The second group of experiments is summarized in Table II and it employed peracetic acid (PAA) in a medium of glacial acetic acid.[12] It is noted in the first place that the bimolecular rate constants were three to four times smaller than those obtained in the PBA oxidations. This difference can be explained in several ways.

Firstly, Overberger and Cummins[3] have shown that the oxidative strength of peracids increases with the electron-withdrawing character of the group attached to the percarboxy group, and of the phenyl and the methyl groups the former is recognized to be more electron-withdrawing. Secondly, it can be safely assumed that the sulfoxide is more strongly solvated in acetic acid than in acetone, and the higher degree of solvation would tend to inhibit to some degree the successful collisions with the peracid. Overberger and Cummins[4] and Friess[13] similarly explained the decelerating effect of water on the oxidation reactions of sulfoxides and ketones, respectively. Thirdly, the PAA oxidations were carried out in the presence of small amounts of sulfuric acid and the latter was shown to be a negative catalyst. The inhibiting effect of sulfuric acid is worthy of further consideration. It is noted that the magnitude of the effect of sulfuric acid is not very great and that it seems to approach a constant value when the concentration of sulfuric acid exceeds that of phenyl sulfoxide. We attribute the effect of sulfuric acid to the salt formation with the sulfoxide, and the close association of the two ions, or the strong solvation of the sulfoxidonium ion[14] by acetic acid explains the observed decrease in the rate constant. If the sulfuric acid were involved in the formation of a complex with PAA then one would expect a positive catalytic effect.[4] Rather surprising results were obtained when benzoic acid was added to the PAA oxidation experiments (Table II). The rate constants calculated on the basis of a bimolecular rate law were very large during the initial period, then decreased rapidly, and at approximately 50% reaction they approached a constant value. It is difficult to suggest a clear cut explanation of these results because of the complexity of the reaction mixture. However, it seems reasonable to assume an equilibrium between PAA and benzoic acid, and the simultaneous oxidation of phenyl sulfoxide by PAA and PBA. Since the initial values of the oxidation rates were higher than those obtained when PBA in acetone was employed, it is possible that under these conditions there is also made a contribution by a sulfuric acid-catalyzed PBA oxidation. The latter would have a better chance in the polar medium of acetic acid than in the medium of acetone.

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[12] The kinetics of the oxidation of phenyl sulfoxide by PAA was previously investigated by J. Böeseken and E. Arrias [*Rec. trav. chim.*, **54**, 711 (1935)]. These investigators also found the reaction to obey the bimolecular rate law but their rate constant varied considerably from one experiment to another. Thus, in two experiments at 24° they obtained rate constants of 7.2 and 4.45 ($\times 10^{-3}$) and variations such as these were attributed to the spontaneous decomposition of PAA since the rate constants seemed to increase as higher concentrations of PAA were employed. These difficulties are largely avoided in this study since the PAA employed here contained a stabilizer which makes spontaneous decomposition negligible over the period of two hours.

[13] S. L. Friess, THIS JOURNAL, **71**, 2571 (1949).

[14] H. H. Szmant and G. A. Brost, *ibid.*, **73**, 4175 (1951).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY]

Ferrocene Derivatives. Part I. The Direct Synthesis of Substituted Ferrocenes

BY P. L. PAUSON[1]

RECEIVED SEPTEMBER 14, 1953

A series of phenyl-substituted ferrocenes is prepared from the corresponding phenyl-substituted cyclopentadienes. Use of a mixture of cyclopentadiene and phenylcyclopentadiene affords the monophenylferrocene. The preparation of 1,1'-dibenzhydrylferrocene from benzhydrylcyclopentadiene provides direct proof that both rings are substituted in the diacylation of ferrocene. Phenylcyclopentadiene and 1,2,3-triphenylcyclopentadiene have been obtained for the first time.

