ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE MONSANTO CHEMICAL CO., DAYTON, O.]

π-Complexes of the Transition Metals. XVI. Addition Reactions of Triphenylchromium and Olefins[1]

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Organochromium reagents can be added across highly reactive, unsaturated bond systems, *e.g.*, disubstituted acetylenes. Addition reactions of triphenylchromium and olefins also occur, provided the olefinic system is capable of complexing with chromium. The phenylation of bicyclo[2,2,1]heptadiene-2,5 and of maleic anhydride, giving *exo*-5-phenyl-bicyclo[2,2,1]-heptene-2, *exo,exo*-2,5-diphenylbicyclo[2,2,1]heptane and α-phenyl-β-benzoylpropionic acid, respectively, is described.

The cyclization of acetylenes to aromatic, polyaromatic and cyclopentadiene rings on organometallic centers has been described in earlier papers.[3] Applying the concept of a stepwise replacement of the coördinating solvent ligands of transition metal organometallics, we were successful in adding aryl groups of triarylchromium complexes to the triple bonds of disubstituted acetylenes. Thus, the styrene derivative, 2-mesityl-2-butene, was formed from trimesitylchromium and 2-butyne, and the stilbene, *cis*-dimethyl diphenylmaleate, arose from addition of triphenylchromium to dimethyl acetylenedicarboxylate.[4] We now report addition reactions of triphenylchromium and certain olefins.

In experiments spanning a wide range of olefinic structure no evidence for the cyclization of olefins on the triphenylchromium complex, as occurs with acetylenes, was found. Instead, the organochromium reagent added to the site of unsaturation when the olefin was capable of complexing with chromium. The 2,2,1-bicyclic diene and conjugated olefin system met this specification.

Bicyclo[2,2,1]heptadiene-2,5 was treated at room temperature in tetrahydrofuran with triphenylchromium. The reaction product consisted essentially of two fractions, the monophenylated bicyclo-[2,2,1]heptene-2 and the diphenylated bicyclo-[2,2,1]heptane, the result of the addition of one and two phenyl groups, respectively, by the organometallic compound to the diene system. The former substance *exo*-5-phenylbicyclo[2,2,1]heptene-2, formed in much the greater amount, is a liquid which was converted to a crystalline phenyl azide, m.p. 144–146°, the sole derivative product. The second fraction, assigned the structure of *exo,exo*-2,5-diphenylbicyclo[2,2,1]heptane, is a solid, m.p. 85–87°, having no detectable unsaturated properties. An attempt to phenylate further the monophenylated hydrocarbon by a second treatment with triphenylchromium was unsuccessful, an experimental fact which has a bearing on the mode of formation of these phenylated hydrocarbons.

A monophenylated derivative of the bicycloheptadiene was prepared some years ago by Alder and Rickert as one of the products of the addition of cyclopentadiene and styrene in the presence of acetylenedicarboxylic acid.[5] This is now formulated as *endo*-5-phenylbicyclo[2.2.1]heptene-2 which gave a phenyl azide adduct melting between 134–135°. The discrepancy in melting points between their phenyl azide and ours is explained by the assumption that the triphenylchromium–bicycloheptadiene addition results exclusively in the *exo*-phenylated form.

Experimental support for the assignment of the *exo* configuration to our product is derived from a repetition of the Alder–Rickert preparation and isolation from their product mixture of a phenyl azide, although in small amount, which melted undepressed at 145° with our azide and whose infrared spectrum was superimposable on that of ours. The main product, as reported, gave the phenyl azide melting at 133–135°. The eutectic temperature of the two azides was 110° accounting for the 110–130° melting crystalline product initially obtained by us by the azidization of the Alder–Rickert hydrocarbon mixture and subsequent separation into the two forms.

The structure of the diphenylated bicycloheptane, isolated in small amount, has been elucidated by means of X-ray diffraction and optical measurements. Oscillation and Weissenberg photographs were taken with CuKα radiation round the three principal axes. The crystals are orthorhombic with $a = 19.70$, $b = 6.95$, $c = 10.64$ Å. The density measured by flotation in a solution of potassium carbonate is 1.11. Thus there are four molecules in the unit cell. The following systematic absences occur amongst the diffracted X-ray spectra: hkl for $k + l$ odd; $0kl$ for k odd and l odd; $h0l$ for h odd and l odd; $hk0$ for k odd. These absences lead unambiguously to the space group $Aba2$ (C_{2v}^{17}). Since there are eight general positions in this space group, and only four molecules in the unit cell, the molecule itself must possess symmetry. The only possibility is a twofold axis. Thus the molecule must be 2,5-diphenylbicycloheptane, either with both phenyl substituents in the *endo* position or both in the *exo* position. That the molecule is in the *exo,exo* form is suggested by the previous chemical evidence. This conclusion is confirmed by the cell dimensions, since four mole-

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[1] Paper XV, T. F. Burger and H. Zeiss, *Chemistry & Industry*, 183 (1962).

