Experimental Part

Materials.—Most of the compounds employed for the spectral measurements were either described elsewhere[4,6,7,9] or else available from other investigations in progress.[8,9] We are indebted to Dr. S. B. Soloway of the Shell Development Co. for the *exo-exo* fused alcohol[6] X and to Dr. J. Abell of the California Research Corp. for a sample of cyclododecanol. Also, we are grateful to Professor Prelog of the E.T.H., Zurich, Switzerland, who kindly made a sample of cyclodecanol available to us through Dr. Richard Heck, and to Professor Robert L. Scott for some useful comments concerning the theory.

Spectral Measurements.—Measurements in the C–H stretching region were carried out on 10% solutions in carbon tetrachloride with a Beckman IR-4 spectrophotometer equipped with lithium fluoride optics. Observed frequencies were corrected by means of a calibration of the instrument with a polystyrene film.[23]

(23) E. K. Plyler, L. R. Blaine and M. Nowak. *J. Research Nat. Bur. Standards*, **58**, 195 (1957).

Tetrasubstituted Cyclooctatetraenes: Catalytic Cyclotetramerization of Propiolic Acid Esters With Tetrakis-(phosphorus trihalide)-Nickel(0) Complexes[1]

By Joseph R. Leto and Marilyn F. Leto

Cyclotetramerization of methyl or ethyl propiolate to form positional isomers of tetracarbomethoxy- or tetracarbethoxy-cyclooctatetraene is catalyzed in hydrocarbon solvents by tetrakis-(phosphorus trihalide–nickel(0) complexes. 1,2,4,6- and 1,3,5,7-substitution on the cyclooctatetraene ring was established mainly from proton magnetic resonance spectra. Partial hydrogenation of the 1,2,4,6-isomers yields the cyclooct-7-enes, whereas total hydrogenation of the 1,2,4,6- and 1,3,5,-7-isomers yields the cyclooctanes. Saponification of cyclooctatetraene-, cyclooctene- and cyclooctane-carboxyesters yields the corresponding acids. This type of catalysis has been attempted using a wide variety of other unsaturated monomers and other zero valent complexes, but has been found to be extremely limited in scope. The reaction provides, however, a useful route to a rare class of compounds.

Introduction

The carbonyls of iron, cobalt and nickel, as well as many of their organic and inorganic derivatives, have proved to be quite active as polymerization catalysts for acetylenic compounds. However, the catalytic activity of a particular metal carbonyl derivative for polymerizing a given monomer is sometimes remarkably specific. This report describes a further example of such specific catalytic activity and the novel products obtained.

Reppe[2] has discussed the cyclotrimerization of monosubstituted acetylenes in the presence of zero valent nickel-carbonyl-phosphine catalysts to give trisubstituted aromatic products. With the catalyst $Ni(CO)_2[P(C_6H_5)_3]_2$, for example, propargyl alcohol was cyclized to a mixture of 1,2,4- and 1,3,5-trimethylolbenzene. Similarly, the highly reactive ethyl ester of propiolic acid undergoes aromatization[3] to give a mixture of 1,2,4-

$$3RC\equiv CH \xrightarrow{Ni(CO)_2(P(C_6H_5)_3)_2}$$

and 1,3,5-tricarbethoxybenzene. In most cases the unsymmetrical isomer is favored. The nature of these cyclizations with nickel-carbonyl-phosphine catalysts has been under investigation in this Laboratory. It has been found[4a,4b] that catalyst activation in these trimerizations most probably

(1) Presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

(2) J. W. Reppe and W. J. Schweckendiek, *Ann.*, **560**, 104 (1948).

(3) L. S. Meriwether, E. C. Colthup, G. W. Kennerly and R. N. Reusch, *J. Org. Chem.*, in press.

(4) (a) L. S. Meriwether and M. L. Fiene, *J. Am. Chem. Soc.*, **81**, 1200 (1959); (b) L. S. Meriwether, E. C. Colthup, M. L. Fiene, G. W. Kennerly and R. N. Reusch, Abstracts of Papers, 138th Meeting, American Chemical Society, New York, N. Y., September, 1960, p. 67-P.

proceeds by way of a tricoördinated nickel(0) species, and that the dissociation of carbon monoxide followed by coördination of an acetylene molecule is responsible for catalytic activity. Whether or not this activity requires the presence

$$Ni(CO)_2(PR_3)_2 \rightleftharpoons [Ni(CO)(PR_3)_2] + CO$$
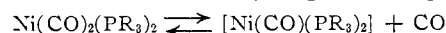
of CO ligand(s) in the original nickel complex is uncertain.

The CO-free tetrakis-(phosphorus trihalide)–nickel(0) complexes, $Ni(PX_3)_4$ (X = F, Cl, Br), have now been investigated as catalytic initiators for acetylene cyclizations. Preliminary P^{31} nuclear magnetic resonance (n.m.r.) studies of phosphine exchange in these complexes in solution indicate that one or more of the phosphine ligands is subject to a reversible dissociation producing a ligand-

$$Ni(PX_3)_4 \rightleftharpoons [Ni(PX_3)_n] + (4-n)PX_3$$
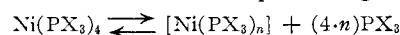
deficient nickel(0) species containing only phosphines. The ability of these tetrakis complexes to catalyze the formation of novel cyclic products has been demonstrated in this work.

Results and Discussion

Cyclization Reactions.—We have found that in the presence of each of the three different tetrakis-(phosphorus trihalide)–nickel(0) compounds mentioned above, as well as the tetrakis-(phenyldichlorophosphine) analog, cyclization of ethyl propiolate proceeds in a fashion different from the trimerization reactions, forming a mixture of stable tetramers in addition to the aromatic trimers. These tetramers have been identified as 1,2,4,6- and 1,3,5,7-tetracarbethoxycyclooctatetraene (I and II). The reaction is carried out at room temperature under a blanket of nitrogen by adding $Ni(PCl_3)_4$ in cyclohexane or benzene to $HC\equiv CCOO-C_2H_5$ in the same solvent. Under these conditions the temperature rises 50–60°, and 73% of the

TABLE I

SCOPE OF CATALYTIC CYCLIZATION REACTIONS

1. Monomers forming both tetramers and trimers with $Ni(PCl_3)_4$　　$HC\equiv CCOOC_2H_5$,[a] $HC\equiv CCOOCH_3$,[a] $CH_2=C=CH_2$[b]

$CH_2=CHCH=CH_2$[c]

