nace and collected in Dry Ice traps. The crude pyrolysate was washed free of acetic acid with 10% sodium carbonate solution, dried over magnesium sulfate and distilled *in vacuo*. After distilling the desired diene II, b.p. 66–69° (16 mm.), the unreacted I was recycled through the furnace. Three such passes were made to give 51.0 g. of crude II, which was redistilled to give 33.4 g. of II (46%). Purification of II was effected by chromatographing on silica gel to give II showing b.p. 73–4° (18 mm.), $n^{20}_{D}$ 1.4550, $d^{20}_{20}$ 0.943.

*Anal.* Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.60, 68.56; H, 8.50, 8.51.

Quantitative hydrogenation of II with Adams catalyst in glacial acetic acid required 99.5% of two molar equivalents of hydrogen.

**Adduct of II with 1,4-Naphthoquinone.**—When 1.40 g. (0.01 mole) of II and 1.58 g. (0.01 mole) of 1,4-naphthoquinone in 15 ml. of benzene was heated under reflux overnight, a colorless solution was obtained. Upon addition of hexane the adduct precipitated which after repeated recrystallization from hexane gave 2.06 g. (69%) of a white crystalline solid; m.p. 95–96°.

*Anal.* Calcd. for $C_{16}H_{18}O_4$: C, 72.96; H, 5.44. Found: C, 72.82; H, 5.52.

**Adduct of II with Maleic Anhydride.**—When 1.66 g. (0.117 mole) of II was heated with 1.15 g. (0.117 mole) of maleic anhydride in benzene much polymeric material and an oil were formed. The oil was hydrolyzed in boiling water to give 0.8 g. of an acid. The acid was recrystallized from benzene–hexane; m.p. 145–146°. The hydrolyzed adduct strongly depressed the melting point of authentic maleic acid.

*Anal.* Calcd. for $C_{12}H_{16}O_6$: C, 56.22; H, 5.80; neut. equiv., 128.12. Found: C, 55.95, 55.85; H, 5.78, 5.98; neut. equiv., 127.8.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

# A Mechanism Study of the Reducing Action of Grignard Reagents on Fluorinated Carbonyl Compounds[1]

BY E. T. MCBEE, O. R. PIERCE AND D. D. MEYER

RECEIVED JULY 6, 1954

A study of the coördination of magnesium bromide with a series of compounds has shown that acetone, propionaldehyde and ethyl acetate form stable complexes in the ratio of 2:1 with magnesium bromide in phenetole, acetonitrile forms a 1:1 complex, but that methyl pentafluoroethyl ketone, heptafluorobutyraldehyde, ethyl trifluoroacetate and heptafluorobutyronitrile form no stable complexes. Possible mechanisms for the reaction of Grignard reagents with fluorinated compounds are discussed, and the effect of temperature and solvent are noted.

## Discussion

Earlier papers[2,3] have reported large amounts of reduction products from the reaction of fluorinated carbonyl compounds with a series of Grignard reagents. These results were unexpected because of the absence of the large steric factor usually associated with reactions of this type, and were attributed to the inductive effect of the perfluoro alkyl group.

A mechanism for the reduction of a sterically hindered carbonyl compound by a Grignard reagent involving a six-membered cyclic intermediate was first suggested by Whitmore.[4] He postulated that a coördination compound was formed between the oxygen of the carbonyl group and the magnesium of the organometallic compound, followed by a shift of a beta hydrogen atom with its electrons. This is consistent with the fact that reduction is observed only in Grignard reagents that possess a hydrogen atom beta to the magnesium,[5] and that the predicted unsaturated hydrocarbon is formed in each reduction reaction.[6,7]

Studies were undertaken to determine the applicability of the cyclic mechanism to the reduction of perfluoro carbonyl compounds with Grignard reagents.

The ability of propiophenone and heptafluorobutyrophenone to coördinate with magnesium bromide was studied by means of infrared spectra. The carbonyl absorption peak of propiophenone was shifted from 5.90 to 6.05 μ when compared in ether and in magnesium bromide etherate, whereas that of the heptafluorobutyrophenone remained at 5.85 μ in both solvents.

