and Mitchell[11] have reported trapping benzocyclobutadiene as the Diels–Alder adduct with cyclopentadiene. These authors assigned the *endo* geometry to the liquid adduct XI on the basis of the Alder rule. Comparison of the various spectra of IV and XI[12] confirmed this structural relationship completely.

Chemically IV and XI behaved similarly and the following comparative reactions are summarized in Chart I. The *exo* isomer IV reacted readily

CHART I
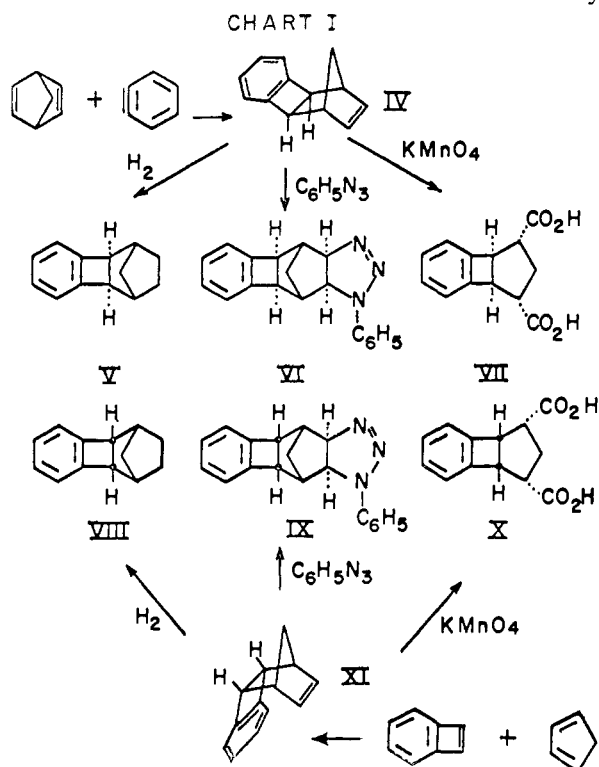
with phenyl azide[13] in pentane to give the white, crystalline triazole VI, m.p. 156.4–157.0°. The *endo* isomer XI gave a similar adduct IX, m.p. 132°.[11] Chromatography of both VI and IX on alumina showed that only a single product was formed in high yield in each case. Oxidation of IV with potassium permanganate in dry acetone gave a 72.5% yield of the crystalline diacid VII, m.p. 181.5–182.5°, while the isomeric diacid X, m.p. 239–240°, was obtained from XI in 36% yield under the same conditions.[11]

Catalytic hydrogenation of IV with 10% palladium-on-carbon in ethanol at 30° required 98.5% of one mole of hydrogen and afforded a high yield of the *exo*-dihydro derivative V. The same dihydro compound V was obtained using platinum oxide at 30° in glacial acetic acid and 98.6% of one mole of hydrogen was required. With the latter

(11) M. P. Cava and M. J. Mitchell, *J. Am. Chem. Soc.* **81**, 5409 (1959); also see C. N. Nenitzescu, M. Avram and D. Dinu, *Ber.*, **90**, 2541 (1957).

(12) A sample of pure XI was kindly supplied by Professor M. P. Cava and was used in subsequent experiments in this work.

(13) A reaction characteristic of the bicycloheptene type of double bond; see K. Alder and G. Stein, *Ann.*, **504**, 216 (1933).

catalyst at 70° additional hydrogen uptake occurred slowly and ceased after one mole was absorbed. V.p.c. analysis of the product showed only the *exo*-dihydro compound V (52%) and a completely saturated hydrocarbon (39%) as indicated by the n.m.r. spectrum. This saturated product was not further studied. Hydrogenation of the *endo* isomer XI using either 10% palladium-on-carbon in ethanol or platinum oxide in glacial acetic acid at 30° required 99 and 102%, respectively, of one mole of hydrogen, and both reductions afforded the *endo*-dihydro derivative VIII in high yield. Interestingly, the *endo* isomer was hydrogenated considerably faster than the *exo* isomer under the same conditions. At 80° with platinum oxide in glacial acetic acid the *endo*-dihydro compound VIII was completely resistant to further hydrogenation as shown by the total recovery of VIII. Previously Cava and Mitchell[11] reported that XI absorbed one mole of hydrogen rapidly and a second mole more slowly to give a tetrahydro derivative XII.[14]


XII
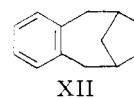
When benzyne was generated from *o*-fluorobromobenzene and magnesium in the presence of bicyclo[2.2.1]heptene, there was isolated by v.p.c. in 10% yield the *exo*-dihydro compound V. No other products boiling in the expected range for 1:1 adducts were detected by v.p.c. analysis of the crude product. The infrared and proton n.m.r. spectra of the product were identical with those of the hydrogenation product of IV. The limits of detection would have shown the presence of *endo*-dihydro derivative VIII in amounts of 0.5%. It is therefore concluded that no more than 0.5% of VIII could have been formed in the addition of benzyne to bicyclo[2.2.1]heptene. This result further confirms the structures assigned to IV and V.
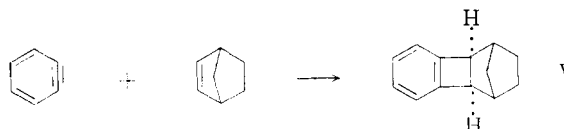
In view of the more complicated reactions of benzyne with less reactive, unstrained olefins, which seem to involve hydrogen abstraction (see below), the clean formation of cycloadducts with these bicyclic olefins is striking. Other multicenter addition reactions[9,10] to bicycloheptene double bonds occur exclusively with *exo* geometry, and this has been ascribed to the ease of steric approach to the less hindered side of the double bond. That the cycloadditions of benzyne to olefins in

(14) The properties of Cava's reported[11] tetrahydro derivative are identical with those of the authentic *endo*-dihydro compound VIII obtained in this work. In a private communication Professor Cava has informed the writer that he has reached the same conclusion and further that the course of hydrogenation of XI is complicated by the fact that the products seem to depend on the quantity of catalyst employed. With massive amounts of platinum oxide, VIII undergoes further hydrogenation, possibly to XII. As indicated above, when the hydrogenation of V was forced, slow hydrogen uptake occurred with the formation of a saturated product, showing the complexity of the reactions of these systems under the conditions of catalytic hydrogenation.