2. Inactive monomers

$HC\equiv CR$: R = -H, $-C_5H_{11}$, $-C_6H_5$, -COOH, -COOK, $-CH_2Cl$, $-CH_2OH$, $-CH_2OCOCH_3$, $-CONH_2$, -CN

$RC\equiv CR$: R = $-COOC_2H_5$, $-C_2H_5$

$CH_2=CHR$: R = -H, $-COOC_2H_5$, -CN

$HC\equiv C(CH_2)_3C\equiv CH$

3. Catalysts forming both tetramers and trimers (in order of reactivity with ethyl propiolate)　　$Ni(PCl_3)_4 > Ni(PF_3)_4 \gg Ni(PBr_3)_4 \sim Ni(C_6H_5PCl_2)_4$

4. Catalysts forming only trimers　　$Ni[P(OC_2H_5)_3]_4 > Ni(CNC_6H_5)_4$

5. Inactive catalysts　　$Ni(C_5H_6)_2$, $Zn[OP(C_6H_5)_3]_4$ $(ClO_4)_2$ [isoelectronic with $Ni(0)$]

[a] Forms cyclooctatetraene and benzene derivatives. [b] Forms cyclooctane and cyclohexane derivatives. [c] Forms tetrameric and trimeric hydrocarbons of unknown structure.

monomer is converted in 3 minutes. Processing of the product mixture produces massive yellow crystals of I in moderate yield (28%), and pale yellow needles of II in small yield (1%), the principal product (71%) being a mixture of 1,2,4- and 1,3,5-tricarbethoxybenzene.

I, R = C_2H_5

III, R = CH_3

IV, R = $3CH_3$, $1C_2H_5$ (undetd. disposition)

IX, R = H

II, R = C_2H_5
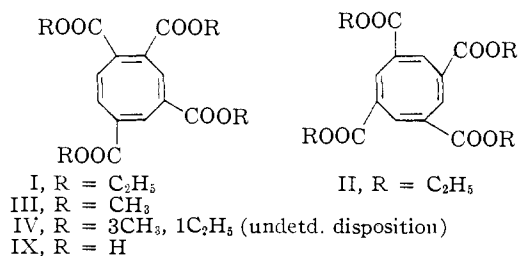
With methyl propiolate 66% of the monomer is converted in 11 minutes, but only one tetramer, III, is obtained. The yield is 83%, the remaining product (17%) being 1,2,4-tricarbomethoxybenzene.

$Ni(PF_3)_4$ causes a 53% conversion of ethyl propiolate to a mixture of I (30%) and aromatic trimers (70%), while with $Ni(PBr_3)_4$ and $Ni(C_6H_5PCl_2)_4$, only a 1% total conversion of monomer is observed, even under fairly strenuous conditions. However, compound I can be isolated from these reactions, along with the trimers. In reactions with the propiolate esters, addition of five moles of PCl_3 for each mole of $Ni(PCl_3)_4$ catalyst present caused the total conversion to drop to about 29%, but did not affect the product distribution. This fact supports the dissociation theory outlined above. With the other catalysts, added free phosphine did not appear to affect the reaction in any way.

The molar ratio of monomer to catalyst in all of the experiments was around 1000. Initial reaction temperatures were not critical, but were limited by thermal decomposition of the catalyst. Molecular oxygen was found to inhibit reaction by decomposing the catalysts irreversibly.

Scope.—Attempts were made to initiate a cyclotetramerization with $Ni(PCl_3)_4$ or $Ni(PF_3)_4$ in a wide variety of unsaturated monomers. Of the acetylenic compounds (see Table I) chosen on the basis of the reactivity of their triple bond in other reactions, only methyl and ethyl propiolate reacted. Of the ethylenic compounds, allene

reacted to give a 24% yield of a mixture of 1,2,4- and 1,3,5-triexomethylenecyclohexane and 1,3,5,7-tetraexomethylene cyclooctane. The catalytic formation of these compounds from allene using a nickel-carbonyl-phosphine catalyst has recently been described by Benson and Lindsey.[5] Butadiene-1,3 also reacts, apparently to give cyclic trimers and tetramers, which are under investigation and will be the subject of a later report.

Co-tetramerization of ethyl propiolate with methyl propiolate was achieved in an equimolar mixture of the two, with the formation of all possible mixed methyl/ethyl esters of the cyclooctatetraene and benzene products. The cyclooctatetraene derivative with 3 methyl groups and 1 ethyl group (IV) was isolated and characterized. However, attempts to copolymerize the propiolate esters with acetylenes which are inactive alone were unsuccessful. In general, the effect of other acetylenes seems to be to decompose the catalyst, or to coördinate with it in some way which inhibits further reaction. Color changes taking place in these mixed systems bear this out.

If the active catalyst for polymerization is indeed a ligand-deficient nickel species which accepts an acetylene to start the cyclization, and if this resulting complex is stable with respect to the original ligand-deficient species, then the inactive acetylene would have the effect of removing the active catalyst as it was formed. Why the propiolates do not inhibit in this way is unknown. The observed failure of propiolate to compete successfully with other acetylenes for the nickel species in the attempted copolymerizations is in distinct opposition to their extreme reactivity with these species when present alone.

The electron-withdrawing power of the group R in $HC\equiv CR$ might be thought an important factor in these reactions. However, the carboxyethyl or carboxymethyl group in the active propiolates have Taft σ^*-values which are intermediate compared with the other R groups in Table I. The operation of an unusual steric effect with the propiolates also appears unlikely. Thus it seems unwise at this time to speculate further on the apparently unique cyclization reaction of propiolate esters as compared with other monosubstituted acetylenes.

(5) R. E. Benson and R. V. Lindsey, Jr., J. Am. Chem. Soc., 81, 1247 (1959).

In an effort to extend the scope of this reaction to other catalysts, four carbonyl-free tetrakis complexes were investigated for reactivity with ethyl propiolate (see Table I). In no case was there any formation of cyclooctatetraene products. The triethyl phosphite and phenyl isonitrile complexes caused 100% and 3% conversion, respectively, to the mixture of 1,2,4- and 1,3,5-tricarbethoxybenzene. The cyclopentadiene and phosphine oxide complexes showed no activity whatever. In comparing those catalysts which form tetramers and trimers with those which form only trimers or are inactive, there is no striking difference in the electronic environment of the phosphorus atoms (P^{31} resonance),[6] in the nickel–ligand force constants (Raman[7,8] and far-infrared[9]), or in the electronic energy levels of the molecule as a whole (ultraviolet).[9]

The unique activity of the complexes possessing a nickel–phosphorus–halogen system might be explained on the basis of π-bonding effects in the ligands. It is known from the strength of their *trans* effect in planar Pt(II) complexes,[10] for example, that the phosphorus halides form stronger π-bonds with transition metals than do the phosphites. This fact could increase the catalytic activity of the Ni–P–X complexes in two ways: (1) by decreasing the Ni–P σ-bond strength, thus facilitating phosphine dissociation; or (2) by stabilizing the resulting ligand-deficient nickel species, thus favoring acetylene conjugation with the nickel catalyst.

