

H, 8.92; mol wt, 316. Found: C, 90.77; H, 8.94; mol wt (mass spectrum), 316.

The ^1H nmr spectrum showed the presence of 5.4 methyl groups, 2.0 different ring methylene groups, and 1.0 olefinic hydrogen to 8.0 aromatic hydrogens. The fractional methyl is probably an impurity. The compound showed a sharp peak (broad base) by vpc.

B.—2-Chloro-4-methylpentene-1 and -2 (59.3 g) were added dropwise over a period of 2.5 hr to a vigorously stirred mixture of 70 g of AlCl_3 in 234 g of benzene while carbon monoxide was rapidly bubbled in at 23–26° during the addition period and for 1.25 hr thereafter. Hydrolysis and work-up of the oil layer by vacuum distillation gave 25.2 g of a fraction, bp 160–180° (0.1 mm), which upon redistillation gave XIX as a heart cut, bp 152–157° (0.1 mm), n_D^{20} 1.5619. No indanones were detected in any of the other fractions.

2,5-Dimethyl-1,4-bis(β -chloro-*t*-butyl)benzene (XXI).—Methallyl chloride (181 g, 2.0 moles) was added dropwise over a period of 5.5 hr to a vigorously stirred mixture of 318 g (3.0 moles) of *p*-xylene and 200 g (2.0 moles) of 96% sulfuric acid while maintaining the temperature at 20–21°. Stirring was continued for 16 hr thereafter at 20–25°. The lower acid layer was then removed and the crystalline solid separated from the oil, then washed, dried, and recrystallized from 350 ml of boiling ethanol to give 66.5 g (11.5% yield) of XXI, mp 117°. No attempt to obtain more XXI from the oil was made.

Reaction of XXI with CO and Benzene.—A solution of 66.5 g of XXI in 300 ml of benzene was added dropwise over a period of 2.5 hr to a stirred slurry of 70 g (0.5 mole) of AlCl_3 and 200 ml of benzene at 19–20°. Carbon monoxide was bubbled in continuously and in excess during the halide addition and for 1 hr thereafter. After decomposition with 400 g of ice, the oil

(29) A. D. Petrov, V. N. Gramenitskaya, A. S. Lebedeva, and G. I. Nitkin, *Chem. Abstr.*, **59**, 482 (1963).

layer was separated, washed, dried over Na_2SO_4 , and distilled under vacuum to yield (a) 13 g, bp 70–90° (0.1 mm), n_D^{20} 1.5354; (b) 30 g, bp 90–105° (0.1 mm), n_D^{20} 1.5410; and (c) 20.2 g, bp 105–130° (0.1 mm), n_D^{20} 1.5527. Each fraction showed ketone present. The fractions a, b, and c were combined, mixed with 100 ml of low-boiling ligroin, and cooled in a Dry Ice chest overnight. The crystalline product was removed and recrystallized from ligroin at 0° to give 35.7 g of pure 2,2-dimethylindanone (V), mp 41–42°, and showed no melting point depression on admixture with an authentic sample of same.

Registry No.—V, 10489-28-8; V 2,4-dinitrophenylhydrazone, 13864-82-9; V semicarbazone, 13970-33-7; IX, 10474-34-7; IX 2,4-dinitrophenylhydrazone 13864-84-1; IX oxime, 13864-85-2; XIII, 10474-35-8; XIII 2,4-dinitrophenylhydrazone, 10474-73-4; XVII, 10474-33-6; XVIII, 13864-88-5; XVIII 2,4-dinitrophenylhydrazone, 13864-89-6; XIX, 13864-90-9; XX 2,4-dinitrophenylhydrazone, 13864-91-0; XX, 13970-34-8; XXIV, 1961-97-3; XXIVa (2,3-diphenylindene), 5324-00-5; 2-methyl-2-phenylindanone-1, 10474-32-5; its 2,4-dinitrophenylhydrazone, 13864-95-4; its oxime, 13864-96-5; 1,1-diphenylpropene-1, 778-66-5; carbon monoxide, 630-08-0.