CHART II
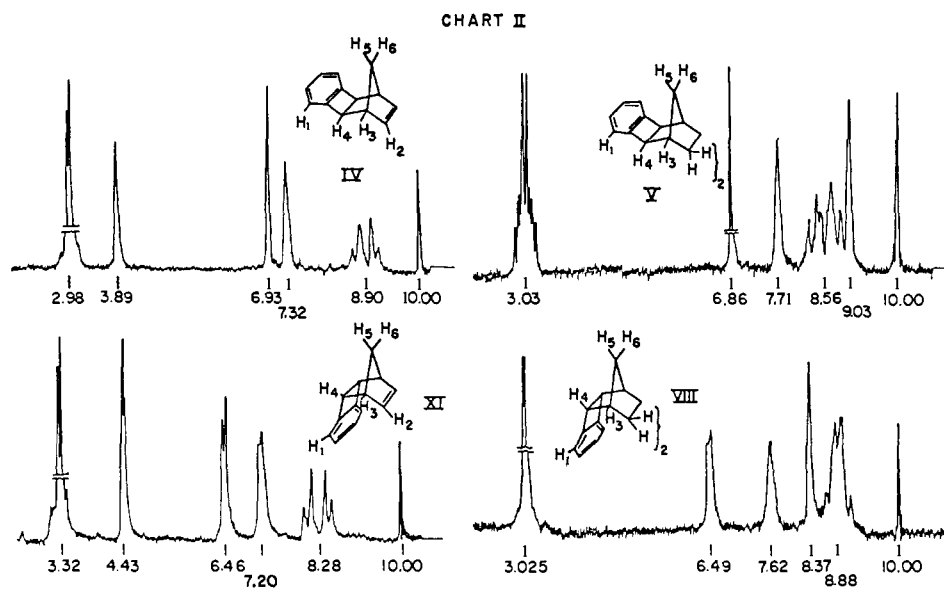
PROTON n-m-r SPECTRA OBTAINED AT 56.4 Mc.(SPINNING) RESONANCE
FREQUENCIES IN TERMS OF τ (p.p.m.) RELATIVE TO TETRAMETHYLSILANE (10.00)

the bicycloheptene system also occur with exclusive *exo* geometry is surprising since it implies that benzyne is more highly discriminating and thus more sensitive to steric controls than has been previously expected. It is also apparent that no unusual electronic effects need be invoked to explain the fact that cycloaddition occurs with bicyclo[2.2.1]heptadiene, since the same mode of reaction (and resultant geometry) is observed with bicyclo[2.2.1]heptene.[15]

Spectra.—The infrared spectra of IV and XI were very similar over most of the spectrum. The *exo* isomer IV showed olefin absorption at 6.39 μ and the *endo* isomer XI had a corresponding band at 6.33 μ.[16] The 5–6 μ region in the spectra of IV and XI was in very good agreement with that expected for *o*-disubstituted benzene derivatives. This region has been shown to be the most useful for the determination of the relative orientation of substituted benzenes.[17] Thus, isomer IV showed bands at 5.14, 5.25, 5.35, 5.41 and 5.56 μ while the corresponding bands in isomer XI were at 5.12, 5.24, 5.35, 5.42 and 5.55 μ. Both isomers had

(15) If benzyne is best represented by a polar structure II, it might have been anticipated that stepwise addition to bicyclo[2.2.1]heptene would have resulted in the formation of products derived from classical carbonium ion rearrangements in this system.
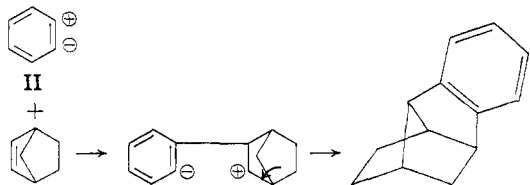
(16) Although some confusion exists in the literature concerning the (C=C) stretching vibration in bicyclo[2.2.1]heptene derivatives, the band at 6.38 μ in bicyclo[2.2.1]heptene has been assigned to this vibration by P. v. R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958). Other examples of strained bicyclo[2.2.1]heptene double bonds absorbing at 6.38–6.39 μ have been found in these laboratories (H. E. Simmons and R. D. Smith, in press).

(17) C. W. Young, R. B. DuVall and N. Wright. *Anal. Chem.*, **23**, 709 (1951).

similar relative intensity patterns, and the positions of the absorptions correspond well with those of a typical *o*-disubstituted benzene derivative. For example, *o*-dichlorobenzene absorbs at 5.12, 5.21, 5.30, 5.45 and 5.56 μ.[17] Compound IV exhibited bands at 12.04, 12.41, 13.01, 13.57 and 14.34 μ which seemed more in accord with a monosubstituted phenyl derivative, while XI had bands at 11.91, 12.40, 13.17 and 13.8 μ which were in agreement with Cava's assigned benzocyclobutene structure. However, upon catalytic hydrogenation the long wave length regions of the dihydro compounds V and VIII became quite similar. Compound V showed two strong bands at 13.21 and 13.76 μ, and VIII exhibited the corresponding bands at 13.26 and 13.94 μ. The olefinic (C=C) stretching bands at 6.39 and 6.33 μ were absent in the dihydro derivatives.

The ultraviolet spectra of IV and XI were characteristic and quite similar to that of the benzenoid model, *o*-xylene. A characteristic dis-

—————IV—————		—————XI—————	
λ, mμ	ε	λ, mμ	ε
301	8.4	308(sh)	13.4
276	2970	275	2450
269	2770	269	2300
263	1730	262	1430

tinction is observed in the extinction coefficients, the strained bicyclic derivatives absorbing approximately seven times more strongly (*o*-xylene, λmax 266 mμ (ε 415) for the center of this group of bands). The appearance of the very weak long wave length band at ~300 mμ in both hydrocarbons may be associated with the strained character of IV and XI, since these bands were absent or of very low intensity in the hydrogenation products, V and VIII.