Some type of specific interaction between a halogen atom and the propiolate to promote activity of the latter is also conceivable. However, in the absence of kinetic data on the reaction or more information about the transition state involved it is not possible to judge the importance of the effects mentioned above.

Reactions of the Tetracarboxyesters of Cyclooctatetraene.—Partial hydrogenation of I and III may be carried out at room temperature and atmospheric pressure over Pd–C catalyst to give the 1,2,4,6-tetracarboxyesters of cyclooct-7-ene in 100% yields (compounds V and VI). The uptake of 3 moles of hydrogen is complete in one hour, and hydrogenation may be stopped at this point.

ROOC COOR

ROOC COOR
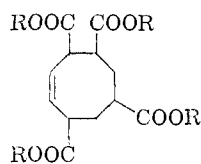
V, R = CH₃
VI, R = C₂H₅
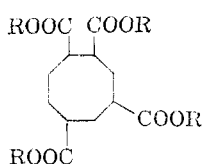
VII, R = CH₃
VIII, R = C₂H₅

Further uptake of one mole of hydrogen to form the cyclooctane derivatives VII and VIII in 100% yield is complete in 72 hours. This peculiar hydrogenation course is comparable to that of the parent

(6) L. S. Meriwether and J. R. Leto, *J. Am. Chem. Soc.*, **83**, in press (1961).

(7) L. A. Woodward and J. R. Hall, *Nature*, **181**, 831 (1958).

(8) M. Bigorgne, *Compt. rend.*, **251**, 3484 (1960).

(9) J. R. Leto, unpublished results.

(10) E. A. Magnusson, *Revs. Pure and Appl. Chem. (Australia)*, **7**, 195 (1957).

hydrocarbon itself.[11] All of the cyclooctenes and cyclooctanes reported here are high boiling liquids.

Hydrogenation of II under similar conditions produces the corresponding cyclooctane in 100% yield in about 10 minutes. In this case, no cyclooctene intermediate could be isolated. In comparing the hydrogenation of the two isomers I and II, it was found that the relative rate of absorption of the first three moles of hydrogen for the asymmetric isomer I is about twice that for the symmetric isomer II, both in cyclohexane.

Saponification of either I or III with KOH in ethanol yields the same acid upon acidification, cyclooctatetraene-1,2,4,6-tetracarboxylic acid (IX), in 100% yield. Titration of this high-melting crystalline acid shows four inflections, corresponding to the successive pK_a values for the acid groups shown in Table II. The other tetraacid compounds in Table II are formed in nearly quantitative yield by saponification and acidification of the corresponding methyl or ethyl esters V, VII and II.

TABLE II

pK_a VALUES FOR VARIOUS TETRA-ACIDS IN WATER

Compound	pK_a values (successive)
IX	5.98, 4.72, 3.93, 3.40 (all ±0.05)
Acid from V	6.85, 5.3, 4.35, 3.45 (all ±0.1)
Acid from VII	6.35, 5.2, 4.45, 3.5 (all ±0.1)
Acid from II	4.5 (only one inflection)

Structure.—The evidence by which a tetrasubstituted cyclooctatetraene structure was assigned to these compounds follows: (1) Determination of the molecular weight and elemental analysis showed compounds I, II and III to be tetramers of the propiolate monomer used.

(2) Aromatic and linear structures for these tetramers were ruled out on the basis of their n.m.r. and infrared spectra. All aromatic formulations for a tetramer of a propiolate ester, one of which is shown as X, contain both a tetrasubstituted benzene ring and a double bond conjugated to the ring and to a carbonyl group. However the n.m.r.

COOR

ROOC CH=CHCOOR

ROOC

X

ROOC ROOC COOR

CH=CHCH=CCH=CC≡CCOOR

XI
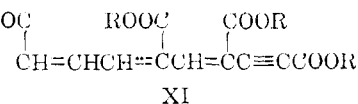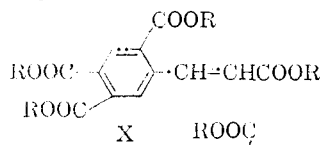
spectra of the tetramers (see Experimental) show no peaks in the conjugated aromatic ring proton region, nor do the infrared spectra (Fig. 1) of the tetramers possess ring C–H band systems which are characteristic of tetrasubstituted benzenes. A linear tetramer of a propiolate ester, such as XI above, might be found in a series of Nieuwland-type[12] condensations and would contain 3 double bonds and one terminal triple bond. The terminal double bond in this compound would absorb strongly in the region of 955–980 cm.$^{-1}$.[13] Absorp-

(11) L. Craig, *Chem. Revs.*, **49**, 103 (1951).

(12) J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold Publishing Corp., New York, N. Y., 1945.