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A Method for Manual Generation of Correct von Baeyer Names of Polycyclic Hydrocarbons

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A general method for naming bridged polycyclic hydrocarbons by the IUPAC 1957 rules (the von Baeyer system) is described in terms of representing the structure of the molecule in terms of a planar graph (a Schlegel diagram). Symmetry elements of the molecule are easily seen by this depiction. The largest possible circuit of the planar graph is determined and the circuit is numbered in such a way as to satisfy IUPAC rule A-32.31. The method, as described, is not limited in scope since it can be applied to the systematic naming of all bridged hydrocarbons. Numerous examples from the current chemical literature of incorrectly named compounds are described and their correct von Baeyer names are given as examples of this system.

Recent advances in the syntheses of regular, three-dimensional, organic solids (polyhedranes¹ and prismanes²) and symmetrically bridged hydrocarbons (adamantane,³ congressane (diamantane),⁴ and triamantane⁵) introduce the possibility of an overabundance of trivial names to the nomenclature of bridged hydrocarbons if there is no systematic means for naming them. Although it is possible to name all of the complex polyhedranes synthesized to date by the Definitive Rules for Nomenclature of Organic Chemistry of the International Union of Pure and Applied Chemistry, commonly referred to as the IUPAC 1957 rules,⁶ it will eventually be necessary to extend this system.⁷

It is the purpose of this paper to outline and discuss a general method for naming polyhedranes in conformity with the IUPAC nomenclature rules. Numerous examples from the literature of incorrectly named structures will be described in terms of this method, and a number of molecules of potential existence will be named.

It is interesting to note that the nomenclature for bridged hydrocarbons can be entirely independent of esoteric trivial names. Most bridged hydrocarbons capable of existence can be drawn as planar graphs,⁸ and it is possible to establish a general method for naming these compounds by first drawing them in two-

(1) Cubane: P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.*, **86**, 962, 3157 (1964).

(2) Hexasubstituted triprismane: H. G. Viehe, R. Merenyi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem.*, **76**, 922 (1964).

(3) S. Landa and V. Machacek, *Collection Czech. Chem. Commun.*, **5**, 1 (1933); P. von R. Schleyer, *J. Am. Chem. Soc.*, **79**, 3292 (1957).

(4) C. Cupas, P. von R. Schleyer, and D. J. Trecker, *ibid.*, **87**, 917 (1965).

(5) V. Z. Williams, P. von R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *ibid.*, **88**, 3862 (1966).

(6) "IUPAC Nomenclature of Organic Chemistry, 1957," Butterworth and Co. Ltd., London, 1958; *J. Am. Chem. Soc.*, **82**, 5534 (1960).

(7) Errors in nomenclature of bridged hydrocarbons have already received critical attention: viz., J. Meinwald and J. K. Crandall, *ibid.*, **88**, 1292 (1966); K. Conrow, *J. Chem. Doc.*, **6**, 206 (1966).

(8) A planar graph is a set of points connected by lines in such a way that it is possible to draw a graph on a plane without having any pair of edges intersect. The method described in this paper is also applicable to those compounds which cannot be drawn as planar graphs.

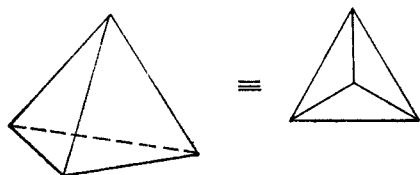


Figure 1.—Tetrahedrane.

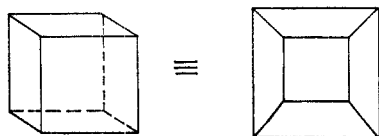


Figure 2.—Cubane.