The proton n.m.r. spectra of IV, V, VIII and XI provide strong evidence for the assigned structures and are shown in Chart II. Some of the fine structure due to spin–spin coupling has not been fully

TABLE I
PROTON N.M.R. ASSIGNMENTS[a]

Com-pound	H_1		H_2		H_3		H_4		H_5,H_6	
IV	2.98	(4)	3.89	(2)	7.32	(2)	6.93	(2)	8.90[b]	(2)
V	3.03	(4)	8.56[c]	(4)	7.71	(2)	6.86	(2)	9.03	(2)
XI	3.32	(4)	4.43	(2)	7.20	(2)	6.46	(2)	8.28[b]	(2)
VIII	3.025	(4)	8.88[c]	(4)	7.62	(2)	6.49	(2)	8.37	(2)

[a] Hydrogen subscripts refer to notation in Chart II. τ-Values are given in p.p.m. relative to tetramethylsilane (10.00); only multiplet centers are indicated. Values in parentheses are relative peak areas. [b] These figures refer to the center of the four line spectrum of the two non-equivalent protons. [c] Multiplet from ethano bridge.

reproduced in Chart II. The observed frequencies and assignments are summarized in Table I. The aromatic protons (H_1) of the four hydrocarbons occur at frequencies close to that of o-xylene (τ 2.99).[18] The vinyl protons of IV (τ 3.89) and XI (τ 4.43) occur at higher field than those in bicyclo-[2.2.1]heptadiene (τ 3.35),[18] and show fine structure in both cases. The fairly constant line assigned to H_3 varied over the range τ 7.20–7.71, which includes bridgehead bicycloheptane protons (endo-dicyclopentadiene, τ 7.20, and bicyclo[2.2.1]-heptene, τ 7 22).[18] In IV and XI, H_3 shows very fine multiplet structure with splittings of the magnitude observed in the vinyl protons (H_2), and the broader multiplet structure of H_3 in V and VIII presumably arises from spin–spin coupling with the protons of the ethano bridge and H_4 (see below). The bridgehead protons (H_4) on the four-membered ring also occur over a narrow range in the four hydrocarbons (τ 6.46–6.93). In the exo isomers IV and V, H_4 is a very sharp singlet indicating the geometry is correct for no splitting by H_3, the only adjacent proton. However in XI and VIII, H_4 is a resolved, unsymmetrical doublet, showing splitting by H_3 alone in this pair. This is just the hydrocarbon pair indicated above which shows the largest splittings of H_3, in complete agreement with the expectation that both H_2 and H_4 split H_3 in XI and VIII. It is interesting that the methylene bridges (H_5,H_6) appear as the characteristic four line pattern for the spin–spin coupling of two non-equivalent protons in the olefins IV and XI, and the coupling constants are equal in both isomers: $J_{5,6}{}^{IV} = J_{5,6}{}^{XI} = 8$ c.p.s. However in both dihydro derivatives V and VIII, the methylene bridge protons appear as a single peak with barely detectable fine structure (τ 9.02 (V), τ 8.37 (VIII)). This is understandable in the endo isomer VIII, where both H_5 and H_6 see essentially the same proton environment; however, the collapse of H_5 and H_6 to a single peak in the exo isomer V cannot be so easily rationalized.[19] It is also interesting that the center of the H_5,H_6 multiplet in the exo isomer IV shows considerably more shielding of the methylene protons (τ 8.90) than in the endo isomer XI (τ 8.28). This is in complete accord with the previously observed interatomic diamagnetic shielding of protons lying on or near the 6-fold axis of a benzene ring,[20] and lends strong support to the as-

(18) "NMR SUMMARY," G. V. D. Tiers, Minnesota Mining and Manufacturing Co., St. Paul, Minn.

(19) A detailed analysis of the spectra of the hydrocarbons discussed above will be given in a forthcoming publication by Dr. W. D. Phillips and the writer.

signed structures. Presumably the doublet at $\tau \sim 9$ belongs to H_5.

Other Olefin–Benzyne Reactions.—To investigate the behavior of benzyne with other olefins, o-fluorobromobenzene was treated with magnesium in tetrahydrofuran in the presence of a moderate excess of the olefin. Wittig[5,6] has shown that many systems containing conjugated double bonds undergo Diels–Alder reactions with benzyne, for example, furan, anthracene and simple 1,3-dienes.[6e] In this work 1,3-cyclohexadiene gave a mixture of two products in 46% yield consisting of the expected Diels–Alder adduct XIII (65%) and another 1:1 adduct XIV (35%). The structure of XIII was assigned by analogy to Wittig's results and on the basis of its infrared and n.m.r. spectrum. Although this second product could not be isolated in a pure state by v.p.c., the n.m.r. spectrum of the

XIII   XIV

crude material showed bands that were in accord with those expected of a benzocyclobutene structure (see Experimental).

With simple monoölefins benzyne underwent an interesting hydrogen abstraction reaction. Thus 1-octene gave a 17% yield of trans-1-phenyl-2-octene, which may have arisen by the following cyclic mechanism. The reaction mixture contained other products in small amounts which
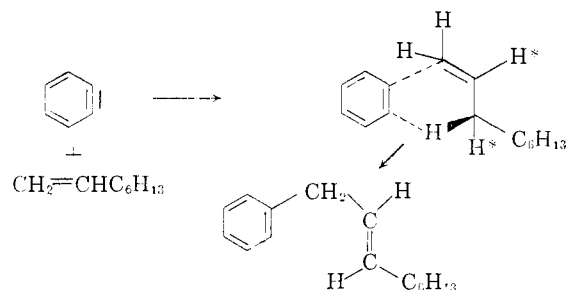

could not be separated in a pure state; however, trans-1-phenyl-2-octene was the only major product and was isolated by v.p.c. The structure of trans-1-phenyl-2-octene was based on analysis, physical constants, ultraviolet spectrum (γ_{max} 250 mμ, ϵ 660), catalytic hydrogenation to 1-phenyl-octane and oxidation to phenylacetic acid in 76% yield. The infrared spectrum of the isolated product had bands at 5.98 μ and 10.33 μ both of which have been extensively used for characterizing trans-olefins of the type $RCH{=}CHR$. The formation of phenyl substituted hydrocarbons in the reaction of benzyne with simple olefins is in marked contrast to the relatively clean cycloaddition observed with strained bicyclic olefins. Since no skeletal rearrangements are involved in the latter reactions,[15] the implication is that stepwise ionic addition is not occurring, and the transition states may be best represented as the four-center type. For this reason the reaction of benzyne