The discovery that the reaction of cyclopentadienylmagnesium bromide with ferric chloride results in the formation of ferrocene (biscyclopentadienyliron(II)),[2] was followed by the demonstration[3] that a variety of both mono- and disubstituted derivatives can be prepared from this compound by acylation under Friedel–Crafts conditions. This method, however, has obvious limitations; to obtain aryl-substituted derivatives in particular, other methods are necessary. After an unsuccessful attempt to introduce phenyl groups into ferrocene by reaction with benzoyl peroxide, it was decided to examine the possibility of preparing the desired products directly from suitably substituted cyclopentadienes.

The preparation of dibenzoferrocene (bis-indenyliron(II)) from indenyllithium has recently been described,[4] but no other application of this reaction to a substituted cyclopentadiene has been reported. It is now shown that derivatives of ferrocene substituted by aryl or alkyl groups in both rings may be obtained readily in this way. Moreover, one example is given to show that monosubstituted derivatives likewise can be obtained if a mixture of the appropriately substituted cyclopentadiene with unsubstituted cyclopentadiene is used in the Grignard reaction.

Of the seven possible cyclopentadienes bearing phenyl substituents (excluding isomers with two

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[1] Chemistry Department, The University, Sheffield 10, England.

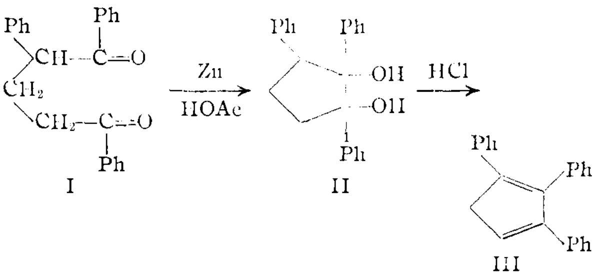
[2] T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

[3] R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

[4] P. L. Pauson and G. Wilkinson, *ibid.*, **76**, 2024 (1953).

groups attached to the same carbon atom), five previously have been described.[5-8] In the course of the present work it became necessary to synthesize the remaining two.

The preparation of 1,2,3-triphenylcyclopentadiene followed closely the methods previously used for the 1,2,4-isomer.[7] 1,2,5-Triphenylpentane-1,5-dione[9] (I) was reduced with zinc and acetic acid[7,8] to 1,2,3-triphenylcyclopentane-1,2-diol (II) which was smoothly dehydrated by hydrochloric acid in boiling ethanol solution[7,8a] to yield the desired diene III. Its infrared spectrum is shown in Fig. 1 together with that of the 1,2,4-isomer.



I II III

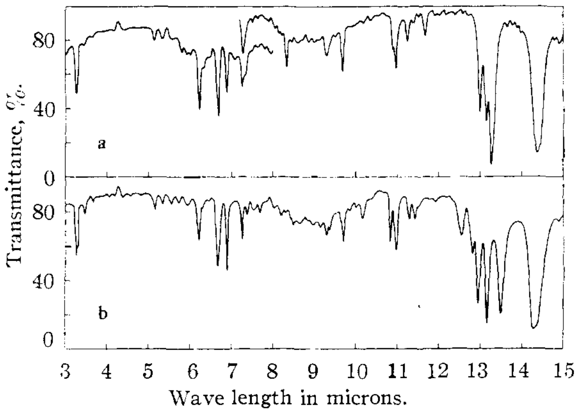
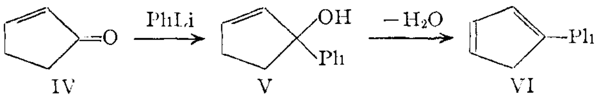


Fig. 1.—Spectra of (a) 1,2,4—(IX) and (b) 1,2,3-triphenylcyclopentadiene (III) in CCl_4 (20 mg./cc.; 3–8 μ) and in CS_2 (15 mg./cc.; 7–15 μ).

To obtain phenylcyclopentadiene (VI), cyclopentenone (IV) was treated with phenyllithium to given 1-phenyl-2-cyclopentene-1-ol (V) which lost water on distillation to yield VI. Although this method is rapid and simple, the yields are only moderate and the search for a better method is therefore being continued.