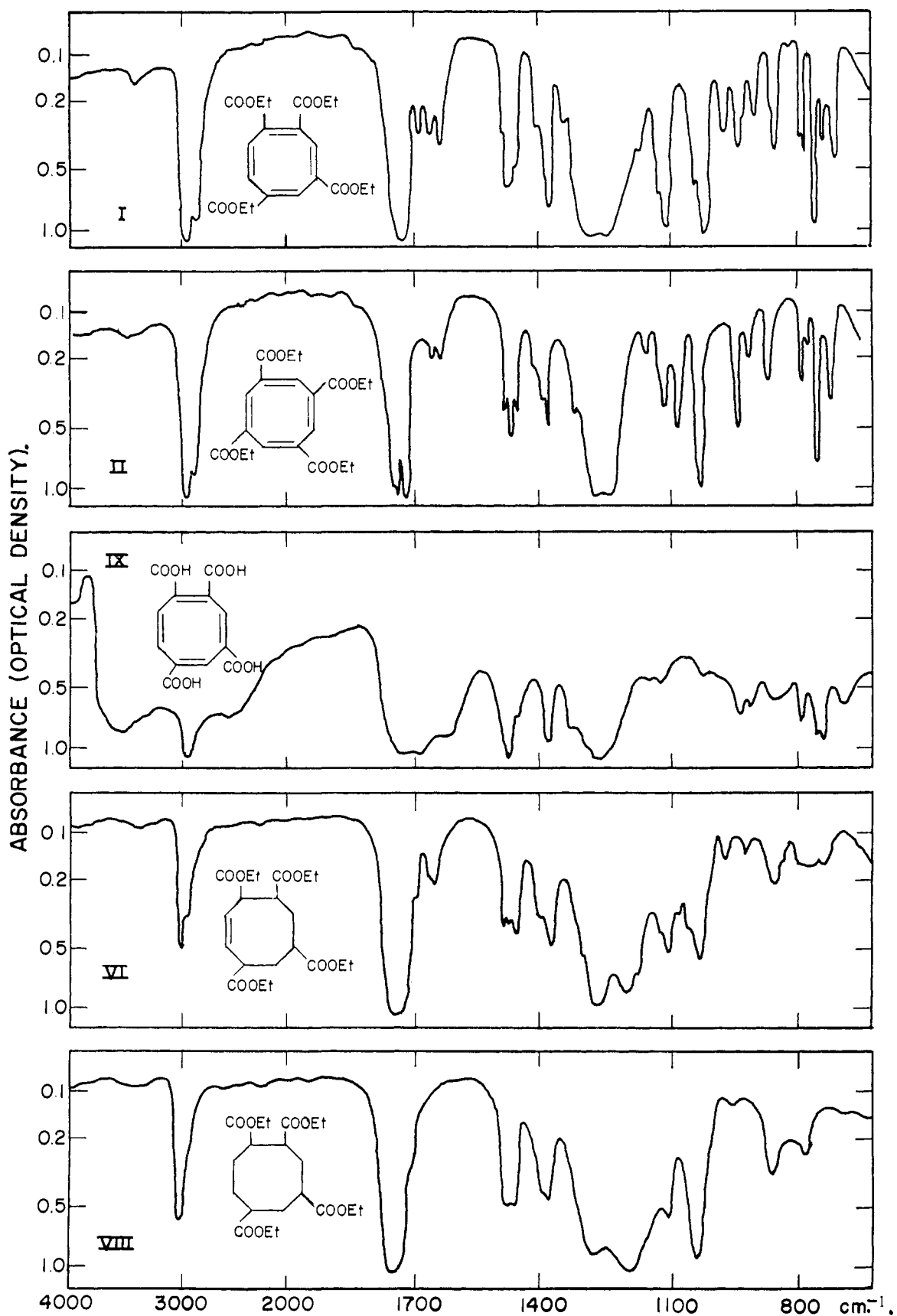(13) J. L. H. Allen, G. D. Meakins and M. C. Whiting, *J. Chem. Soc.*, 1874 (1955).

Fig. 1.—Infrared spectra of five new tetrasubstituted eight-membered carbocycles.

tion of this type is absent in the tetramers. Further, the terminal triple bond would absorb in the region 2170–2260 cm.$^{-1}$, and conjugation with the carbonyl group would be expected to enhance the intensity of such an unsymmetrically disubstituted triple bond. No absorption in the infrared near this region is present.

(3) Uptake of four moles of hydrogen under the mild conditions employed, to give a completely saturated compound, would not be expected for either formulation X or XI.

(4) All of the tetramers have infrared modes at 1630 and 795 cm.$^{-1}$, bands which are present in cycloöctatetraene and its derivatives. In addition, the proton resonance of compound I as well as its ultraviolet spectrum (see Experimental) are consistent with this structure.

(5) Finally, upon pyrolysis I cleaves to form primarily 1,2,4-tricarbethoxybenzene and ethyl propiolate. It thus appears that a typical valence tautomeric equilibrium[11] between the monocyclic and bicyclic structures is involved. Although both
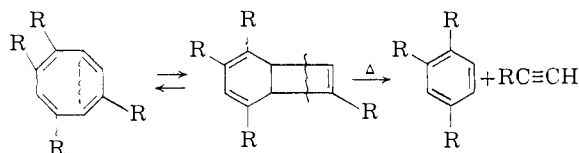
1,2,5,6- and 1,2,4,7-tetrasubstituted cycloöctatetraenes (as well as the 1,2,4,6-isomer shown) may also cleave to give a 1,2,4-trisubstituted benzene, the former two isomers are ruled out on other grounds (see below). A stabilized bicyclo[4.2.0] system for I, II and III is excluded on the basis of spectroscopic evidence.

The cycloöctatetraene structure to which we are thus led is somewhat surprising in view of the mild conditions of homogeneous catalysis employed. Cyclizations and copolymerizations of acetylene[14] and substituted acetylenes[11,15,16] are well established and remain a field of active interest.[17,18] However, most of these syntheses are high-temperature, high-pressure heterogeneous reactions employing a Ni(II) salt as catalyst. Furthermore, until 1958, no example of simple tetrasubstitution on a cycloöctatetraene ring was to be found, although about a dozen tetra- and higher-substituted fused-ring benzo-cycloöctatetraenes have been described.[11] Recently, White[19] and Criegee[20] have reported tetraphenyl- and octamethylcycloöctatetraenes. respectively, but these syntheses also involved high temperature pyrolyses through hypothetical cyclobutadiene intermediates.

Attempts to prepare either a silver nitrate or a maleic anhydride adduct of I were unsuccessful (see Experimental). Evidently the four electron-withdrawing ring substituents prevent such adducts from forming in the usual manner.

Positional Isomerism.—From the propiolate monomer, it is possible to build only four tetrasubstituted cyclooctatetraene structures, i.e., those with 1,3,5,7-, 1,2,5,6-, 1,2,4,7- and 1,2,4,6-substitution on the ring. For compound I, the first two are rejected for the same reason: the n.m.r. spectrum of I shows two different kinds of unsaturated ring protons, whereas only one kind would be predicted. Next, it was established that the double bond in the octene compound VI is unsubstituted. Disubstitution of this double bond is impossible because of the presence of ring-unsaturated protons. Monosubstitution was also rejected because neither the infrared nor ultraviolet spectrum of this compound shows any conjugated carbonyl absorption (see Experimental). Of the two remaining isomers, the n.m.r. data support the 1,2,4,6-structure for VI. Although the area ratio of saturated ring CH$_2$ to saturated CH is 1:1 and could arise from either octene isomer, the fact that there are two grossly different kinds of ethyl groups in an asymmetric ratio other than 2:2 precludes the symmetrical 1,2,4,7-isomer (see Experimental).

The 1,3,5,7-structure is written for the low-yield tetramer II since it is the only structure consistent with both n.m.r. and hydrogenation data.

No attempt was made to determine the geometrical isomerism in these compounds.

Acknowledgments.—The coöperation of the Research Service Department of the Stamford Laboratories is gratefully acknowledged. The authors wish also to express their appreciation to Dr. L. S. Meriwether for several pertinent discussions.

Experimental

Most of the acetylenic compounds were available commercially. They were purified by fractional distillation until their boiling points and refractive indices agreed with the literature values. Propargyl acetate,[21] propiolonitrile[22] and propiolamide[22] were prepared by published methods. Potassium propiolate was prepared by neutralizing a solution of propiolic acid in ethanol with potassium hydroxide in ethanol, collecting the salt, washing, and drying; yield 73%, white crystals, m.p. 195°. The gaseous ethylenic compounds and acetylene were dried and distilled prior to use.