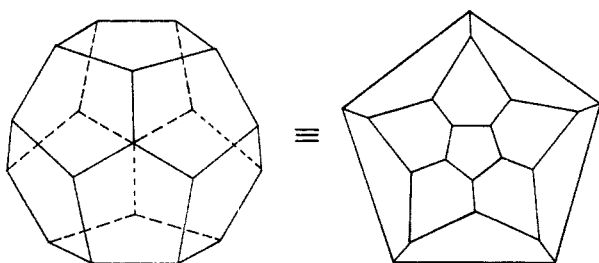


Figure 3.—Dodecahedrane.

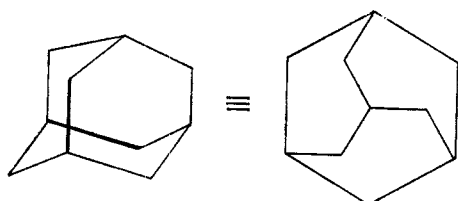


Figure 4.—Adamantane.

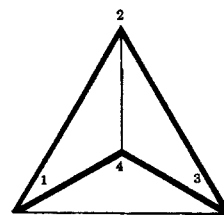
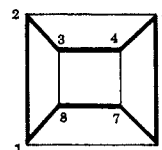
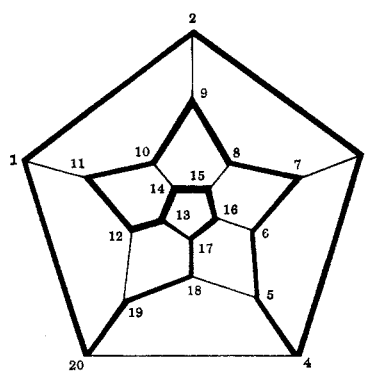
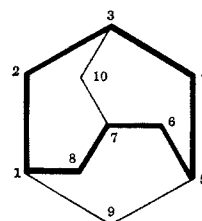
dimensional form. Figures 1–4 depict the carbon skeletons of tetrahedrane, quadriprismane (cubane), dodecahedrane, and adamantane, and their relative planar graphs.

The effect of a planar graph is the same as that produced by allowing a polyhedron to rest on one of its faces and have the observer view it from below with the perspective exaggerated so that all of the other faces appear to lie within the one nearest the observer. This type of representation, called a Schlegel diagram, is a very convenient way of representing any polyhedron as a system of polygons all lying within one polygon which is one face of the solid.⁹

The organic polyhedron, having been drawn in the form of a Schlegel diagram, can be easily visualized as a bridged hydrocarbon by finding a route, an arc, which passes through each carbon once and only once and returns to its starting point. An arc which returns to its starting point is called a circuit. A circuit which passes through every vertex once and only once is called a Hamiltonian line. Hamiltonian lines are drawn (in heavy print) through tetrahedrane^{10a} (Figure 5), cubane¹ (Figure 6), and dodecahedrane^{10b} (Fig-

(9) A. F. Wells, "The Third Dimension in Chemistry," Oxford University Press, London, 1956, p 28.

(10) (a) The tricyclo[1.1.0.0^{2,4}]butane system (S. Masamune and M. Kato, *J. Am. Chem. Soc.*, **87**, 4190 (1965)); (b) triquinacene (R. B. Woodward, T. Fukunaga, and R. C. Kelly, *ibid.*, **86**, 3162 (1964)).

Figure 5.—Tricyclo[1.1.0.0^{2,4}]butane.Figure 6.—Pentacyclo[4.2.0.0^{2,5,0^3,8,0^4,7}]octane.Figure 7.—Undecacyclo[9.9.0.0^{2,9,0^3,7,0^4,20,0^5,18,0^6,16,0^8,15,0^10,14,0^12,19,0^13,17}]eicosane.Figure 8.—Tricyclo[3.3.1.1^{3,7}]decane.

ure 7) in order to number and name the polyhedra as bridged hydrocarbons. A Hamiltonian line cannot be drawn through adamantane,³ but a circuit (Figure 8) can be drawn, allowing the remaining carbons to be numbered as secondary bridges.