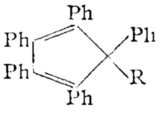
IV V VI

The preparation of ferrocene derivatives was first attempted with the readily available 1,3-diphenylcyclopentadiene.[5] This readily formed the corresponding Grignard reagent on treatment with ethylmagnesium bromide and on treatment of this solution with ethereal ferric chloride, the orange-red 1,3,1′,3′-tetraphenylferrocene was obtained; it was readily separated from unchanged hydrocarbon by fractional crystallization from acetone in which it is less soluble.

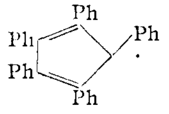
1,2,4-Triphenylcyclopentadiene[7] behaved similarly, and the red 1,2,4,1′,2′,4′-hexaphenylferrocene was obtained after removal of unchanged hydrocarbon by sublimation.

However, when the same reaction sequence was applied to 1,2,3,4-tetraphenylcyclopentadiene,[8] no ferrocene derivative could be isolated. To ensure that this failure was not the result of failure to obtain the intermediate Grignard reagent, the hydrocarbon was first converted to the corresponding bromine[10]; this underwent halogen–metal exchange smoothly when treated with a solution of phenyllithium, but again the desired product could not be obtained after treatment of the tetraphenylcyclopentadienyllithium with ferric chloride.

It was considered of particular interest to test the next higher member of this series, 1,2,3,4,5-pentaphenylcyclopentadiene (VII, R = H),[8c] in view of the known stability of the corresponding free radical VIII.[8c] However, neither reaction of the bromide (VII, R = Br)[8c] with phenyllithium to yield the lithium derivative (VII, R = Li) followed by treatment with ethereal ferric chloride nor interaction of the radical VIII with iron pentacarbonyl afforded the desired ferrocene derivative.



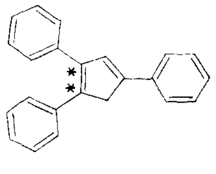
VII



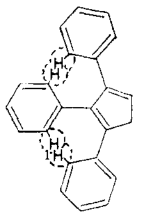
VIII

These unexpected failures led to the consideration of the possibility that steric factors might be responsible for preventing the reaction of the tetra- and pentaphenylcyclopentadienyllithium with ferric chloride.

It can readily be ascertained from models that in these substances the phenyl groups cannot all be coplanar with each other and with the five-membered ring owing to interference between the hydrogen atoms in the *ortho* positions. Instead, the molecules most probably assume a propeller-like configuration. When only two phenyl groups are adjacent as in 1,2,4-triphenylcyclopentadiene (IX), this effect can be minimized by a slight increase of the angles (*), but with three adjacent phenyl groups as in 1,2,3-triphenylcyclopentadiene (III), at least the central one must be rotated appreciably out of the plane of the cyclopentadiene ring.



IX



III

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[5] N. L. Drake and J. R. Adams, This Journal, **61**, 1326 (1939).

[6] C. F. H. Allen, J. E. Jones and J. A. Van Allan, *J. Org. Chem.*, **11**, 268 (1946).

[7] J. Wislicenus and F. H. Newman, *Ann.*, **302**, 237 (1898).

[8] (a) J. Wislicenus and H. Carpenter, *ibid.*, **302**, 223 (1898); (b) F. B. Auerbach, *Ber.*, **36**, 933 (1903); (c) K. Ziegler and B. Schnell, *Ann.*, **445**, 266 (1925); (d) W. Dilthey, W. Braun, O. Trösken, *J. prakt. Chem.*, [2] **139**, 1 (1933).

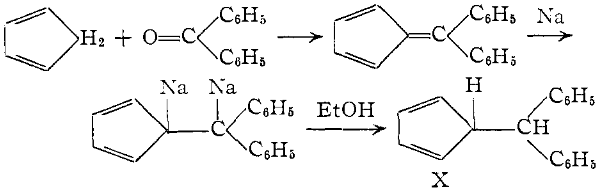
[9] C. F. H. Allen and W. E. Barker, This Journal, **54**, 736 (1932).

[10] H. Kainer, *Ann.*, **578**, 232 (1952).