The metal complexes Ni(PCl$_3$)$_4$, Ni(PF$_3$)$_4$ and Ni(PBr$_3$)$_4$ were prepared according to the directions of Wilkinson.[23,24] The PCl$_3$ and PBr$_3$ complexes were freshly crystallized before use from −80° petroleum ether and 20° PBr$_3$, respectively. The PF$_3$ complex, prepared by fluorination of Ni-(PCl$_3$)$_4$ with SbF$_3$, was distilled before use. Ni(C$_6$H$_5$PCl$_2$)$_4$ was prepared following the method of Sacco.[25] Ni[P(OC$_2$H$_5$)$_3$]$_4$ was prepared[26] by slowly warming a mixture of Ni-(CO)$_4$ and triethyl phosphite from −80° to reflux (180°) and the chilling after CO evolution ceased (18 hr.). Traces of monocarbonyl impurity were removed by crystallization from absolute ethanol; yield 32% (based on Ni(CO)$_4$) of

(14) (a) K. Kammermeyer, "Polymerization of Acetylene to Cyclooctatetraene," Hobart Publ. Co., Wash., D. C., 1947. (b) J. W. Reppe, "Acetylene Chemistry," P. B. Report 18852-S, I.G. Farben Industrie. A.G. (O.T.S. Translation, 1949). (c) A. C. Cope and L. L. Estes, Jr., J. Am. Chem. Soc., 72, 1128 (1950).

(15) J. W. Reppe, Ann., 560, 1 (1948).

(16) A. C. Cope and H. C. Campbell, J. Am. Chem. Soc., 73, 3536 (1951); A. C. Cope, M. Burg and S. W. Fenton, ibid., 74, 173 (1952).

(17) A. C. Cope, et al., ibid., 80, 5505 (1958), paper XLIV and previous papers in this series.

(18) French Patent 1,182,299 (assigned to Badische Anilin und Soda-Fabrik A.G.) June, 1959.

(19) E. H. White and H. C. Dunathan, Abstracts of 134th A.C.S. Meeting, Chicago, Ill., 1958, p. 41P.

(20) R. Criegee, Angew. Chem., 71, 70 (1959).

(21) E. Heilbron, J. Chem. Soc., 88 (1945).

(22) P. Saggiomo, J. Org. Chem., 22, 1171 (1957).

(23) J. W. Irvine and G. Wilkinson. J. Am. Chem. Soc., 73, 5501 (1951).

(24) G. Wilkinson, Science, 113, 742 (1951).

(25) F. Sacco, Ann. Chim. (Rome), 44, 134 (1954).

(26) M. Bigorgne, Laboratoire dem Chimie minerale. E.N.S.C.P. (Paris), private communication.

white crystals, m.p. 107°. Ni(CNC₆H₅)₄ was synthesized from phenyl isonitrile[27] and Ni(CO)₄ according to the directions of Klages[28] and Hieber.[29] Ni(C₅H₆)₂ was prepared by the method of Fischer[30] from cyclopentadiene and Ni(CO)₄. Zn[OP(C₆H₅)₃]₄(ClO₄)₂ was synthesized[31] from zinc perchlorate and the phosphine oxide in ethanol.

Analytical or pure grade reagents and solvents were used throughout the experiments. Infrared spectra were obtained with a Perkin–Elmer model 21 infrared spectrometer, and certain regions of interest were recorded on a Beckman IR 4 instrument. Ultraviolet spectra were obtained with a Cary model 11 spectrophotometer. Refractive indices were measured on an Abbe refractometer. Melting points are uncorrected and were taken on a Fisher–Johns block. Boiling point determinations were made using the inverted capillary technique.

A. Cyclization of Propiolate Esters. Procedure.—To a stirred solution of propiolate ester and solvent under dry nitrogen in a flask fitted with a reflux condenser, thermometer, vaccine cap and gas inlet tube, was added by means of a syringe a weighed amount of metal complex in a small volume of solvent. When the temperature of addition was below 20°, the reaction mixtures turned bright yellow; on warming to 25° a color change to dark orange occurred, accompanied by a rise in temperature. Aliquots of the reaction mixture were taken periodically and examined in the infrared for disappearance of the 2125 cm.⁻¹ acetylenic band of the propiolate. The processing was similar for all runs, and is described below. Cyclization of the propiolate with the four active catalysts listed in Table I as well as attempted cyclizations and cocyclizations of the other acet·ylenic and liquid ethylenic monomers listed in Table I, were all carried out in the fashion described. If a monomer did not react at 25°, the temperature was raised to reflux to promote reaction.

1,2,4,6-Tetracarbethoxycyclooctatetraene (I).—Ethyl propiolate (21.3 g., 217 mmoles) was treated with Ni(PCl₃)₄ (0.26 g., 0.43 mmole) in 250 ml. of cyclohexane. At 25°, the temperature rose 46° in 5 min., and infrared analysis showed 70% reaction of starting monomer. The dark orange reaction mixture was filtered to remove catalyst decomposition products, and solvent and unreacted propiolate were removed by evaporation under reduced pressure. The red-brown viscous residue (15.5 g.) was dissolved in 50 ml. of refluxing absolute ethanol, and chilled. Large yellow crystals and a lighter yellow powder precipitated overnight. The two crude solids were separated, to give 4.31 g. of crude I (29% of reacted propiolate) and 0.19 g. of crude 1,3,5,7-tetracarbethoxycyclooctatetraene (II) (1.3% of reacted propiolate). One recrystallization from ethanol yielded 3.15 g. of pure I as yellow crystals, m.p. 83.5–84°.

Anal. Calcd. for C₂₀H₂₄O₈: C, 61.22; H, 6.17; O, 32.61; mol. wt., 392.4. Found: C, 61.30; H, 6.45; O, 33.09; mol. wt., 390 ± 5 (cryoscopic in benzene).

Repeated crystallizations from ethanol yielded 0.12 g. of pure II as light yellow needles, m.p. 130.5–131°.

Anal. Found: C, 60.99; H, 6.95.

Alcohol was removed from the mother liquor which gave I and II, leaving 9.85 g. of a brown residue, which was extracted several times with light petroleum. The yellow extractates were chilled to −80° to precipitate 9.28 g. of a clear yellow viscous oil, which upon standing deposited 0.1 g. of white crystals. The oil was identified as 1,2,4-tricarbethoxybenzene, b.p. 176° (1.5 mm.), by comparison of its infrared spectrum with that of an authentic sample, and the white crystals, m.p. 135–136°, were identified as 1,3,5-tricarbethoxybenzene.