(20) J. S. Waugh and R. W. Fessenden, J. Am. Chem. Soc., 79, 846 (1957).

with 1-octene has been written as a concerted process as pictured above, in which a hydrogen atom is transferred to benzyne with near simultaneity in timing with the formation of the carbon–carbon bond. Molecular models indicate that approach of the benzyne molecule to the olefin in the direction of maximum overlap favors the configuration with the bulky alkyl group (C_6H_{13}) away from the entering benzyne on steric grounds. This transition state predicts the product olefin to be of the *trans* configuration, the two starred hydrogen atoms becoming the olefinic hydrogens. This was seen to be the case experimentally. The author is grateful to Professor J. F. Bunnett for pointing out the steric consequences of this addition reaction.

In a recent publication Arnett[21] has reported that benzyne generated from *o*-fluorobromobenzene and magnesium reacted with 2,5-dimethyl-2,4-hexadiene to give a compound characterized as 2,5-dimethyl-3-phenyl-1,4-hexadiene[22] and none of the expected Diels–Alder adduct was detected. The formation of the unconjugated diene was interpreted as occurring by a cyclic process similar to that suggested above for the formation of 1-phenyl-2-octene.
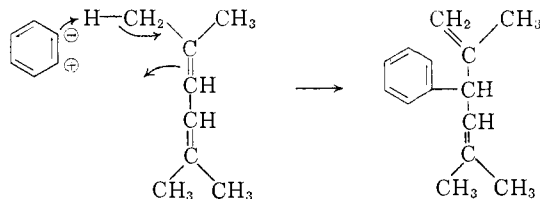
Benzyne reacted with cyclohexene to give a complex mixture of products from which 3-phenylcyclohexene was isolated in 18% yield by v.p.c. 1,5-Cyclooctadiene gave a complex mixture of products, from which after catalytic hydrogenation phenylcyclooctane could be isolated. Clean products could not be isolated from the reactions of benzyne with ethylene, allene, styrene, 5-decyne, diphenylacetylene, benzene and naphthalene. Interestingly, tetrafluoroethylene reacted with *o*-fluorobromobenzene and magnesium in tetrahydrofuran in a closed system to give a low yield of *o*-fluoro-α,β,β-trifluorostyrene. Apparently the intermediate Grignard reagent, *o*-fluorophenylmagnesium bromide, exists for an appreciable time, long enough for the usual addition reaction to fluoroolefins.[23] The only other product isolated from the reaction was triphenylene.
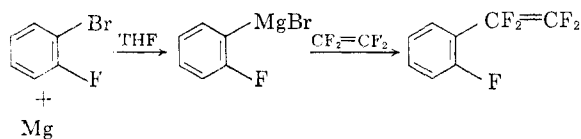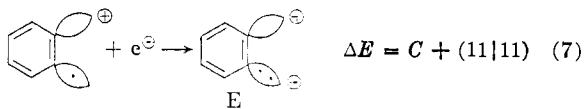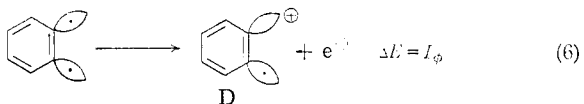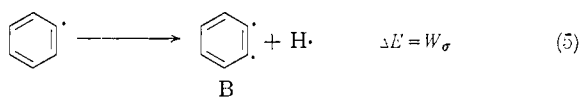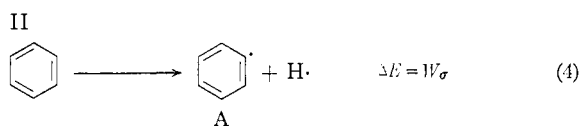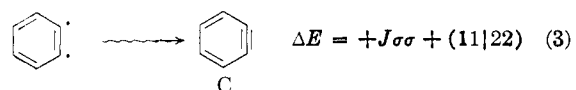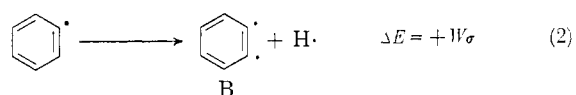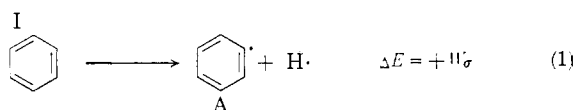
Structure of Benzyne.—Detailed calculations considering deformation of the regular hexagonal

(21) E. M. Arnett, *J. Org. Chem.*, **25**, 324 (1960).

(22) This product was isolated with difficulty by distillation,[21] and in view of our findings that the apparently homogeneous distillates from all of the reactions of benzyne with olefins actually contain several components as shown by v.p.c., it is possible that products isomeric with 2,5-dimethyl-3-phenyl-1,4-hexadiene may also have been formed.