To test these views, III was synthesized as described above. Although this compound reacted vigorously with methyl- or ethyllithium, being converted to the corresponding lithium derivative, the second step, reaction with ferric chloride again failed, in strong contrast to the behavior of the isomeric compound IX. This observation thus lends strong support to the view that steric effects interfere with the formation[11] of ferrocene derivatives from cyclopentadienes bearing three or more adjacent phenyl substituents. In this connection, the differences in the infrared spectra (Fig. 1) may be of interest. (Note the absence in III of the medium strong band at 8.32 μ, the presence of additional bands at 10.16 μ (weak) and 12.55 μ (medium) and the shift of the 13.3 μ (strong) band (of IX) to 13.5 μ.)

To complete the series, phenylcyclopentadiene was converted to the corresponding Grignard reagent with ethylmagnesium bromide and then with ferric chloride to 1,1′-diphenylferrocene. Further, as an example of the applicability of this method to the preparation of unsymmetrical ferrocene derivatives, a mixture of cyclopentadiene and phenylcyclopentadiene was converted to a mixture of the corresponding Grignard reagents and allowed to react with ferric chloride. An excess of cyclopentadiene was used in this experiment and, under these conditions, the products where chiefly ferrocene and phenylferrocene with only a trace of the diphenyl derivative. The products were readily separated chromatographically on alumina using petroleum ether as solvent.

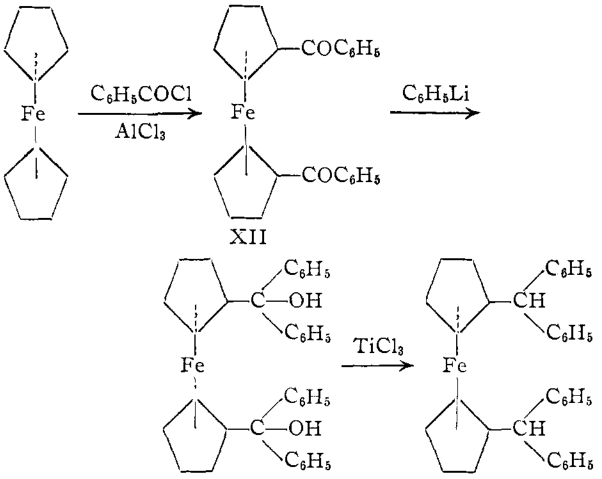
Special methods are necessary for the preparation of each of the phenyl-substituted cyclopentadiene derivatives used in the above syntheses. However, a general method is available for the preparation of certain alkyl-substituted cyclopentadienes which may be exemplified by Schlenk and Bergmann's preparation[12] of benzhydrylcyclopentadiene (X) by the route illustrated



X

It was deemed worthwhile to demonstrate the usefulness of such alkyl-substituted cyclopentadienes in the preparation of ferrocenes. Indeed it was found that X was smoothly converted to 1,1′-dibenzhydrylferrocene (XI). The particular choice of X was dictated by the fortunate circumstance that Woodward and Csendes[13] had independently synthesized XI by the route.

Direct comparison of the two products[13] left no doubt as to their identity. Thus whereas the dibenzoyl (XII) and other diacyl ferrocenes[3,14] formed as the principal products from ferrocene under Friedel–Crafts conditions had always been formulated as those in which both rings are substituted, the present synthesis of dibenzhydrylferrocene (XI) provides the first direct proof of the correctness of this assumption.



XII

XI

The infrared spectrum of XI is shown in Fig. 2 together with those of mono-, di-, tetra- and hexaphenylferrocene. XI has all the separate absorbing units present in tetraphenylferrocene, but sepa-