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[3] *Cf.* H. Zeiss, "Organometallic Chemistry," Reinhold Publ. Corp., New York, N. Y., 1960, pp. 411–414, for detailed discussion and appropriate references.

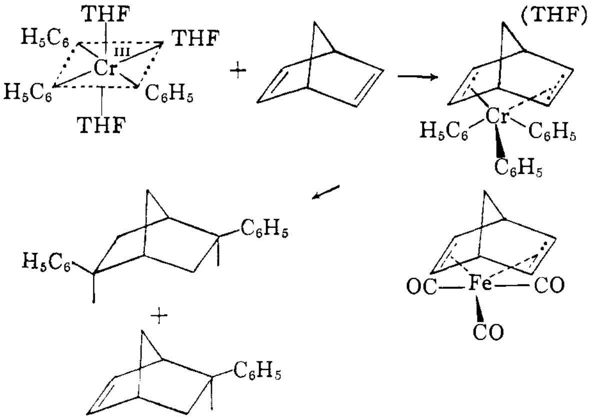
[4] W. Metlesics and H. Zeiss, *J. Am. Chem. Soc.*, **81**, 4117 (1959).

[5] K. Alder and H. F. Rickert, *Ber.*, **71**, 379 (1938).

cules of an *endo,endo* form could not fit into a cell of this size, and also by the high (presumably positive) birefringence of the crystals, which is consistent with the long *exo,exo*-molecules lying roughly parallel to each other and to the long [*a*] axis.

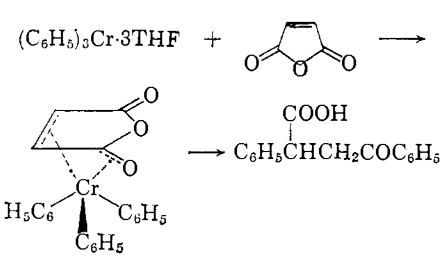
An explanation of the *exo* addition of phenyl groups by triphenylchromium to bicycloheptadiene lies in the assumption of an initial complexing of the diene system with the σ-bonded phenylchromium compound, the result of a displacement of coördinating solvent molecules by the diene. This intermediate π-complex is somewhat analogous in structure to the cyclobutadiene–chromium complex proposed for the formation of aromatic, polyaromatic and cyclopentadiene rings from the aryl- and alkyl-chromium reagents and acetylenes.[3]

The actuality of this intermediate is supported by the existence of the tricarbonyliron complex of bicyclo[2,2,1]heptadiene-2,5.[6] However, the phenyl–chromium bond is considerably more labile than that of a carbonyl–metal, particularly in the presence of other reactive centers, and, since the *endo* position is blocked in the intermediate, only *exo* addition is open to the phenyl group. Hydrolysis of the complex then supplies the proton in the final product.



Failure to phenylate further the monophenylbicycloheptene with triphenylchromium is also an argument for the existence of this intermediate as a reaction requirement. Simple olefins, *e.g.*, hexenes, cyclohexene, isoprene or even stilbene and styrene, do not undergo appreciable addition reactions with triphenylchromium, a fact attributable to the lack of coördinating power of these olefins with chromium.

Another olefinic system which permits a similar interpretation is that provided by maleic anhydride. The product of the reaction of this substance with triphenylchromium is α-phenyl-β-benzoylpropionic acid, isolated as its methyl ester. The formation of this substance may be superficially described as the result of a 1,4-addition of triphenylchromium to the α,β-unsaturated ester[7] but perhaps better interpreted in terms of the formation of an intermediate, internally reactive π-complex.



The preceding examples and arguments lend weight to the concept of the π-complex as an essential, catalytic intermediate in metal–organic reactions. The internal reactivity of these intermediates provides the drive in coördination synthesis, and their geometry determines the structure of the final products.

Experimental[8]

Addition of Triphenylchromium to Bicyclo[2,2,1]heptadiene-2,5.—Triphenylchromium was prepared by treating 15 g. (0.095 mole) of anhydrous chromium(III) trichloride in 500 ml. of tetrahydrofuran with 250 ml. of a 1 *M* solution of phenyl Grignard (0.25 mole) in tetrahydrofuran at −20°. To this mixture 11.5 g. (0.125 mole) of bicycloheptadiene (Shell Chemical Co., previously filtered through basic alumina and distilled at atmospheric pressure) was added at room temperature and left standing overnight. After 18 hours the initial reddish-brown color of the solution had turned to green, and a small amount of green flocks which had deposited were filtered and discarded. The solvent was removed *in vacuo*, the residue treated with 5% sulfuric acid and then extracted with ether. The ether solution was washed with aqueous sodium bicarbonate, dried over sodium sulfate, and then freed for the most part of ether. The residue was distilled over a small column, the main fraction of 6–8 g. boiling between 114–116° (15 mm.). The infrared spectrum of this product indicated reasonable purity and contained absorptions consistent with the **5-phenylbicyclo[2,2,1]heptene-2** structure.

Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.68; H, 8.14.

In another experiment in which 0.045 mole of triphenylchromium and 0.092 mole of bicycloheptadiene were allowed to react, 4.5 g. of this hydrocarbon was isolated in similar fashion.

The phenylazide adduct of ***exo*****-5-phenylbicyclo[2,2,1]heptene-2** was prepared by dissolving equal amounts of the hydrocarbon and phenyl azide in ethyl acetate. After standing for some time, white crystals of the adduct appeared as the sole product, m.p. 114–146°. This adduct melted undepressed with a sample of the phenyl azide adduct of 5-phenylbicyclo[2,2,1]heptene-2 prepared according to Alder and Rickert (*vide infra*).[5]

Anal. Calcd. for $C_{19}H_{19}N_3$: C, 78.86; H, 6.62; N, 14.52. Found: C, 78.67; H, 6.69; N, 14.43.

The distillation residue from the isolation of monophenylbicycloheptene above was transferred to a ball tube and distilled at a bath temperature of 200° (0.5 mm.), giving a pale yellow oil which crystallized on scratching. Recrystallization from ethanol yielded 0.6–1 g. of white leaflets, m.p. 85–87°, of ***exo,exo*****-2,5-diphenylbicyclo[2,2,1]heptane.**

Anal. Calcd. for $C_{19}H_{20}$: C, 91.88; H, 8.12; mol. wt., 248. Found: C, 92.01; H, 8.06; mol. wt., 236 (Rast).

5-Phenylbicyclo[2,2,1]heptene-2.[5]—Freshly distilled cyclopentadiene (115 g.), 1.6 g. of acetylenedicarboxylic acid and 180 g. of styrene were heated at 190° for 15 hours in a 500-ml. steel bomb. After several fractional distillations the main fraction, a colorless liquid, boiling between 113–115°

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[6] R. Burton, M. L. H. Green, E. W. Abel and G. Wilkinson *Chemistry & Industry*, 1592 (1958); R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

[7] Phenyl Grignard adds similarly to maleic anhydride, but in this case the major product is desylacetophenone: D. S. Tarbell, *ibid.*, **60**, 215 (1938). This would indicate that diphenylmagnesium is capable of complexing such systems also.

[8] All work was carried out under G.E. lamp-grade nitrogen. Melting points were determined on the Kofler hot-stage. Analyses were performed by the Schwartzkopf Microanalytical Laboratories, Woodside 66, N. Y.

(14 mm.), was obtained. The infrared spectrum of this product, while containing absorptions attributable to those of phenylbicycloheptane, was definitely different from that of the hydrocarbon isolated from the addition of triphenylchromium to bicycloheptadiene. Several attempts to separate the main fraction into components by vapor phase chromatography were unsuccessful.

The product was then dissolved with an equal amount of phenyl azide in ethyl acetate. After 3 days standing and frequent scratching, a crop of white crystals, m.p. 110–130°, was deposited. Recrystallization of this mixture from ethyl acetate gave as first fraction a small amount of adduct, m.p. 143–145°, melting undepressed with and showing a superimposable infrared spectrum with that of 5-phenylbicyclo-[2,2,1] heptene-2 obtained above from addition of triphenylchromium to the bicycloheptadiene.

A second fraction was obtainable from the 110–130° product by chromatography with ether on a basic alumina column. The first eluted fractions melted between 133–135° corresponding with the phenyl azide derivative prepared by Alder and Rickert from *endo*-5-phenylbicyclo [2,2,1]heptene-2, m.p. 134–135°. The eutectic temperature for the 145°- and 135°-melting azides was found to be 110°. A semiquantitative study of infrared spectra revealed that the 110–130° azide mixture contained the 145°- and 135°-azides in a ratio of about 1:1. According to the infrared spectrum of the parent hydrocarbon mixture, a large excess of the 135° azide would have been expected in the 110–130° azide mixture had it not been for its greater solubility in ethyl acetate and methanol.