(23) S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

symmetry will certainly be necessary to give an adequate description of the benzyne molecule in the ground state. Some crude considerations, however, are of interest, for they provide an initial basis for an understanding of the structure and reactivity of this hydrocarbon. When two *ortho*-hydrogen atoms are removed from benzene, the resulting diradical I can be considered a canonical structure in resonance with the dipolar structures II and III, providing spin conservation is observed. The orbitals emphasized in I–III are part of the σ-framework and are essentially orthogonal to the π-electron system of the ring. The relative importance of the structures I and II in the wave function describing the ground state of the molecule can be roughly estimated if the π-electrons are considered only slightly perturbed (no ring deformation). Consider the following formalizations

$$\Delta E = +\text{''}\sigma \quad (1)$$

$$\Delta E = +W_\sigma \quad (2)$$

$$\Delta E = +J_{\sigma\sigma} + (11|22) \quad (3)$$

$$\Delta E = W_\sigma \quad (4)$$

$$\Delta E = W_\sigma \quad (5)$$

$$\Delta E = I_\phi \quad (6)$$

$$\Delta E = C + (11|11) \quad (7)$$

In I: (1) is the dissociation of benzene to phenyl radical (A) with the attendant energy change W_σ. (2) is a second dissociation of an *ortho*-hydrogen atom to give the hypothetical, uninteracted diradical (B), the energy change being again approximately W_σ. In (3) interaction is allowed to give benzyne (C), introducing $J_{\sigma\sigma}$, the exchange interaction of the two sp^2 hybrid orbitals, and (11|22), the two-center coulomb repulsion integral.

In II: (4) and (5) are as before, and (6) is the ionization of one of the uninteracted electrons, a process whose energy change approximates that of the ionization potential of phenyl radical, I_ϕ. In process 7 the electron is returned to D in a manner to give the dipolar form E. This process is attended by a decrease in the coulomb electro-

static energy of opposite charges at a distance of 1.39 Å. and an increase given by the appropriate one-center coulomb repulsion integral $(11|11)$, since the two electrons now exist in the same orbital.

If we compare the energy of the diradical canonical structure (I or B) with that of a dipolar structure (II, III or E), it is readily seen that

$$\Delta E = E_E - E_B = I_\phi + C + (11|11) \qquad (8)$$

$(11|11)$ is approximately equal to $+10.5$ e.v.,[24,25] $C = -10.4$ e.v. at 1.39 Å., and I_ϕ can be taken to be approximately $+11.2$ e.v.[25] Substituting these values in (8) gives $\Delta E = E_E - E_B = +11.3$ e.v., showing that the *canonical structure* II is very much less stable than I.

If electron interaction is allowed in I (B) as shown in (3), we can estimate the gain in energy.

$$\Delta E = E_E - E_C = I_\phi + C + (11|11) - (11|22) - J_{\sigma\sigma} \qquad (9)$$

The exchange integral J_{bond} is known to be roughly proportional to S^2_{bond}, where S is the overlap integral. For the π-bond in ethylene, $S_{\pi,\pi} = +0.250$ and $J_{\pi,\pi} \sim 0.063$. In benzyne, calculation by the method of Mulliken[26] shows that $S_{\sigma\sigma} = 0.125$ and hence $J_{\sigma\sigma} \sim 0.016$. The exchange integral in ethylene is negative and has a value near -3.2 e.v.,[24] so that we estimate $J_{\sigma\sigma} \cong -0.8$ e.v. in benzyne. The two-center coulomb repulsion integral $(11|22)$ has the value $+7.3$ e.v. at 1.39 Å.[24] Substituting these values in (9) gives

$$\Delta E = E_E - E_C = +4.0 - J_{\sigma\sigma} = +4.8 \text{ e.v.}$$

If benzyne is of distorted hexagonal geometry, so that $J_{\sigma\sigma}$ becomes more negative as overlap increases, the ionic structures become even less important.
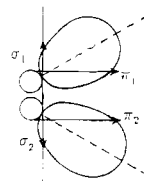
It is thus estimated that the canonical structures II and III are probably much less stable than covalent structure I. The overlap integral for two pure sp^2 orbitals of the hexagonal geometry assumed in our model of benzyne $(S_{\sigma\sigma} = 0.125)$ is larger than might have been anticipated and leads to an exchange interaction about one-fourth as strong as found in a pure π-bond. It seems reasonable, therefore, to speak of a new "bond" in benzyne, and it can be seen from the simple decomposition of the vector components of the two sp^2 orbitals forming the new bond in benzyne that the most significant overlap is due to the π-components (π_1, π_2). The σ-components (σ_1, σ_2) are directed for minimum overlap. The new bond cannot be considered a π-bond in the usual sense, since the positive overlap receives contributions from both σ- and π-electron distributions. A referee has pointed out that the bond could be described as

approximately $^2/_3$ π and $^1/_3$ σ, however it must be emphasized that this is a consequence of the assumed geometry. The actual benzyne molecule is probably considerably distorted in seeking the configuration of lowest potential energy.

Recently Huisgen, Mack and Möbius[27] have presented evidence that benzyne intermediates are truly halogen-free when generated by the reaction of aryl halides and strong bases. In discussing the electronic structure of benzyne these authors consider the new bond in terms of the limiting structures involving pure sp^2 hybrids and pure p-orbitals. They conclude that although their preferred representation of the intermediate "is not completely correct," it strongly emphasizes the

"aromatic character" of benzyne. This view agrees with our conclusions above.

These results suggest that benzyne might best be considered a truly aromatic hydrocarbon with one multiple bond of high energy content, whose reactivity might more nearly resemble that of a very strained olefin than that of a polar species such as II. The high reactivity of benzyne in Diels–Alder reactions,[6] homopolymerizations,[5] and possible hydrogen abstraction reactions[4] is in accord with this view. The formation of a cyclobutane derivative from the reaction with strained olefins appears to be the first example of this kind of addition observed for benzyne.[28] Although the mechanism(s) of cycloaddition reactions is not known with certainty,[29] benzyne as pictured above might well be expected to undergo such reactions with appropriate olefins.

Experimental[30]

o-Fluorobromobenzene was prepared by the pyrolysis of o-bromobenzenediazonium fluoroborate. Large-scale pyrolyses of 200-g. batches of the salt gave 80% yields of pure o-fluorobromobenzene (b.p. 157°, $n^{25}D$ 1.5346). The overall yield from o-bromoaniline was 72%, a considerable improvement over the reported[31] yield (40%). The olefins

(24) R. Pariser, *J. Chem. Phys.*, **21**, 568 (1953), has shown that theoretical values of $(11|11)$ based on the convenient Slater orbitals are much too large but that the empirical relation $(11|11) = I - A$, where I is the ionization potential and A the electron affinity, gives a much better estimate of the one-center coulomb repulsion integral. Also see R. Pariser and R. G. Parr, *ibid.*, **21**, 466, 767 (1953).