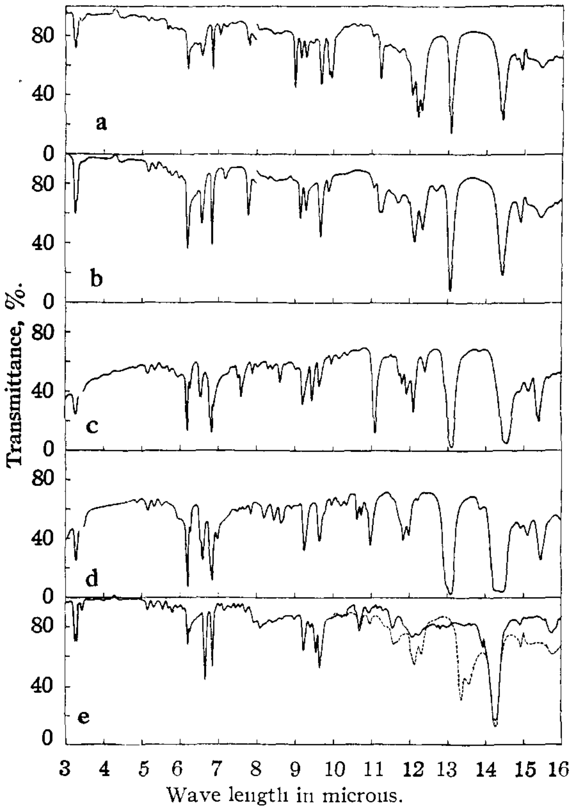


Fig. 2.—a, phenylferrocene (20 mg./cc.) in CCl_4 (3–8 μ) and in CS_2 (8–16 μ); b, 1,1′-diphenylferrocene in CCl_4 (30 mg./cc.; 3–8 μ) and in CS_2 (20 mg./cc.; 8–16 μ); c, 1,3,1′,3′-tetraphenylferrocene, solid in KI; d, 1,2,4,1′,2′,4′-hexaphenylferrocene, solid in KI; e, 1,1′-dibenzhydrylferrocene (XI) (20 mg./cc.) in CCl_4 — and in CS_2 ---------

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[11] There is no basis for believing that the products would be unstable if formed. Only interference with their formation under the usual reaction conditions is here postulated.

[12] W. Schlenk and E. Bergmann, *Ann.*, **463**, 1 (1928).

[13] Private communication; the author is grateful to Professor R. B. Woodward for permission to quote these unpublished results and to Dr. E. Csendes for a sample of the product.

[14] M. Rosenblum, Thesis, Harvard University, 1953.

rated from each other by the methine groups; thus conjugation is prevented and several of the characteristic bands of tetraphenylferrocene are therefore lacking in XI. Indeed there is a closer similarity between the spectra of the polyphenylferrocenes and their parent hydrocarbons as is seen by comparing the spectrum of 1,2,4-triphenylcyclopentadiene (Fig. 1a) with that of the derived iron compound (Fig. 2d). The most striking differences between these two compounds are the absence of the medium strong band at 7.25 μ and the presence of the additional bands at 8.65, 12.0 and 15.5 μ as well as the merging of the bands at 13.0–13.3 μ into a single broad band. At least some of these features are common to all the phenylferrocenes and must result from interactions of the hydrocarbon radical with the metal atom. Comparison of the phenyl-substituted ferrocene derivatives among themselves reveals the most striking differences in the case of the monophenyl derivative. In this substance, four bands can clearly be distinguished: at 7.05, 9.0, 9.95 and 12.21 μ which are absent in the others. However, these correspond exactly to the main absorption regions of ferrocene itself. It has already been observed by Professor R. B. Woodward and his collaborators[13,14] that the bands near 9.0 and 9.95 μ are retained in all monosubstitution derivatives of ferrocene, but disappear when both rings bear substituents[15]; the present observation is in good agreement with these results.

Experimental

1,2,3-Triphenylcyclopentane-1,2-diol (II).—To 1,2,5-triphenylpentane-1,5-dione (I)[9] (18 g.) dissolved in boiling glacial acetic acid (500 cc.), zinc (90 g.) was added in portions over three hours. The mixture was maintained at reflux for a further two hours after complete addition, filtered hot and poured on ice. The zinc residues were extracted with a further 200 cc. of hot acetic acid. The product was collected (if oily, crystallization may be induced by trituration with methanol) and recrystallized from cyclohexane. It forms large white prisms (9 g., 50%), m.p. 132.5-133.5°.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.6; H, 6.7. Found: C, 83.8; H, 6.7.