A more quantitative determination of the coördination between carbonyl compounds and magnesium bromide was then carried out by measuring the vapor pressure of a series of compounds in phenetole. Henry's law constants were determined for acetone, propionaldehyde, ethyl acetate, acetonitrile, methyl pentafluoroethyl ketone, heptafluorobutyraldehyde, ethyl trifluoroacetate and heptafluorobutyronitrile. The plot of pressure as ordinate *vs.* number of millimoles of compound added (or mole fraction) gave the expected straight line curve going through the origin for all of the compounds tested, in agreement with the equation $P = kN$, Table I.

In the presence of a small amount of magnesium bromide, the curves for acetone, propionaldehyde and ethyl acetate were shifted along the abscissa

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[1] This paper represents part of a thesis submitted by D. D. Meyer to the Graduate School, Purdue University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] K. N. Campbell, J. D. Knobloch and B. K. Campbell, THIS JOURNAL, **72**, 4380 (1950).

[3] E. T. McBee, O. R. Pierce and J. F. Higgins, *ibid.*, **74**, 1736 (1952).

[4] F. C. Whitmore, paper presented before the Atlantic City meeting of the American Chemical Society, April, 1943.

[5] F. C. Whitmore and S. George, THIS JOURNAL, **64**, 1239 (1942).

[6] C. R. Noller, *ibid.*, **53**, 635 (1931).

[7] H. S. Mosher and E. LaCombe, *ibid.*, **72**, 3994 (1950), observed that partial asymmetric reduction was obtained in the reaction between methyl *t*-butyl ketone and (+)-2-methylbutylmagnesium chloride, which is further evidence for a cyclic intermediate. Swain and Boyles[8] found that the amount of addition product was increased at the expense of the reduction product if diisopropyl ketone was stirred with magnesium bromide etherate before being treated with *n*-propylmagnesium bromide. This is also in accord with the Whitmore mechanism, since the magnesium bromide is a stronger coördinating agent than the Grignard reagent and would preferentially coördinate with the carbonyl oxygen of the ketone.

[8] C. G. Swain and H. B. Boyles, *ibid.*, **73**, 870 (1951).

Table I

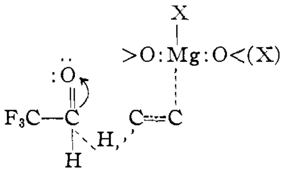
Henry's Law Constants, $P = kN$

| Carbonyl compd. in phenetole | $MgBr_2$ added, mmoles | $k$ (mm.) | Carbonyl compd. in phenetole | $MgBr_2$ added, mmoles | $k$ (mm.) |
|---|---|---|---|---|---|
| $CH_3COCH_3$ | 0.0 | 87.6 | $CH_3CO_2C_2H_5$ | 0.0 | 37.0 |
| $CH_3COCH_3$ | .149 | 87.6 | $CH_3CO_2C_2H_5$ | .090 | 35.6 |
| $CH_3COC_2F_5$ | .0 | 769 | $CF_3CO_2C_2H_5$ | .0 | 183 |
| $CH_3COC_2F_5$ | .018 | 769 | $CF_3CO_2C_2H_5$ | .074 | 183 |
| $C_2H_5CHO$ | .0 | 150 | $CH_3CN$ | .0 | 75.2 |
| $C_2H_5CHO$ | .037 | 149 | $CH_3CN$ | .067 | 68.3 |
| $C_3F_7CHO$ | .0 | 1868 | $C_3F_7CN$ | .0 | 6391 |
| $C_3F_7CHO$ | .035 | 1868 | $C_3F_7CN$ | .097 | 6391 |

from the origin to a point corresponding to a complex between two molecules of the carbonyl compound and one molecule of magnesium bromide. After all of the bromide had been used up in complex formation, the further addition of the carbonyl compounds gave the regular pressure increases observed in the initial experiments, and the slopes of the two lines were the same. Acetonitrile gave a shift along the abscissa which corresponds to a 1:1 complex with magnesium bromide. These results corroborate Swain's explanation for the magnesium bromide effect on diisopropyl ketone, discussed earlier. All of the fluorinated compounds tested gave curves that coincided exactly with those observed when no magnesium halide was present. Thus, it appears that a complex of the type observed for the common carbonyl compounds is not formed in the fluorinated series.

The cyclic mechanism of Whitmore does not apply to the reducing reaction of Grignard reagents on perfluoro compounds, therefore, unless there are very small amounts of unstable complexes formed which were not detected by the experimental conditions used. If any of these complexes were present, the driving force for the shift of the Grignard beta hydride ion should be very large because the positive character of the carbonyl carbon would be increased both by the large inductive effect of the fluorine atoms and the polarizing effect of complex formation.