(25) R. S. Mulliken, *ibid.*, **2**, 782 (1934), gives for the sp^2 valence state $I = 11.22$ e.v., $A = 0.69$ e.v. so that $(11/11) = +10.5$ e.v. Accurate values of I and A for an sp^2 electron *in a molecule* are not known, but they can be approximated for our purposes by considering the corresponding values for an isolated carbon atom in the sp^2 valence state.

(26) R. S. Mulliken, *ibid.*, **19**, 900 (1951).

(27) R. Huisgen, W. Mack and L. Möbius, *Tetrahedron*, **9**, 29 (1960).

(28) The dimerization of benzyne to biphenylene[6] can be considered a special case of cycloaddition, although the formation of triphenylene may not be associated with direct trimerization.[2]

(29) J. D. Roberts and C. M. Sharts, "Organic Reactions," Vol. 12, Cyclobutane Derivatives from Thermal Cycloaddition Reactions," in press.

(30) All melting points are corrected and boiling points are uncorrected. Infrared spectra were determined on a Perkin–Elmer model 21 double beam infrared spectrometer equipped with NaCl optics (2–15 μ). Spectra were obtained on pure liquids or in potassium bromide wafers. The proton n.m.r. spectra were obtained using a Varian high resolution n.m.r. spectrometer and electromagnet at a frequency of 56.4 Mc. The spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of tetramethylsilane as an internal standard. The usual spinning techniques were used to obtain the highest resolution.

(31) E. Bergmann, L. Engel and S. Sandor, *Z. physik. Chem.*, **10B**, 106 (1930).

employed in this work were commercial samples and were purified before use until their physical constants were in agreement with reliable literature values.

Reaction of Benzyne with Bicyclo[2.2.1]heptadiene.— Five milliliters of a solution of o-fluorobromobenzene (40.0 g., 0.228 mole) in dry tetrahydrofuran (40 ml.) was added dropwise to a solution of freshly distilled bicyclo[2.2.1]-heptadiene (40.0 g., 0.436 mole) and magnesium (5.60 g., 0.230 mole) in tetrahydrofuran (160 ml.) in a 500-ml. three-necked flask equipped with a magnetic stirrer, pressure-equalized dropping funnel and reflux condenser (calcium chloride tube). The system was initially flushed with nitrogen and stirred and heated until reaction began. The remaining o-fluorobromobenzene solution was added at a rate to maintain vigorous reflux. When the addition was completed, the orange reaction mixture was heated under reflux for an additional 30 minutes. The reaction mixture was poured into a separatory funnel containing 200 ml. of cold 10% hydrochloric acid, and the mixture was extracted with three 50-ml. portions of pentane. The combined pentane extracts were washed successively with 100 ml. of water, 100 ml. of saturated sodium bicarbonate solution and 100 ml. of water. The pentane solution was dried over anhydrous magnesium sulfate and the pentane was removed by distillation. Fractionation of the residue gave 8.2 g. of a colorless oil, b.p. 63–69° (0.9 mm.). Several grams of triphenylene could be recovered from the distillation residue. Analytical v.p.c. of the oil showed that it consisted of two components, ret. times 9.75 and 12.0 min. The products were separated on a preparative column (6-ft. copper tubing, $^3/_4$ in. dia.) packed with firebrick coated with 15% "tetrafluoroalkylpyromellitate" operated at 180° with a helium flow rate of 600 ml./min. The product of retention time 9.75 min. was separated in the pure state and weighed 5.6 g. (14.7%). The sample of pure exo-3,4-benzotricyclo[4.2.1.0^{2,5}]nona-3,7-diene (IV) had b.p. 69–70° (0.75 mm.), n^{25}D 1.5676.

Anal. Calcd. for $C_{13}H_{12}$: C, 92.81; H, 7.19. Found: C, 92.76; H, 7.15.

In other runs yields of purified IV were as high as 21%. The minor component of the reaction mixture (ret. time 12.0 min.) partially crystallized. It was saturated as determined by its failure to decolorize potassium permanganate solution, but it could not be obtained sufficiently pure for characterization.

Hydrogenation of IV.—A sample of IV (1.0000 g., 5.945 mmoles) in 95% ethanol (20 ml.) was hydrogenated in the presence of 100 mg. of 10% palladium-on-carbon at 30° and atmospheric pressure and required 0.0116 g. (97.5% of one mole of hydrogen). The catalyst was removed by filtration and the ethanol was distilled. The residue was dissolved in pentane and passed through a short column of alumina. After evaporation of the pentane the residue was fractionated through a micro-column to give 0.87 g. (86%) of pure exo-3,4-benzotricyclo[4.2.1.0^{2,5}]non-3-ene (V).

Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.68; H, 8.22.

When a sample of IV (0.4648 g., 0.002763 mole) was hydrogenated in 20 ml. of glacial acetic acid over 20 mg. of reduced platinum oxide at 30°, 98.6% of one mole of hydrogen was absorbed. The product was worked up as above and afforded 0.423 g. (90%) of pure V. Hydrogenation over platinum oxide ceased cleanly at 30°; however, at 50° slow uptake began and approximately one additional mole of hydrogen was absorbed. When this reaction mixture was worked up and analyzed by v.p.c. (12-ft. copper tubing ($^3/_4$ in. diameter) packed with firebrick coated with 30% "tetrafluoroalkyl pyromellitate," operated at 150° with a helium flow rate = 600 ml./min.), compound V (ret. time 60.75 min.) was isolated in 52% yield along with a second product (ret. time 49.9 min.) in 39% yield. The latter compound partially crystallized on standing and appeared to be a mixture which could not be separated by v.p.c. This product did not decolorize potassium permanganate solution, and the n.m.r. spectrum showed no olefinic or aromatic protons.

The infrared spectrum of V showed the absence of olefinic absorption at 6.39 μ and was in accord with the assigned structure.