Evaporation of the mother liquors leaves an oil which failed to crystallize and was therefore not examined further; it may contain some of the stereoisomers of the above diol as well as the straight chain diol corresponding to I.

1,2,3-Triphenylcyclopentadiene (III).—The above diol (8.2 g.) was heated with a mixture of ethanol (200 cc., 95%) and concentrated hydrochloric acid (20 cc.) on a steam-bath for 2 hours under reflux. The product gradually crystallized from the hot solution and was collected by filtration after cooling (6.1 g.). Further heating (1 hour) and concentration of the solution to 100 cc. yielded a further quantity of slightly less pure product (0.9 g.) (total yield 7 g., 96%). Recrystallization from ethanol gave long, fine, pale yellow (almost colorless) needles, m.p. 157–159° (in a sealed evacuated tube).

Anal. Calcd. for $C_{23}H_{18}$: C, 93.9; H, 6.1. Found: C, 94.1; H, 6.2.

Phenylcyclopentadiene (VI).—To a solution of phenyllithium (excess) prepared in ether from bromobenzene (35 g.) and lithium (3 g.) was added an ether solution of 2-cyclopentene-1-one (10 g.) at 0°. After complete addition the mixture was allowed to warm to room temperature over 1 hour and stirred at that temperature for a further hour, the entire reaction being conducted in a nitrogen atmosphere. The solution was poured on ice, washed with water, dried and evaporated to yield a viscous oil (11 g.) which crystallized partially when kept at 0°. Its infrared spectrum indicated the presence of a ketone (probably 3-phenylcyclopentanone arising from 1,4-addition of the phenyllithium) as an impurity. Distillation resulted in loss of approximately the quantity of water calculated for V. (Double distillation was employed to effect complete dehydration. Complete dehydration also resulted in one step when copper bronze was added, but this procedure resulted in more extensive resinification.) The main fraction distilled at 180–220° (3.2 g.) and was used for the following experiments without further purification.

1,1′-Diphenylferrocene.—Crude phenylcyclopentadiene (0.65 g.) dissolved in ether was added to phenyllithium (10 cc., 0.5 *N* solution in ether) and the mixture stirred under nitrogen for 1 hour. An ether solution of ferric chloride (0.25 g.) was then added and the mixture left overnight. After pouring the product on ice–HCl, separating the ethereal layer, washing, drying and evaporating, a benzene solution of the residue was passed through a short column of alumina to remove tarry impurities. Crystallization of the eluate from light petroleum yielded orange leaflets, m.p. 154°.

Anal. Calcd. for $C_{22}H_{18}Fe$: C, 78.1; H, 5.4. Found: C, 77.6; H, 5.8.

Phenylferrocene.—To methyllithium prepared from lithium (1.4 g.) and methyl iodide (14 g.) in ether (100 cc.) under nitrogen, phenylcyclopentadiene (4 g.) diluted with ether (20 cc.) was added dropwise at room temperature and followed after 30 minutes by cyclopentadiene (4 g.) in ether (20 cc.), the mixture being stirred throughout. After a further hour, the mixture was cooled to 0° and an ether solution of ferric chloride (5 g.) slowly added. After leaving overnight and working up as described for the diphenylferrocene (above), the crude product was subjected to chromatography on alumina using light petroleum as solvent. Ferrocene passes through the column rapidly and is followed more slowly by the monophenyl derivative, the diphenyl compound being held even more strongly; complete separation was readily achieved on an 8-inch column. Monophenylferrocene formed orange crystals from light petroleum m.p. 109-110°.

Anal. Calcd. for $C_{16}H_{14}Fe$: C, 73.3; H, 5.4. Found: C, 73.6; H, 5.7.

1,3,1′,3′-Tetraphenylferrocene.—1,3-Diphenylcyclopentadiene (3 g.) dissolved in benzene (50 cc.) was added to ethylmagnesium bromide, prepared in ether from ethyl bromide (1.5 g.) and magnesium (0.32 g.), and the solution was refluxed for 4 hours. After cooling to 0°, an ether solution of ferric chloride (0.7 g.) was added and the mixture left at room temperature overnight. After working up in the usual manner, the product was crystallized from acetone. Deep orange-red flat prisms of 1,3,1′,3′-hexaphenylferrocene separated leaving unchanged hydrocarbon in solution. After recrystallization from the same solvent the product had m.p. 220–222°.