A possible mechanism for the reduction of the perfluoro carbonyl compounds may involve a transfer of a hydrogen with its electrons intermolecularly from the Grignard reagent to the compound being reduced, somewhat similar to the mechanism postulated by Doering[9] for the base-catalyzed carbinol–carbonyl equilibrium. The driving force for this reaction is again the enhanced positive character of the carbonyl carbon due to the inductive effect of the fluorine atoms. The reaction may be aided by the presence of ionic species of the type $[RMgX_2]^-$ in a Grignard solution[10] which would assist in the expulsion of a hydride ion because of the influence of the negative charge, or by the solvation of the magnesium atom which would weaken the carbon–magnesium bond and tend to leave the carbon with an unshared pair of electrons that could form the olefin and eliminate a beta hydrogen with its electrons. This is actually a coöperative effect in which the ether attached to the magnesium (or the negative charge on the anion $[RMgX_2]^-$) and the positive carbonyl carbon aid in breaking the carbon–magnesium bond and the carbon–hydrogen bond, respectively. Each fission assists the other and the two together constitute a single synchronous process. It is conceivable that the magnesium halide portion of the Grignard reagent could approach the carbonyl oxygen during this process, and then the formation of the alkoxide salt would be a further aid to reaction. This, however, imposes a rigid orientation on the transition state of the reaction.



It would appear from the data at hand that the addition reaction of fluorinated carbonyl compounds with Grignard reagents proceeds by a direct attack on the uncomplexed fluorine compound. In effect, the fluorine accomplishes the same end result as does the initial complexing between a molecule of Grignard reagent and a non-fluorinated carbonyl compound in the addition reaction suggested by Swain[8]; that is, it decreases the electron density on the carbonyl carbon to such an extent that an attack by the nucleophilic portion of the organomagnesium compound is possible.

In the reaction of a fluorinated carbonyl compound with a Grignard reagent, the amount of addition is greatly decreased in going from the trifluoromethyl to the pentafluoroethyl compounds, and only slightly decreased in going from the pentafluoroethyl to the heptafluoropropyl compounds.[3] Bender[11] observed similar variations in the amounts of sodium alkoxide addition compounds with trifluoroacetic, pentafluoropropionic and heptafluorobutyric acids, and attributed it to F-strain. This same explanation can be used to explain the decrease in the amount of Grignard addition compounds and the corresponding increase in the reduction reaction as the length of the perfluoro group is increased. Thus, increase in reduction is probably due to steric influences rather than an increased inductive effect. Supporting evidence for this assumption is found in the similarity of the ionization constants for trifluoroacetic and heptafluorobutyric acids, which are $5.9 \times 10^{-1}$ and $6.8 \times 10^{-1}$, respectively.[12]

The amount of addition and reduction products formed in the reaction between ethylmagnesium iodide and pentafluoropropionaldehyde or heptafluorobutyraldehyde is not changed significantly when the reaction temperature is changed from 0 to −70° (Table II).

The effect of solvent on the reaction of ethylmagnesium iodide with pentafluoropropionaldehyde is reported in Table II. The yields of reduction and addition products under identical reaction conditions are similar in anisole, diethyl ether and triethylamine. Lewis and Wright[13] found that a

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[9] W. von E. Doering and T. C. Aschner, This Journal, **75**, 393 (1953).

[10] W. V. Evans and E. Field, *ibid.*, **58**, 720 (1936).

[11] M. L. Bender, *ibid.*, **75**, 5986 (1953).

[12] A. L. Henne and C. J. Fox, *ibid.*, **73**, 2323 (1951).

[13] R. N. Lewis and J. R. Wright, *ibid.*, **74**, 1253 (1952).

TABLE II

THE REACTION OF ETHYLMAGNESIUM IODIDE WITH FLUORINATED ALDEHYDES

| Aldehyde | Solvent | Temp., °C. | Redn., % | Addn., % |
|---|---|---|---|---|
| $C_2F_5CHO$ | Ether | 0 | 55 | 34[b] |
| $C_2F_5CHO$ | Ether | −70 | 54 | 28 |
| $C_3F_7CHO$ | Ether | 0 | 61 | 19[b] |
| $C_3F_7CHO$ | Ether | −70 | 54 | 20 |
| $C_2F_5CHO$[a] | Ether | 0 | 16 | 51 |
| $C_2F_5CHO$ | Anisole | 0 | 58 | 30 |
| $C_2F_5CHO$ | Pyridine | 0 | 20 | 39 |
| $C_2F_5CHO$ | Triethylamine | 0 | 57 | 30 |