1,2,4,6-Tetracarbomethoxycyclooctatetraene (III).—Methyl propiolate (4.53 g., 54 mmoles) and Ni(PCl₃)₄ (0.0325 g., 0.053 mmole) were stirred together in 60 ml. of cyclohexane at 22°. After a 3-minute induction period, a 33° rise in temperature took place in 11 min., and infrared analysis showed 93% reaction of monomer. The reaction mixture consisted of a cloudy yellow solution and an insoluble brown viscous material. The yellow solution was

decanted and filtered, and the solvent and unreacted monomer removed under reduced pressure. The viscous yellow oil which remained was identified as 1,2,4-tricarbomethoxybenzene, b.p. 103° (0.1 mm.). Hot absolute ethanol was added to the viscous brown material. At reflux, light crystalline flakes were precipitated and filtered, giving 1.1 g. of crude III. No attempt was made to isolate all of the product. The solid was recrystallized from ethanol, giving pure III as cream platelets, m.p. 182.5–183°.

Anal. Calcd. for C₁₆H₁₆O₈: C, 57.14; H, 4.80. Found: C, 57.26; H, 5.01.

In a similar run, 6.6 g. of reaction products was obtained from 10 g. of methyl propiolate. Following the same procedure, 5.4 g. of crude III (83% reacted propiolate) and 1.1 g. of 1,2,4-tricarbomethoxybenzene (17% reacted propiolate) were obtained.

Monocarbethoxytricarbomethoxycyclooctatetraene (IV).—Methyl propiolate (2.27 g., 27 mmoles) and ethyl propiolate (2.65 g., 27 mmoles) were dissolved in 55 ml. of cyclohexane and nitrogen was passed through the solution for 20 minutes; Ni(PCl₃)₄ (0.0364 g., 0.06 mmole) in 1 ml. of solvent was added at 19°. A 42° rise in temperature in 15 min. was accompanied by an 89% disappearance of the monomers (by infrared analysis). The reaction mixture consisted of a yellow solution and a brown precipitate. After filtration and evaporation of the solution, a dark orange viscous oil remained which was extracted with petroleum ether. The extracts were chilled at −80°, depositing about 2 ml. of a canary-yellow oil. Mass spectroscopic analysis of this yellow oil showed "parent" mass peaks for all possible methyl, ethyl and mixed methyl/ethyl tetrameric and trimeric products.

The brown precipitate from the reaction mixture was dissolved in a minimum of hot absolute ethanol, from which IV was precipitated as cream plates, m.p. 146°.

Anal. Calcd. for C₁₇H₁₈O₈ (3CH₃,1C₂H₅): C, 58.28; H, 5.18. Found: C, 58.26; H, 4.90.

The particular distribution of the four carboxyesters on the ring was not determined.

B. Attempted Adduct Formation.—Several attempts to prepare the AgNO₃ addition complex of I were made. Finely ground AgNO₃ (0.262 g., 1.54 mmoles) was added to a refluxing solution of I (0.296 g., 0.75 mmole) in 10 ml. of abs. ethanol and refluxed for 1 hour; Compound I (0.298 g., 0.76 mmole) was added to a refluxing solution of AgNO₃ (0.261 g., 1.53 mmoles) in ethanol and refluxed for 1 hour; and Compound I (0.303 g., 0.77 mmole) and AgNO₃ (0.329 g., 1.94 mmoles) in ethanol were brought to reflux together and maintained at that temperature for 1 hour. In all cases only starting materials were recovered.

Attempts were also made to prepare a maleic anhydride adduct of I. Maleic anhydride (0.0752 g., 0.78 mmole) and Compound I (0.309 g., 0.78 mmole) were refluxed for 18 hours in 10 ml. of toluene. The solution was concentrated to 5 ml. and stored in a freezer. After several days a small amount of maleic acid (0.02 g.) was precipitated. The remainder of the solution contained only starting materials.

In a separate run, maleic anhydride (0.235 g., 2.4 mmoles) and I (0.611 g., 1.56 mmoles) were dissolved in 50 ml. of cyclohexane and placed in a quartz flask. Continuous irradiation with the ultraviolet light from a low pressure Xenon arc for 67 hours at 60° resulted only in the recovery of the starting materials.

C. Hydrogenation.—The hydrogenation experiments were carried out at room temperature and 760 mm. pressure on a vacuum line employing standard manometric techniques. Solvent and catalyst (5% Pd/C) were stirred under H₂ for 2 hours, after which the unsaturated compound was added in solution.

1,2,4,6-Tetracarbomethoxycycloöct-7-ene (V).—Hydrogenation of III (0.5914 g., 1.76 mmoles) in 70 ml. of ethyl acetate in the presence of 0.1 g. of prereduced Pd–C catalyst was stopped after the absorption of 5.35 mmoles of hydrogen (101% of 3 moles/mole) in 70 min. After removal of the catalyst and evaporation of the solvent, 0.475 g. of V remained as a colorless liquid, b.p. 135° (0.1 mm.) n²⁵D 1.489.

Anal. Calcd. for C₁₆H₂₂O₈: C, 56.13; H, 6.48. Found: C, 55.74; H, 6.78.

1,2,4,6-Tetracarbethoxycycloöct-7-ene (VI).—Hydrogenation of I (0.1927 g., 0.492 mmole) in 52 ml. of cyclo-

(27) W. Wiegrebe, *et al.*, *Ber.*, **83**, 506 (1950).

(28) F. Klages and K. Mönkemeyer, *ibid.*, **85**, 109 (1950).

(29) W. Hieber and C. Böckly, *Z. anorg. Chem.*, **262**, 344 (1950).

(30) E. O. Fischer, *Ber.*, **92**, 1423 (1959).

(31) We thank Dr. E. Bannister, M.I.T., for a generous sample of this compound.

hexane was stopped after the absorption of 1.47 mmoles of hydrogen in 45 min.; VI was isolated as a colorless liquid, b.p. 185° (0.1 mm.), n^{25}D 1.479.

Anal. Calcd. for $C_{20}H_{30}O_8$: C, 60.28; H, 7.59. Found: C, 60.15; H. 7.35.

1,2,4,6-Tetracarbomethoxycyclo̊octane (VII).—Hydrogenation of III (0.5619 g., 1.66 moles) in 70 ml. of ethyl acetate absorbed 3 moles of hydrogen in 70 min., and over a period of 72 hours absorbed the remaining mole of hydrogen (total: 6.64 mmoles of hydrogen); VII was isolated as a colorless liquid, b.p. 180° (0.25 mm.), n^{25}D 1.474.

Anal. Calcd. for $C_{16}H_{24}O_8$: C, 55.80; H, 7.02. Found: C, 55.47; H, 7.27.

1,2,4,6-Tetracarbethoxycyclo̊octane (VIII) was prepared similarly. Four moles of hydrogen per mole of I were absorbed in 66 hours in cyclohexane; VIII remained as a colorless liquid, b.p. 163° (0.25 mm.), n^{25}D 1.467.