It is possible to begin the numbering of complex bridged hydrocarbons at any position on the circuit; however, there is usually only one correct way to number the molecule. As an example, the molecule shown in Figure 9 has been synthesized by Masamune^{11a} who has given it the trivial name "basketene." Masamune has given its IUPAC name as pentacyclo[4.2.2.0^{2,5,0^3,8,0^4,7}]deca-9-ene and *Chemical Abstracts*^{11b} has named the molecule in the same fashion. If "basketene" is drawn in the form of a planar graph, it is an easy matter to show that a Hamiltonian line may be drawn through the graph (Figure 10). (Actually, the Hamiltonian line may be drawn in four different ways, but the sym-

(11) (a) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Letters*, 1017 (1966); (b) *Chem. Abstr.*, **64**, 788A (1966).

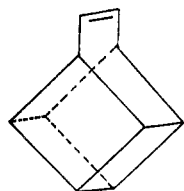


Figure 9.—Basketene.

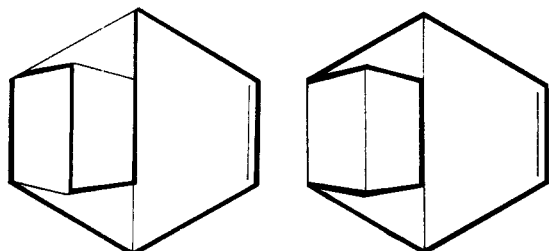


Figure 10.—Hamiltonian lines of basketene.

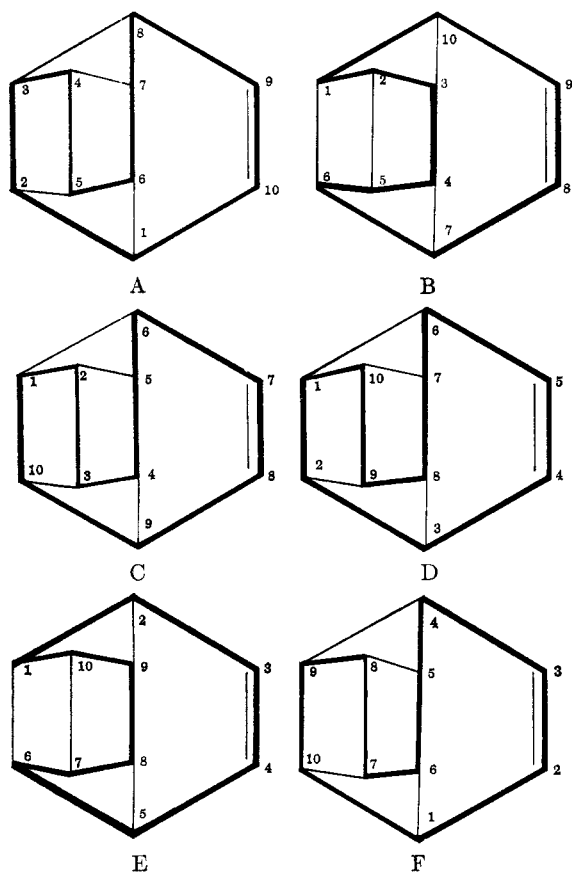


Figure 11.—(A) pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-ene;¹⁴ (B) pentacyclo[4.4.0.0^{2,5}.0^{3,10}.0^{4,7}]dec-8-ene; (C) pentacyclo[4.4.0.0^{2,5}.0^{3,10}.0^{4,9}]dec-7-ene; (D) pentacyclo[4.4.0.0^{2,9}.0^{3,8}.0^{7,10}]dec-4-ene; (E) pentacyclo[4.4.0.0^{2,9}.0^{5,8}.0^{7,10}]dec-3-ene; and (F) pentacyclo[4.4.0.0^{4,9}.0^{5,8}.0^{7,10}]dec-2-ene.

metry¹² of "basketene" is such that two pairs of Hamiltonian lines are equivalent, or degenerate.) Because a Hamiltonian line may be drawn through "basketene," the main ring contains all of the carbon atoms in the

(12) "Basketene" has two planes of symmetry and one twofold axis of symmetry. The two planes of symmetry are depicted by the following planar graphs.