[a] With added magnesium bromide. [b] Reference 3.

strongly basic solvent retards the reaction between ethylmagnesium bromide and benzophenone because a solvent molecule cannot easily be displaced from the Grignard reagent by the ketone to form the ketone–Grignard coördination compound which is an intermediate in the reaction. Since this effect of basicity of the solvent is not observed in the reaction of a perfluoro aldehyde with ethylmagnesium iodide, additional support must be given to a reaction mechanism which does not involve an intermediate formed by the coördination of the two reactants.

The ratio of reduction and addition products is reversed when pyridine is used as a solvent, or when magnesium bromide is added to the aldehyde before it is treated with a Grignard reagent. The explanation for these results may be in the polarity of the solvents. Pyridine has a dipole moment of 2.26 *D* compared to 0.90 *D* for triethylamine, which is a much stronger base than pyridine. Magnesium bromide in ether forms the oily, viscous liquid magnesium bromide dietherate which is insoluble in ether. The heterogeneity of the reaction media could cause the change in products in this case.

Methyllithium gave the expected secondary alcohol when treated with fluoral, and ethyllithium gave the addition product with heptafluorobutyraldehyde. The latter experiment is to be compared with 61% reduction product and 19% addition product in the corresponding Grignard reaction, and is in agreement with other observations by many workers that alkyllithium compounds give no reduction products of sterically hindered carbonyl compounds (Table III).

TABLE III

THE REACTION OF ALKYLLITHIUMS WITH FLUORINATED ALDEHYDES IN ETHER AT 0°

| Aldehyde | RLi | Redn., % | Addn., % |
|---|---|---|---|
| $CF_3CHO$ | $CH_3Li$ | 0 | 70 |
| $C_3F_7CHO$ | $C_2H_5Li$ | 0 | 68 |

**Acknowledgment.**—The authors wish to express their gratitude to the Westinghouse Electric Corporation, the Carbide and Carbon Chemicals Company and the Purdue Research Foundation for support of this work.

## Experimental

**Henry's Law Measurements.**—High vacuum equipment and methods[14] were adapted to the determination of Henry's law constants. The apparatus is shown in Fig. 1.

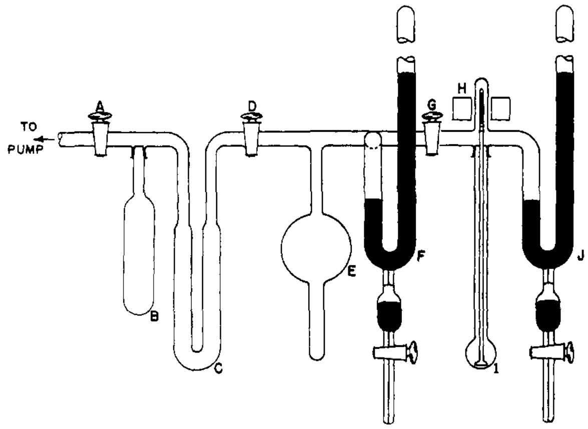

Fig. 1.—Apparatus used for coördination studies.

In a typical experiment, a weighed amount of phenetole (and magnesium bromide, if it was to be used) was introduced into the reaction tube I, and the tube was connected to the line by means of a ground glass joint. The phenetole was frozen in liquid nitrogen, the system was evacuated, and stopcock G was closed while the solvent was allowed to warm to room temperature. It was then refrozen, G was opened and the system again evacuated to remove dissolved gases from the liquid. This process was repeated three times, and mercury was introduced into the manometer J from the reservoir before the phenetole was allowed to warm up after the final degassing. With G closed, the rest of the system was opened to the air and a small amount of the carbonyl compound to be tested was added to tube B, the tube was reconnected to the line by a ground glass joint, and the degassing procedure used for the phenetole was repeated. After the system had been evacuated for the final time, stopcocks A and D were closed, mercury was introduced in the manometer F, and the U-tube C was surrounded by an ethylene dichloride slurry. Stopcock D was opened and some of the carbonyl compound was allowed to distil into E, which was cooled in a liquid nitrogen bath. D was then closed and E was allowed to warm up to room temperature, and the pressure in the system was read after the mercury in the manometer had been adjusted to the proper height. The volume of E was previously determined by measuring the pressure developed by a known amount of pure methyl chloride, and calculating *V* from the simple gas law.