Anal. Calcd. for $C_{20}H_{32}O_8$: C, 59.98; H, 8.06. Found: C, 59.67; H, 8.07.

Hydrogenation of II in cyclohexane was complete in 10 min. with the absorption of 101% of four molar equivalents of hydrogen. A colorless viscous liquid, was produced, which was characterized as a cyclo̊octane by its infrared spectrum.

D. Pyrolysis of Compound I.—Compound I was melted and held above its melting point while a hot nitrogen stream was allowed to bubble through the melt and carry the compound vapor into the pyrolysis chamber, a 25-mm. Pyrex tube packed with 4-mm. Pyrex beads and glass helices. The chamber was heated by an electric furnace. Three low temperature traps and a flow meter were connected in series at the exit of the chamber to collect products and measure the residence time of the compound in the chamber. After a sufficient quantity of the pyrolysate had been trapped, the gas flow was stopped and the trapped material was washed out with ether, dried over Na_2SO_4, filtered, and analyzed both by infrared and vapor phase chromatographic analysis. The carbonized material in the chamber was also extracted and analyzed as above. Optimum temperature for the melt was found to be 135–150°. Pyrolysis does not occur below 300°, while charring of all vapor takes place at 400°. Pyrolysis temperatures of 340–350° were employed with a residence time of about 120 seconds.

The principal products were ethyl propiolate and 1,2,4-tricarbethoxybenzene, although smaller amounts of 1,3,5-, 1,3- and 1,4-isomers were also detected.

E. Saponification.—Equal amounts of a dilute solution of KOH in absolute ethanol were placed in two flasks, one containing the ester to be saponified, the other to be used as a blank. Both solutions were refluxed for 1 hour, cooled, and titrated with standard HCl, employing a Leeds & Northrup pH meter. The difference in volumes required for the two titrations, multiplied by the acid normality, equaled the meq. of KOH required for the ester. The solution containing the acid anion was then titrated to pH 1.5 to determine the pK_a's of the acid groups. After this, the acid was isolated.

Cyclo̊octatetraene-1,2,4,6-tetracarboxylic Acid (IX).—Compound I (0.2873 g., 0.723 mmole) was saponified in 25 ml. of absolute ethanol containing 1.25 g. of KOH. The ester formed a brown solution immediately upon addition of base. After 1 hour at reflux the solution was cooled and titrated with 0.5 N HCl. Neutralization of 16.33 meq. of KOH occurred at pH 8.75, at which point the solution turned yellow. Neutralization of the blank at pH 7.0 required 19.30 meq. of KOH, so that 2.97 meq. of KOH (102% of 4 moles KOH per mole ester) were required for saponification. Further titration of the solution containing the acid anion showed inflections in the titration curve, indicating successive acidification of carboxylate groups and corresponding to pK_a values as given in Table II. Color changes from yellow through amber, pink, and red were observed during the titration.

The acid product was isolated by removing water and ethanol by evaporation and extracting the resulting solids with diethyl ether in a Soxhlet apparatus. The yellow ether solution was evaporated, and the crude product was recrystallized from ether to yield pure IX as yellow plates, m.p. 267–268° dec.

Anal. Calcd. for $C_{12}H_8O_8$: C, 51.44; H, 2.88; Found: C, 51.44; H, 3.25.

When IX was heated to 100° in dioxane and CCl_4 was added, a white solid precipitated, m.p. 245° dec., which had the infrared spectrum of an anhydride. The white solid dissolves in water to give a yellow solution which is acidic.

In like manner III was saponified to the same acid IX, yellow plates, m.p. 267° dec., with identical infrared spectrum.

Anal. Found: C, 51.57; H, 3.49.

Acid IX which had been prepared from III was re-esterified by refluxing it in ethanol and concentrated sulfuric acid for 1 hour. Water was added, the solution was saturated with $(NH_4)_2SO_4$, and extracted with ether. Evaporation of the ether extract and recrystallization of the crude solid so obtained gave yellow crystals of pure I, m.p. 83.5°.

The ester II formed an intensely blue solution upon addition of KOH in ethanol. After 1 hour of reflux, the solution had turned wine colored. Neutralization occurred at pH 8.25, requiring 95% of 4 moles of KOH per mole of ester, after which only one further inflection was observed. Isolation of the product was carried out as described above, producing light yellow crystals of an acid, m.p. 235–237° dec. The detection of a single inflection in the titration of this carboxylate ion is attributed to its symmetrical structure, with resulting closeness in the pK_a values.

Saponification of the methyl esters V and VII (neutralization occurred at pH 8.75 in both cases, requiring nearly 4 moles of KOH per mole of ester) was carried out as described above. Upon acidification, V produced pale yellow crystals of an acid, m.p. 120–122°, and VII produced white crystals which form an anhydride at 90°.

Proton Resonance Spectra.—The spectra of cyclo̊octatetraene and compounds I, II, III, VI and VIII were measured at high dilution in chloroform-d solution on a Varian 4300B spectrometer at a frequency of 40 Mc. and a field of 9300 gauss. Both benzene external and tetramethylsilane internal references were used. Positive chemical shifts are at higher fields, and all shifts are accurate to ±1 c.p.s. Area ratios (where measured) were determined both by counting squares and by cutting out the trace in question and weighing the paper. Data are presented below. Chemical shifts are in parts per million (p.p.m.) from benzene.

Compound	Olefinic ring CH	Ester CH₂	Aliphatic ring CH	CH₂	Ester CH₃
C_8H_8	−0.85	.....	.....	.....	.....
I	− .90⎫[a] − .70⎭	+2.28[b]	.....	.....	+5.25[c]
II	− .95	+2.25[d]	.....	.....	+5.22[e]
III	− .90⎫[a] − .75⎭	.....	.....	.....	+5.15⎫[f] +5.22⎭
VI	− .70⎫[a] − .50⎭	+2.27[g]	+4.13[h]	+4.50[h]	+5.22[k]
VIII	....	+2.25[d]	+4.10[j]	+4.52[j]	+5.22[e]

[a] Not coupled. [b] Two quartets, equal area, 2 c.p.s. coupling. [c] Two triplets, equal area, 2 c.p.s. coupling. [d] One quartet, 2 c.p.s. coupling. [e] One triplet, 2 c.p.s. coupling. [f] Two singlets, not coupled. [g] Two quartets, area ratio 3:1, coupling 3 c.p.s. [h] Area ratio CH/CH_2 = 1:1. [j] Area ratio CH/CH_2 = 1:2. [k] Two triplets, area ratio 3:1, coupling 3 c.p.s.