Hydrogenation of XI.—A sample of pure XI[12] (0.2418 g., 0.001438 mole, b.p. 82–84° (2 mm.), n^{25}D 1.5712) in

glacial acetic acid (10 ml.) was hydrogenated at 30° over reduced platinum oxide (20 mg.). The hydrogenation required 102% of one mole of hydrogen and then ceased completely. The product was worked up and isolated as described above. There was obtained 0.225 g. (92%) of pure $endo$-3,4-benzotricyclo[4.2.1.0^{2,5}]non-3-ene (VIII), b.p. 68° (1 mm.), n^{25}D 1.5612.

Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.66; H, 8.24.

When it was attempted to force the hydrogenation under the above conditions by raising the temperature to 80°, no further uptake of hydrogen was detected.

The infrared spectrum of VIII was free of olefinic absorption and was very similar to that of V.

Reaction of IV with Phenyl Azide.—A mixture of phenyl azide (0.12 g., 0.0010 mole) and IV (0.17 g., 0.0010 mole) was allowed to stand in pentane (5 ml.). After 6 hours white crystals began to deposit, and these were filtered off after 48 hours. Recrystallization from hot hexane gave 0.25 g. (87%) of pure exo-9,10-benzo-exo-3,4,5-triazatetra-cyclo[5.4.1.0^{2,6}.0^{8,11}]-5-phenyldodeca-3,9-diene (VI), m.p. 156.4–157.0°.

Anal. Calcd. for $C_{19}H_{17}N_3$: C, 79.40; H, 5.96. Found: C, 79.26; H, 6.05.

The infrared spectrum of VI was very similar to that of the $endo$-exo isomer IX,[11] m.p. 132°. Small samples of VI and IX were chromatographed on neutral alumina using benzene–hexane. Both triazoles were recovered in >95% yield and were shown to be homogeneous.

Oxidation of IV.—A solution of potassium permanganate (0.520 g., 0.00326 mole) in dry acetone (30 ml.) was added dropwise over 20 min. to a stirred solution of IV (0.200 g., 0.00119 mole) in dry acetone (4 ml.). When addition was complete the mixture was stirred for 1 hour at 25° and then was evaporated to a volume of 10 ml. The resulting mixture was diluted with 10 ml. of 1% sodium bisulfite solution and acidified with dilute sulfuric acid to pH 2. This mixture then was extracted eight times with 10-ml. portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and were evaporated to give a crystalline residue. The residue was shaken with 6 ml. of 1% sodium hydroxide solution and 20 ml. of ether. The aqueous layer was separated, filtered, and acidified with concentrated sulfuric acid. The oil which separated crystallized after standing 1 hour at 0°. After recrystallization from hot benzene, there was obtained 0.200 g. (72.5%) of the pure diacid VII, m.p. 181.5–182.5°. The infrared spectrum of VII was similar to that of X[11] and was in complete accord with the assigned structure.

Anal. Calcd. for $C_{13}H_{12}O_4$: C, 67.24; H, 5.21. Found: C, 67.61; H, 5.42.

Reaction of Benzyne with Bicyclo[2.2.1]heptene.— The reaction was carried out essentially as described previously for bicyclo[2.2.1]heptadiene. From the reaction of o-fluorobromobenzene (40.0 g., 0.228 mole), magnesium (5.60 g., 0.230 mole) and bicyclo[2.2.1]heptene (40.0 g., 0.426 mole) in tetrahydrofuran (180 ml.), there was isolated by distillation 3.9 g. of an oil, b.p. 70–72° (1 mm.), which was analyzed and separated into its components by v.p.c. The oil was 98% one component which was separated by preparative v.p.c. (12-ft. column packed with 30% "tetrafluoroalkyl pyromellitate" on "Chromosorb" operated at 175°, helium flow rate 600 ml./min., sample size 1.0 ml.). The major peak showed a retention time of 29.0 min. under these conditions. There was thus obtained 3.7 g. (9.6%) of pure V, whose infrared and proton n.m.r. spectra were identical with those of the hydrogenation product of IV.

Reaction of Benzyne with 1-Octene.—The reaction was carried out under the usual conditions employing o-fluorobromobenzene (50.0 g., 0.286 mole), magnesium (7.2 g., 0.296 mole) and freshly distilled 1-octene (50.0 g., 0.446 mole), b.p. 121–121.5°, n^{25}D 1.4068) in tetrahydrofuran (120 ml.). After workup, distillation afforded 11 g. of an oil, b.p. 85–87° (0.75 mm.). Preparative v.p.c. allowed the separation of the major component of the distillate, and there was isolated 9.2 g. (17%) of 1-phenyl-2-octene, b.p. 87° (0.8 mm.), n^{25}D 1.4986.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.05; H, 10.48.

There was isolated from the distillation residue 4 g. of triphenylene, m.p. 199°, and 2 g. of tetraphenylene, m.p. 241–242°.

The infrared spectrum was in accord with the assigned structure for the major product and showed bands at 5.98 μ (C=C) stretching, and 10.33 μ *trans* out-of-plane (C—H) deformation. These bands have an extensive literature for characterizing *trans* double bonds of the type RCH=CHR. The ultraviolet spectrum showed λ_{max} 250 mμ (ϵ 660) indicating that the benzene ring and double bond are not in conjugation.

Catalytic hydrogenation of the phenyloctene using platinum oxide in ethanol at 33° required 105% of one mole of hydrogen. The product was purified by v.p.c. and had n^{25}D 1.4831 (lit.[32] n^{25}D 1.4831 for 1-phenyloctane). The infrared spectrum of the hydrogenation product was identical to that of an authentic sample of 1-phenyloctane. Oxidation of the phenyloctene with cold potassium permanganate solution led to the isolation of phenylacetic acid in 76% yield (identified as the amide).