Anal. Calcd. for $C_{34}H_{26}Fe$: C, 83.3; H, 5.3. Found: C, 83.2; H, 5.3.

1,2,4,1′,2′,4′-Hexaphenylferrocene.—1,2,4-Triphenylcyclopentadiene (2.5 g.) and benzene (50 cc.) were added to an ether solution of butyllithium (0.012 mole) and refluxed two hours. After cooling in ice, ethereal ferric chloride (0.8 g.) was added and the mixture left overnight. The crude product, isolated in the usual manner, was sublimed under reduced pressure to remove unchanged hydrocarbon. The residue crystallized readily from acetone in red prisms m.p. 227–228°.

Anal. Calcd. for $C_{46}H_{34}Fe$: C, 86.0; H, 5.3. Found: C, 85.7; H, 5.4.

1,1′-Dibenzhydrylferrocene.—Diphenylfulvene was reduced as described by Schlenk and Bergmann[12] and the crude product distilled to give benzhydrylcyclopentadiene as a viscous oil (0.85 g.) which was used without further purification. Its solution in ether (10 cc.) was added to phenyllithium (8 cc. of an 0.5 *N* solution) under nitrogen and the resulting mixture was allowed to stand at room temperature for 1 hour. Ferric chloride (0.2 g.) dissolved in anhydrous ether (10 cc.) was then added at 0° and the mixture kept at room temperature overnight. The product was poured on an ice-ammonium chloride mixture, extracted with ether,

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(15) The band at 7.05 μ is relatively weak and cannot always be observed sufficiently clearly; insufficient data to establish a general rule are available for the 12.2 μ band as most of the spectra have been observed in chloroform or carbon tetrachloride only.

washed, dried and evaporated. The residue was dissolved in cyclohexane and passed through a short column of alumina to remove tarry impurities.

The eluate on evaporation to dryness left yellow crystals, m.p. 161°. Recrystallization from acetone gave the pure 1,1'-dibenzhydrylferrocene as yellow needles, m.p. 162–163°.

Anal. Calcd. for $C_{36}H_{30}Fe$: C, 83.4; H, 5.8. Found: C, 83.7; H, 5.8.

This product was indistinguishable in melting point, mixed melting point and infrared spectrum (determined in carbon tetrachloride solution with a Baird double beam spectrophotometer, Fig. 2e) from a sample supplied by Dr. E. Csendes.[13]

Acknowledgments.—The author is indebted to the du Pont Company for financial support.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, VICTOR CHEMICAL WORKS]

Allyl Esters of Phosphonic Acids. III. Influence of Substituents on Polymerization Characteristics[1]

BY A. D. F. TOY AND ROBERT S. COOPER

RECEIVED DECEMBER 4, 1953

It is well-known that diallyl esters of organic dibasic acids will undergo polymerization to form cross-linked types of glassy resins. It has been shown that the diallyl esters of the arylphosphonic acids undergo polymerization to produce hard, transparent solids which are flame resistant. Further studies covering more than thirty allyl esters of phosphonic acids and other phosphorus-containing allyl derivatives have shown that glassy polymers are not obtained in all cases. The following factors are among those which appear to govern the polymerization characteristics of these compounds: (1) steric hindrance as determined by the size of the substituent group; (2) electrical character of the substituent group and (3) presence or absence of inhibitory groups. The dimethallyl esters polymerize faster than the corresponding diallyl esters. The degree of flame resistance of these phosphorus-containing polymers seems to depend upon their thermal stability rather than upon the phosphorus content of the monomers.