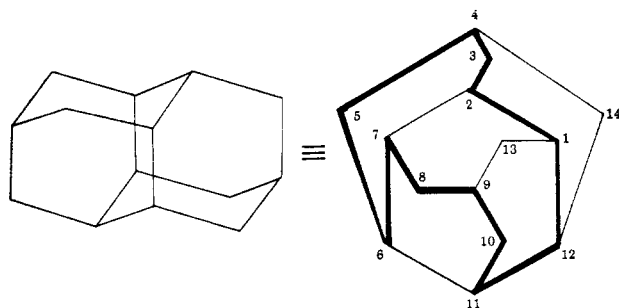
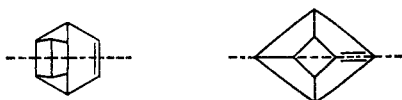
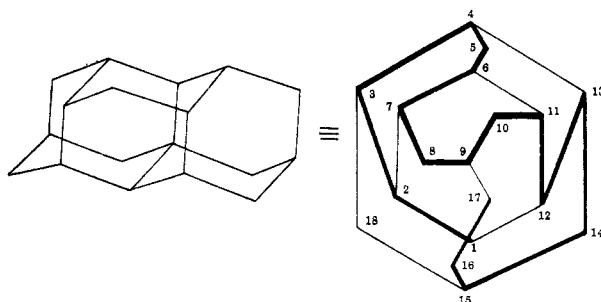
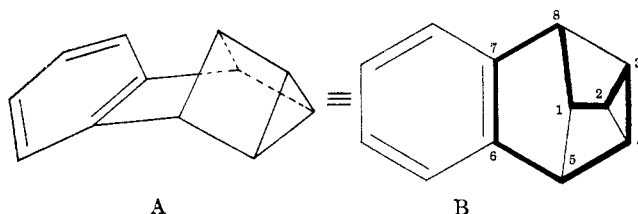
Figure 12.—Pentacyclo[7.3.1.1^{4,12}.0^{2,7}.0^{8,11}]tetradecane.Figure 13.—Heptacyclo[7.7.1.1^{3,15}.0^{1,12}.0^{2,7}.0^{4,13}.0^{6,11}]octadecane.

Figure 14.—(A) 2,3-Benzotetracyclo[3.2.1.0^{5,7}.0^{6,8}]oct-2-ene^{16a} (incorrect); (B) 6,7-benzotetracyclo[3.3.0.0^{2,4}.0^{3,8}]oct-6-ene^{16b} (correct).

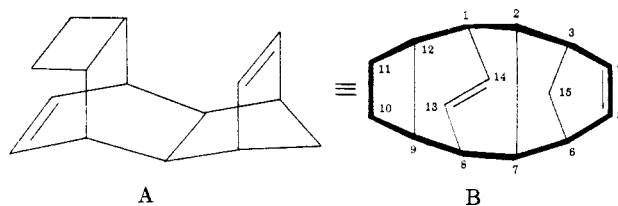


Figure 15.—(A) Pentacyclo[8.2.2^{3,8}.1,0^{2,9}.0^{4,7}]pentadeca-11,14-diene¹⁷ (incorrect); (B) pentacyclo[6.4.2.1^{3,6}.0^{2,7}.0^{9,12}]pentadeca-4,13-diene (correct).

molecular skeleton (IUPAC rule A-32.31:a).¹³ Since no carbon atoms remain to be accounted for, the main bridge must be a zero bridge (A-32.31:b). Since the main ring contains ten carbon atoms, it will be divided as symmetrically as possible if carbons 1 and 6 serve as the major bridgeheads (A-32.31:c).