The points for the curves were obtained by cooling I in a liquid nitrogen-bath, opening stopcock G to admit a small amount of vapor from E, and then placing an ice-bath around I until equilibrium was reached. The pressure on both manometers and the temperature of E were read and recorded after each addition, and from these data and the simple gas law the number of millimoles of added gas could be readily calculated, and plotted against the pressure of I.

All liquids were purified by careful rectification, and the magnesium bromide was prepared according to the directions of Rowley.[15] It was only slightly soluble in the phenetole.

**The Low Temperature Reactions of Ethylmagnesium Iodide with Perfluoro Aldehydes.**—The aldehydes were prepared by the lithium aluminum hydride reduction of the corresponding acids.[16] The Grignard reagent was prepared in the usual manner and filtered through glass wool under nitrogen pressure into a 1-liter, three-necked flask cooled in a Dry Ice-bath and fitted with a Dry Ice reflux condenser, an efficient stirrer and an addition funnel containing an ether solution of the carbonyl compound. Approximately 0.5 mole of Grignard reagent was used to 37.0 g. (0.25 mole) of pentafluoropropionaldehyde or 64.0 g. (0.32 mole) of heptafluorobutyraldehyde, which were added dropwise over a 1-hour period. After an additional hour of stirring, the reaction mixture was allowed to warm up to ice temperatures and hydrolyzed in the flask with 400 ml. of cold 10% aqueous sulfuric acid. The ether layer was separated, dried over Drierite, and distilled to remove the ether. Rectification of the residual liquid gave 20.3 g. (54%) of 2,2,3,3,3-pentafluoropropanol, b.p. 81–83°, $n^{20}_{D}$ <1.3000, and 12.6

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[14] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[15] H. H. Rowley, THIS JOURNAL, **72**, 3305 (1950).

[16] D. R. Husted and A. H. Ahlbrecht, *ibid.*, **74**, 5422 (1952).

g. (28%) of 1,1,1,2,2-pentafluoro-3-pentanol, b.p. 97–98°, $n^{20}_{\mathrm{D}}$ 1.3291 (lit. b.p. 98°, $n^{20}_{\mathrm{D}}$ 1.3280)[17] when pentafluoropropionaldehyde was used; 34.8 g. (54%) of 2,2,3,3,4,4,4-heptafluoro-1-butanol, b.p. 93–95°, $n^{20}_{\mathrm{D}} < 1.3000$ and 14.8 g. (20%) of 4,4,5,5,6,6,6-heptafluoro-3-hexanol, b.p. 114–115°, $n^{20}_{\mathrm{D}}$ 1.3260 (lit. b.p. 113.5°, $n^{20}_{\mathrm{D}}$ 1.3255)[18] were obtained when heptafluorobutyraldehyde was used.

**The Reaction of Ethylmagnesium Iodide with Pentafluoropropionaldehyde in Magnesium Bromide Etherate.**—Magnesium bromide was prepared by slowly adding 96 g. (0.6 mole) of bromine to a well-stirred mixture of 14.6 g. (0.6 g. atom) of magnesium turnings in 300 ml. of dry ether. The aldehyde, 49 g. (0.33 mole), was distilled into this mixture through a gas inlet tube reaching above the surface of the liquid, and stirring was continued for an additional 1.5 hours. The flask was cooled in an ice-bath and approximately 0.6 mole of ethylmagnesium iodide was added dropwise over a two-hour period. Hydrolysis was carried out in the flask with 500 ml. of 15% aqueous sulfuric acid, the product was taken up in ether, dried, and the ether removed by distillation. Rectification of the residual liquid gave 7.8 g. (16%) of 2,2,3,3,3-pentafluoropropanol, b.p. 81–83°, and 30.2 g. (51%) of 1,1,1,2,2-pentafluoro-3-pentanol, b.p. 95–97°.