Ultraviolet Spectra.—The spectra of cyclo̊octatetraene and of compounds I, VI and VIII were measured in cyclohexane solution; absorption maxima are given in mμ, followed by intensity as log_{10} E: C_8H_8: 260 sh(2.52), 278 (2.50); I: 226 (4.46), 316 (3.06); VI, VIII: without feature. The tetrasubstituted tetraene I shows a very intense conjugated carbonyl absorption at 226 mμ, whereas the tetrasubstituted mono-ene shows none. The remaining unsaturation in this latter compound is thus unsubstituted.

Infrared Spectra.—Spectra of all compounds listed in Table I were run either as smears or in KBr matrices. Noteworthy features: (1) the spectra of the cyclo̊octatetraene esters I, III and IV are similar except for the expected methyl and ethyl differences below 1000 cm.$^{-1}$. This indicates similar isomerism for all three. Compound II is similar above 1000 cm.$^{-1}$ to the other tetraenes; below 1000 cm.$^{-1}$, however, it is much simpler, with fewer bands, indicating a more symmetrical isomer. (2) The octenes V

and VI are similar to one another, and show a decrease in complexity and intensity in the C=C region compared with the tetraenes. The presence of ester carbonyl is clearly indicated, but it is difficult to assign an unconjugated/conjugated ratio. (3) The octanes VII and VIII are similar to one another, and have lost all C=C absorptions. (4) The spectra of the acids show very strong OH stretches but no anhydride bands.

High Pressure Reactions.—Reactions of the gaseous monomers listed in Table I were all carried out in similar fashion. A 280-ml. glass-lined autoclave was charged with solid Ni(PCl₃)₄ catalyst and 100 ml. of cyclohexane. The autoclave was then flushed with nitrogen and gaseous monomer was condensed into the chilled reaction vessel, either from a weighed transfer bomb or from the storage tank. Monomer to catalyst ratios were about 700:1 in all cases. The autoclave was then sealed and allowed to warm to 20°, where shaking and a temperature–time program were begun. With acetylene (12 g.), 4.5 hours at 85° produced 0.4 g. of an unidentified aromatic-smelling yellow oil. This product contained no nickel or cyclooctatetraene derivatives, but showed infrared absorption bands at 3380s, 1635m, 1665m, 1175m and 1025s. cm.⁻¹.

With ethylene no reaction was achieved after 4 hours of contact at 120°.

With allene (14.5 g.), 5 hours of contact at 80° produced a bright yellow solution. Absolute ethanol (50 ml.) was added to decompose the remaining catalyst, after which the solution was filtered and evaporated at 25° under high vacuum. As the evaporation proceeded, a yellow solid and a yellow oil were deposited. The combined weight of these products was 3.5 g., or 24%, based on allene. The infrared spectra of both were the same, and were identical with the spectra of a mixture of triexomethylenecyclohexane and tetraexomethylenecyclooctane reported by Benson and Lindsay.[5]

With butadiene (69 g.), a 36-hour contact at 115° followed by a further 36 hours at 150° produced 68.2 g. of a homogeneous yellow oil. After centrifugation to remove inorganic solids, the oil was fractionated at reduced pressure, giving 22.9 of the thermal dimer 4-vinylcyclohexene and 22.8 g. of the g. thermal high polymer polybutadiene. The remaining 22.5 g. consisted of three fractions containing (by mass spectroscopy) butadiene dimer (25%), trimer (50%) and tetramer (25%). The composition of these oligomers is unknown, but it appears they are different from those obtained by Reed[32] and Wilke[33] with other catalyst systems.

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(33) G. Wilke, J. Polymer Sci., 38, 45 (1959).

COMMUNICATIONS TO THE EDITOR

THE CHROMIC ACID OXIDATION OF ORGANOBORANES—A CONVENIENT PROCEDURE FOR CONVERTING OLEFINS INTO KETONES via HYDROBORATION

Sir:

The hydroboration of olefins, with subsequent oxidation of the resulting organoboranes with alkaline hydrogen peroxide, provides a convenient procedure for the conversion of olefins into alcohols.[1] These alcohols can be taken up in ether and converted, without isolation, into the corresponding ketones, by chromic acid oxidation.[2]

It has been reported that the hydroboration of conessine followed by chromic acid oxidation[3] in aqueous acetic acid[4] yielded 3β-dimethylaminoconanin-6-one. Since organoboranes are susceptible to protonolytic cleavage in the presence of acetic acid, but are stable to aqueous mineral acids,[5] we undertook to explore the utility of aqueous chromic acid as a general procedure for the conversion of organoboranes into ketones.

Cyclohexene, hydroborated in diglyme, tetrahydrofuran, or ethyl ether, was treated with aqueous chromic acid. After two hours at 25–35°, 60–65% yields of cyclohexanone were realized. Since the use of ethyl ether greatly facilitated the isolation of the ketone, later studies emphasized

this medium. 1-Methylcyclopentene was converted into 2-methylcyclopentanone in 83% yield, and 1-methylcyclohexene was converted into 2-methylcyclohexanone in 87% yield. Similarly, 1-phenylcyclohexene produced 2-phenylcyclohexanone in 63% yield and α-pinene was converted into isopinocamphone in 72% yield (several per cent. of the epimer, pinocamphone was indicated in the gas chromatogram).

The procedure is exceedingly simple. The olefin is hydroborated in ethyl ether with boron trifluoride-etherate and lithium borohydride or with sodium borohydride in the presence of catalytic quantities of zinc chloride.[6,7] A slight excess (10%) over the theoretical quantity of aqueous chromic acid is added over 15 minutes, the mixture refluxed (35–37°) for two hours, and the product isolated as an ether solution.

This ready oxidation of organoboranes to ketones makes available a convenient general synthesis of 2-alkyl- and 2-arylcycloalkanones:
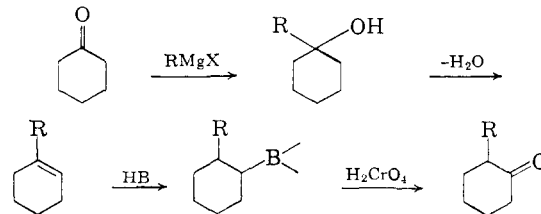
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(2) H. C. Brown and C. P. Garg, ibid., 83, 2952 (1961).

(3) R. Pappo, ibid., 81, 1010 (1959).

(4) R. Pappo, private communication as reported in L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corporation, New York, N. Y., 1959, p. 864.

(5) H. C. Brown and K. Murray, J. Am. Chem. Soc., 81, 4108 (1959).

(6) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover and G. Zweifel, ibid., 82, 4233 (1960).

(7) Alternatively, the lithium aluminum hydride procedure of Sondheimer and his co-workers may be employed to achieve hydroboration in this solvent: S. Wolfe, M. Nussim, Y. Mazur and F. Sondheimer, J. Org. Chem., 24, 1034(1959).