Having applied these three criteria in their proper turn, it is still possible to number the ring in six different ways (Figure 11). Three possibly correct IUPAC names (Figures 11A, 11B, and 11C) can be demonstrated to exist for the parent ring system if rule A-32.31:d is now considered in its proper turn. Con-

(13) The IUPAC rule most often neglected in the literature is rule A-32.31: "When there is a choice, the following criteria are considered in turn until a decision is made: (a) The main ring shall contain as many carbon atoms as possible, two of which must serve as bridgeheads for the main bridge. (b) The main bridge shall be as large as possible. (c) The main ring shall be divided as symmetrically as possible by the main bridge. (d) The superscripts locating the other bridges shall be as small as possible."¹⁶

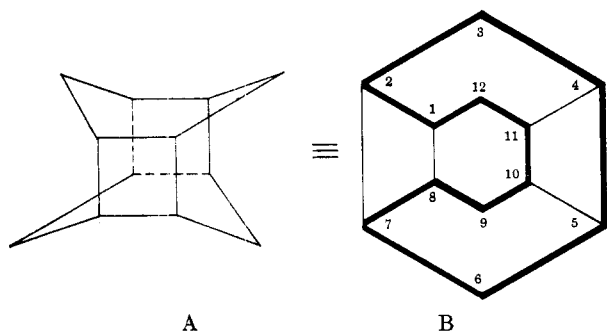


Figure 16.—(A) Pentacyclo[5.3.1.1^{2,6}.0^{3,10}.0^{5,8}]dodecane^{18a} (incorrect); (b) pentacyclo[6.4.0.0^{2,7}.0^{4,11}.0^{5,10}]dodecane^{18b} (correct).

Considering IUPAC rule A-2.2 which demands the placing of substituents at the lowest numbered carbon possible (the same rule which prevents the use of *4-chloropentane* for *2-chloropentane*), the appropriate name of "basketene" is, therefore, pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-ene^{14,15} (Figure 11A).

(14) W. G. Dauben and G. L. Whalen (*Tetrahedron Letters*, 3743 (1966)) correctly named "basketene" as pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]dec-9-ene (Figure 11A).

(15) There are known to the present author three interpretations of rule A-32.31:d, each of which has its own merits, and each, quite often, leads to a different name for the same compound. In the first interpretation, used by the present author, the parent compound is given the name which has, at the first possible difference, the smallest possible number as the *first* member of a pair of superscripts. In the second interpretation, the parent compound is given the name which has the smallest possible number at the first possible difference as the first member of each pair of superscripts and the smallest possible numbers for the positions of substituents on the parent compound. This second interpretation would give precedence to the name in Figure 11C over that in Figure 11A. In the third interpretation, used by *Chemical Abstracts*, the parent compound is given the name which has the smallest possible number at the first possible difference in the superscripts, no matter whether it is the first or second member of a pair of superscripts. This third interpretation would give the compound in Figure 17 the name: *endo,cis,endo*-heptacyclo[8.4.0.0^{2,7}.0^{3,5}.0^{4,8}.0^{9,13}.0^{12,14}]tetradecane.

Note: The sum of the superscripts for the above name is 77 and the sum of superscripts of the name in Figure 17 listed as "correct" is 75.

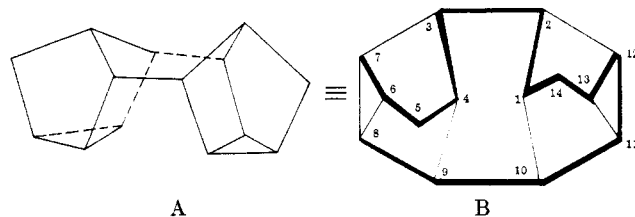


Figure 17.—(A) *endo,cis,endo*-heptacyclo[5.3.1.1^{2,6}.1^{4,12}.1^{9,11}.0^{3,5}.0^{8,10}]tetradecane¹⁹ (incorrect); (B) *endo,cis,endo*-heptacyclo[8.4.0.0^{2,12}.0^{3,7}.0^{4,9}.0^{6,8}.0^{11,13}]tetradecane (correct).