Reaction of Benzyne with 1,3-Cyclohexadiene.—The reaction was carried out under the usual conditions employing *o*-fluorobromobenzene (10.0 g., 0.057 mole), magnesium (1.40 g., 0.058 mole), 1,3-cyclohexadiene (9.1 g., 0.11 mole) and tetrahydrofuran (20 ml.). There was obtained 4.1 g. (46%) of a mixture of 5,6-benzobicyclo[2.2.2]-octa-2,5-diene (XIII) and a second 1:1 adduct (XIV), b.p. 75–80° (1.3 mm.), n^{25}D 1.5677; v.p.c. analysis of the mixture showed the ratio of XIII:XIV was 65:35. A sample of pure XIII was obtained by preparative v.p.c. and had b.p. 79–80° (1 mm.), n^{25}D 1.5657.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 92.20; H, 8.04.

A pure sample of XIV could not be obtained by v.p.c. However, a sample of a mixture of XIII and XIV, in which the latter was enriched, was used for n.m.r. analysis. The lines of the spectrum attributable to XIV could be interpreted on the basis of the assigned structure, and a line

of weight 2 at τ 6.51 indicated the presence of cyclobutane hydrogens in the benzocyclobutene structure.

Reaction of Benzyne with Cyclohexene.—The reaction was carried out under the usual conditions employing *o*-fluorobromobenzene (20.0 g., 0.114 mole), magnesium (2.80 g., 0.115 mole) and cyclohexene (32.0 g., 0.390 mole) in tetrahydrofuran (45 ml.). After workup, distillation afforded 5 g. of a fraction, b.p. 60–65° (0.6 mm.); v.p.c. analysis showed a complex mixture from which 3.3 g. (18%) of fairly pure 3-phenylcyclohexene, b.p. 64–65° (0.55 mm.), n^{25}D 1.5402 (lit.[33] b.p. 235°, n^{20}D 1.5440), was obtained. The infrared and ultraviolet spectra of the product indicated that the benzene ring and double bond are not in conjugation, and this is further confirmed by the low value of the refractive index.[33]

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.75; H, 9.17.

Catalytic hydrogenation of the phenylcyclohexene in ethanol at 33° over platinum oxide required 104% of one mole of hydrogen. The product of the hydrogenation had b.p. 67° (0.5 mm.), n^{25}D 1.5413 (lit.[34] n^{20}D 1.5429), and its infrared spectrum was identical with that of authentic phenylcyclohexane.

Reaction of Tetrafluoroethylene with *o*-Fluorobromobenzene and Magnesium.—*o*-Fluorobromobenzene (10.0 g. 0.057 mole), magnesium (1.40 g., 0.058 mole) and tetrahydrofuran (35 ml.) were sealed in a 100-ml. silver-lined pressure vessel. Tetrafluoroethylene (12.0 g., 0.12 mole) was introduced into the vessel which was then sealed and heated at 65° for 3 hours. After cooling and venting the vessel, the contents were worked up in the usual fashion. Distillation afforded 1.0 g. of *o*-fluoro-α,β,β-trifluorostyrene, b.p. 125°, n^{25}D 1.4441. The n.m.r. fluorine spectrum was entirely in accord with the assigned structure.

Anal. Calcd. for $C_8H_4F_4$: C, 54.56; H, 2.29; F, 43.15. Found: C, 54.29; H, 2.38; F, 43.43.

(32) A. W. Schmidt, *Ber.*, **75**, 1399 (1942).

(33) A. Berlande, *Bull. soc. chim. France*, [V] **9**, 942 (1942). 1-Phenylcyclohexene is reported to have n^{20}D 1.5718.

(34) O. Neunhoffer, *J. prakt. Chem.*, [II] **133**, 95 (1932).

Conformational Analysis. XIII. On the Geometry of the Cyclooctane Ring. The Relative Stabilities of the 1,3-Dimethylcyclooctanes[1,2]

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Infrared studies confirm an earlier suggestion that cyclooctanone exists very largely in a single conformation in the liquid phase at 25°. The pure isomeric *cis*- and *trans*-1,3-dimethylcyclooctanes have been prepared and equilibrated in the presence of a palladium catalyst at 260°. The free energy of the reaction *trans*- ⇌ *cis*-1,3-dimethylcyclooctane was found to be +0.25 kcal./mole. It was concluded that the conformation of the cyclooctane ring which best fits this and other available data is the skewed crown.

Introduction

The conformations of the cyclooctane ring have been the subject of a number of recent papers.[3–8] Three separate conformational structures for cyclooctane have been proposed together with two

additional ones for certain cyclooctane derivatives including cyclooctanone.[9,10] The purpose of the present work is to furnish additional information which bears on this question, and to attempt to reach the correct conclusion as to the conformation of the eight membered ring.

The conformations of the medium rings became of interest as soon as the relative difficulty of their synthesis was noted.[11] In an effort to explain the variation of the carbonyl stretching frequency with ring size in the cyclanones, the "O-inside" and "O-outside" conformations were discussed,

(1) Paper XII, N. L. Allinger and V. Zalkow, *J. Am. Chem. Soc.*, **83**, 1144 (1961).

(2) This work was supported by a research grant from the National Science Foundation.

(3) (a) E. Billeter, T. Bürer and H. H. Günthard, *Helv. Chim. Acta*, **40**, 2046 (1957); (b) T. Bürer and H. H. Günthard, *ibid.*, **40**, 2054 (1957).

(4) R. Kolinski, H. Piotrowska and T. Urbanski, *J. Chem. Soc.*, 2319 (1958).

(5) G. Chiurdoglu, T. Doehaerd and B. Tursch, *Chemistry & Industry*, 1453 (1959).

(6) H. E. Bellis and E. J. Slowinski, Jr., *Spectrochim. Acta*, 1103 (1959).

(7) N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959).

(8) R. Pauncz and D. Ginsburg, *Tetrahedron*, **9**, 40 (1960).

(9) N. L. Allinger and S. Greenberg, *J. Am. Chem. Soc.*, **81**, 5733 (1959).

(10) N. J. Leonard, T. W. Milligan and T. L. Brown, *ibid.*, **82**, 4075 (1960).

(11) For a summary of earlier work, see V. Prelog, *J. Chem. Soc.*, 420 (1950).