It is well-known that the diallyl esters of dibasic acids, such as diallyl phthalate[2,3] and diethylene glycol bis-(allylcarbonate)[4] will undergo polymerization to form cross-linked glassy solids. In previous papers[5,6] of this series, it has been shown that the diallyl esters of arylphosphonic acids also undergo similar polymerization reactions to form hard transparent resins. A unique property of these arylphosphonate polymers is their flame resistance, that is, they are self-extinguishing when removed from a flame. This self-extinguishing characteristic is even retained in copolymers produced by copolymerization with other compatible monomers. It had been assumed that the observed polymerization tendencies of these substances are typical of all diallyl esters and that the self-extinguishing characteristic is due to the phosphorus content. However, further studies in this Laboratory have shown that these generalizations do not always hold. Differences in the polymerization and flame resistant characteristics have been observed among the allyl esters of various phosphonic acids.

This paper constitutes a preliminary report on the influence of substituents on the polymerization characteristics and other properties of the allyl esters of some phosphonic acids and some allyl derivatives of other phosphorus-containing acids.[7]

The diallyl and dimethallyl esters of a series of alkenyl- and alkylphosphonic acids, as well as some derivatives of compounds containing phosphorus–oxygen, phosphorus–sulfur and phosphorus–nitrogen bonds have been studied.

Experimental

The allyl and methallyl esters were prepared by the interaction of the acid chlorides and the alcohols in the presence of a tertiary amine as the condensation agent.[5,8] The alkenylphosphonic dichlorides were prepared using the Woodstock method[9] which involves the action of phosphorus(V) oxide on the addition compound of phosphorus pentachloride and the desired olefin.[10] The alkylphosphonic dichlorides were prepared: (a) by the action of phosphorus pentachloride on the alkylphosphonic acids which in turn were prepared by the hydrolysis of the dialkyl alkylphosphonates obtained by the action of sodium dialkyl phosphites[11] on the alkyl halides[12]; (b) by the hydrolysis of the complex formed by the action of phosphorus trichloride and aluminum chloride and alkyl halide as reported by Clay,[13] and by Kinnear and Perren[14]; and (c) by the action of oxygen on a mixture of phosphorus trichloride and the hydrocarbon as reported by Clayton and Jensen.[15] Other acid chlorides necessary for the preparation of the allyl derivatives of various miscellaneous phosphorus-containing acids were prepared by standard procedures involving the action of phos-

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(1) Presented in part before the Division of Organic Chemistry at the 122nd Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

(2) D. A. Kardashev, N. S. Leznov and V. P. Nuzhdina, *Khimicheskaya Prom.*, No. 2, 5 (1945).

(3) W. Simpson, *J. Soc. Chem. Ind.*, **65**, 107 (1946).

(4) I. E. Muskat and F. Strain, U. S. Patent 2,370,565 (1945).

(5) A. D. F. Toy, THIS JOURNAL, **70**, 186 (1948).

(6) A. D. F. Toy and L. Brown, *Ind. Eng. Chem.*, **40**, 2276 (1948).

(7) Since the presentation of this paper, G. Kamai and V. A. Kukhtin, *Doklady Akad. Nauk. SSSR*, **89**, 309 (1953), have reported the synthesis and polymerization of several unsaturated phosphonates. They have also observed that certain groups attached to the phosphorus atom activate the polymerizability of some allyl phosphonates.

(8) A. D. F. Toy, U. S. Patent 2,425,766 (1947).

(9) W. H. Woodstock, U. S. Patent 2,471,472 (1949).

(10) Commercial grades of isobutylene and diisobutylene were used. In the case of isobutenylphosphonic dichloride, the chlorine content was always found to be 2 to 3% higher than the calculated value; this finding may be attributed to contamination with isochlorobutylphosphonic dichloride. The contaminant may be dehydrochlorinated, however, by heating the crude mixture under reflux until no more hydrogen chloride is evolved; the resulting product is purified by distillation.

(11) A convenient method for the preparation of sodium dialkylphosphite entails the addition of dialkylphosphite to metallic sodium dissolved in liquid ammonia. The completion of the reaction is indicated by the disappearance of the blue color. This reaction has been found to be applicable with diethyl, dibutyl and dioctylphosphites, but not with diallyl phosphite.

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