Further exemplification of this method which involves planar graphs can be shown in the naming of "congressane" and "triamantane." "Congressane" has been described as the "adamantalog" of adamantane.⁴ It is easily numbered and named from its planar graph, as shown in Figure 12 (with the circuit exposed in heavy print). Bisadamantyladamantane ("triamantane"²⁵) can also be named easily from its planar graph (Figure 13).

In Figures 14A–17A are examples of structures which have been incorrectly named in the literature. The structures have been redrawn in the form of planar graphs (Figures 14B–17B)^{16–19} to show the basis for correct IUPAC designations.

It would be helpful to have one interpretation of rule A-32.31:d approved for use by the IUPAC nomenclature committee.

(16) (a) W. H. F. Sasse, P. J. Collin, and G. Sugowdz, *Tetrahedron Letters*, 3373 (1965). (b) "Benzo" nomenclature is described in the IUPAC nomenclature rules for "ortho-fused" systems (rule A-21.3). This paper makes no attempt to cite ambiguities caused by the use of the "ortho-fused" nomenclature system; however, by dropping the "benzo" from the name of the compound in Figure 14B, the name becomes pentacyclo[6.4.0.0^{2,5}.0^{3,7}.0^{4,6}]dodeca-1,9,11-triene.

(17) R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.*, 3062 (1964).

(18) (a) *Chem. Abstr.*, **56**, 1609S (1962); (b) R. C. Cookson, D. A. Cox, and J. Hudec, *J. Chem. Soc.*, 4499 (1961).

(19) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *J. Am. Chem. Soc.*, **88**, 4890 (1966).

Solvent Effects in the Alkylation of Benzene with 1-Dodecene and *trans*-6-Dodecene in the Presence of Hydrogen Fluoride

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Received April 13, 1967

1-Dodecene and *trans*-6-dodecene alkylate benzene in the presence of anhydrous hydrogen fluoride at 0 and 55° to give all five isomeric secondary phenyldodecanes. At both temperatures, the α -olefin affords greater amounts of the 2-phenylalkane and correspondingly smaller amounts of the 5- and 6-phenylalkanes. However, if the alkylation reaction is carried out in the presence of excess *n*-hexane, both olefins afford identical isomer distributions. A significant decrease in the 2-phenyl content of the products is observed at the lower temperature both in the presence and absence of *n*-hexane. In alkylations with either olefin at 55°, the absence of a separate liquid catalyst phase results in a substantial rise in the amount of the 2-phenyl isomer. An explanation for the above behavior is given based on alkylation in both phases of the two-phase reaction mixtures, competitive isomerization and alkylation reactions, and formation of carbonium ions with stabilities and reactivities which are affected by the solvent.

Earlier workers reported the formation of only one phenylalkane in the alkylation of benzene with long-chain α -olefins in the presence of Friedel-Crafts catalysts.^{1,2} Subsequent investigations by many workers have definitely established that isomerization

occurs and that all the possible phenylalkanes are obtained except the 1-phenyl isomer.^{3,4} The generally accepted mechanism for Friedel-Crafts alkylations involves interaction of the olefin with the catalyst to form a carbonium ion, the corresponding ion pair, or a polarized complex. This undergoes

(1) W. S. Emerson, V. E. Lucas, and R. E. Heimsch, *J. Am. Chem. Soc.*, **71**, 1742 (1949).

(2) W. L. Lenneman, R. D. Hites, and V. I. Komarewsky, *J. Org. Chem.*, **19**, 463 (1954).

(3) A. C. Olson, *Ind. Eng. Chem.*, **52**, 833 (1960).

(4) R. D. Swisher, E. F. Kaelble, and S. K. Liu, *J. Org. Chem.*, **26**, 4066 (1961).