Addition of Triphenylchromium to Maleic Anhydride.—To a solution of 0.029 mole of triphenylchromium in tetrahydrofuran was added 5.7 g. (0.059 mole) of maleic anhydride. A spontaneous reaction ensued, the whole mixture reaching a temperature of 40°. After standing for 48 hours the solvent was removed, the residue treated with ice-water and then filtered. A green solid was collected on the filter from which only biphenyl could be extracted with benzene. The infrared spectrum of the remainder indicated it to be a metal salt of a carboxylic acid. Treatment of this green powder with strong hydrochloric acid and extraction with ether overnight yielded a dark brown solution from which organic acids could be removed with aqueous sodium bicarbonate. The alkaline solution was acidified and extracted with ether again overnight. Removal of the ether left 2.25 g. of crude product in the form of a brown, sticky mass which was now esterified by dissolution in 25 ml. of methanol, addition of 3 ml. of concentrated sulfuric acid and refluxing on the steam-bath for 3 hours. This reaction mixture was diluted with water, extracted with ether, and the unesterified acid fraction removed from the ether layer with bicarbonate. The ester fraction was distilled in a ball tube at a bath temperature of 180–250° (0.5 mm.), yielding a yellow oil which crystallized after scratching. Recrystallization from ethanol gave white crystals of methyl α-phenyl-β-benzoylpropionate, m.p. 100–102°.[9]

Anal. Calcd. for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01; CH_3O, 11.5. Found: C, 76.41; H, 6.06; CH_3O, 11.9.

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[9] Rupe, *et al.*, *Ber.*, **28**, 963 (1895), reported m.p. 104°.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, N. Y.]

Reactions of Palladium Compounds with Acetylenes. I. Tetraphenylcyclobutadienepalladium(II) Chloride

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In non-hydroxylic solvents, bis-(benzonitrile)-palladium chloride (I) catalyzes the trimerization of tolan to hexaphenylbenzene. In ethanol–chloroform (3:1), tolan reacts with compound I to give an orange-red complex (A), $(C_{30}H_{25}OPdCl)_x$, which on treatment with hydrogen chloride affords a deep red crystalline complex (B), $(C_{28}H_{20}PdCl_2)_x$. Spectroscopic and degradation studies of complex B show that it is tetraphenylcyclobutadienepalladium(II) chloride. Complex B, which can also be obtained directly by reaction of tolan with palladium chloride, fails to react with tolan, 2-butyne and dimethyl acetylenedicarboxylate. Treatment of B with ethanol converts it to a yellow complex (C), isomeric with complex A. Complex A reacts with bromine to give tetraphenylfuran and it decomposes thermally to 2,3,8-triphenylbenzofulvene and 8-ethoxy-2,3,8-triphenylbenzofulvene. Structures are postulated for complexes A and C, and a mechanism is proposed for the reactions leading to their formation.

Considerable effort has been expended by a large number of workers over the last fifty years in attempts to prepare derivatives of cyclobutadiene.[1] Apart from the preparation of diphenylene and its derivatives[2] this quest has hitherto been fruitless, with the exception of a number of cyclobutadiene–metal complexes which have recently been reported.[3–6] It would seem that one of the most practical and hopeful routes to cyclobutadienes would be by decomposition of suitably stabilized cyclobutadiene–metal complexes. However, the routes used to obtain these metal complexes do not, for the most part, appear to be broadly useful for the preparation of complexes other than the specific ones described.

As yet very little work has been carried out on reactions of acetylenes with palladium compounds; one brief note by Malatesta and co-workers[7] has appeared which describes, *with complete absence of detail*, the preparation of a cyclobutadiene–palladium complex in two steps from tolan (diphenylacetylene) and palladium chloride. Since this is certainly the simplest route yet discovered to cyclobutadiene complexes and one which should be capable of great extension, its reinvestigation was undertaken, preparatory to a more complete study of the route as a general method.

Results

Bis-(benzonitrile)-palladium chloride (I), $(C_6H_5CN)_2PdCl_2$,[8] was chosen as the source of palladium in the present study. This palladium

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[1] W. Baker and J. F. W. McOmie, "Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, p. 43.

[2] W. Baker and J. F. McOmie, *Chem. Soc. Special Publ. No. 12*, 49 (1958).

[3] M. Avram, E. Marica and C. D. Nenitzescu, *Chem. Ber.*, **92**, 1088 (1959); *Tetrahedron Letters*, 21 (1961).

[4] R. Criegee and G. Schroeder, *Ann.*, **623**, 1 (1959).

[5] W. Hübel and E. H. Braye, *J. Inorg. Nucl. Chem.*, **9**, 250 (1959); *cf.* W. Hübel, *et al.*, *ibid.*, **9**, 204 (1959), and R. P. Dodge and V. Schomaker, *Nature*, **186**, 798 (1960).

[6] H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961).

[7] L. Malatesta, G. Santarella, L. Vallarino and F. Zingales, *Angew. Chem.*, **72**, 34 (1960); *Atti. accad. naz. Lincei, Rend. Classe sci. fis. mat. e nat.*, **27**, 230 (1959).

[8] M. S. Kharasch, R. C. Seyler and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).