**The Reaction of Pentafluoropropionaldehyde with Ethylmagnesium Iodide in Pyridine and in Triethylamine.**—The Grignard reagent (0.6 mole) was prepared in the usual manner in ether, and filtered through glass wool with nitrogen pressure into a dry, 1-liter, three-necked flask fitted with a Dry Ice reflux condenser, an efficient stirrer and an addition funnel containing 300 ml. of freshly dried and distilled amine (pyridine or triethylamine). The ether was removed under reduced pressure and the amine was added before the removal was complete. The flask was cooled in an ice-bath, 49 g. (0.33 mole) of aldehyde was distilled in, and the mixture stirred for 1 hour. The reaction mixture was hydrolyzed in the flask by the dropwise addition of 500 ml. of 30% aqueous sulfuric acid. The solution was then made acidic with 50% aqueous sulfuric acid, extracted with ether, dried and rectified to give 10.1 g. (20%) of 1,1,1,2,2-pentafluoropropanol, b.p. 80–82°, and 23.2 g. (39%) of 1,1,1,2,2-pentafluoro-3-pentanol, b.p. 96–98° when pyridine was used. With triethylamine as a solvent the products were 28.5 g. (57%) of 1,1,1,2,2-pentafluoropropanol and 17.8 g. (30%) of 1,1,1,2,2-pentafluoro-3-pentanol.

**The Reaction of Pentafluoropropionaldehyde with Ethylmagnesium Iodide in Anisole.**—The Grignard reagent (0.6 mole) was prepared directly in 500 ml. of dry anisole, and filtered into a three-necked flask, cooled in an ice-bath and fitted with a Dry Ice reflux condenser and an efficient stirrer. Pentafluoropropionaldehyde (49 g., 0.33 mole) was distilled into the reaction flask, stirring was continued for an additional hour, and the mixture was hydrolyzed in the flask with 200 ml. of 10% aqueous sulfuric acid. The product was taken up in ether, dried over Drierite and rectified to give 29.1 g. (58%) of 1,1,1,2,2-pentafluoropropanol and 18.2 g. (30%) of 1,1,1,2,2-pentafluoro-3-pentanol.

**The Reaction of Alkyllithium Compounds with Perfluoro Aldehydes.**—The alkyllithium compounds were prepared in ether in the usual manner with excess lithium,[19] and filtered into a 1-liter, three-necked flask fitted with an efficient stirrer, a Dry Ice reflux condenser and a gas inlet tube or an addition funnel, depending on whether fluoral or heptafluorobutyraldehyde was added. Approximately two moles of organometallic compound was used to one mole of carbonyl compound, and the quantities never exceeded one mole of alkyllithium. The total reaction time varied from 4 to 12 hours at ice temperatures, and the hydrolysis was carried out in the same flask with 20% aqueous sulfuric acid. The product was worked up in the usual manner to give 18.4 g. (70%) of 1,1,1-trifluoro-2-propanol, b.p. 76–78°, $n^{20}_{\mathrm{D}}$ 1.3171, when methyllithium was treated with 23 g. (0.23 mole) of fluoral, and 51.7 g. (68%) of 1,1,1,2,2,3,3-heptafluoro-4-hexanol, b.p. 112–114°, $n^{20}_{\mathrm{D}}$ 1.3250, when ethyllithium was treated with 67 g. (0.33 mole) of heptafluorobutyraldehyde.

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[17] E. T. McBee, J. F. Higgins and O. R. Pierce, This Journal, **74**, 1387 (1952).

[18] E. T. McBee, O. R. Pierce and W. F. Marzluff, *ibid.*, **75**, 1609 (1953).

[19] H. Gilman, *et al.*, *ibid.*, **71**, 1499 (1949).

West Lafayette, Indiana

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[Contribution from the Department of Chemistry, Purdue University]

# 1,2,3,4-Tetrachlorocyclopentadiene. I. The Preparation of the Diene and its Reaction with Aromatic Aldehydes and Dienophiles

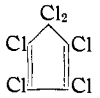
By E. T. McBee, R. K. Meyers[1] and C. F. Baranauckas[2]

Received July 16, 1954

1,2,3,4-Tetrachlorocyclopentadiene has been prepared by reduction of hexachlorocyclopentadiene with zinc dust and hydrochloric acid. The new diene reacts with aromatic aldehydes to give 1,2,3,4-tetrachloro-6-arylfulvenes. It forms adducts with maleic anhydride, cyclopentadiene and *p*-benzoquinone.

## Discussion

When hexachlorocyclopentadiene (I) is reduced with zinc and absolute ethyl alcohol, cyclopentadiene can be isolated from the reaction products. Part of the chlorine is retained on reduction with stannous chloride, as is the case with zinc and hydrochloric acid. The latter reagent affects only the two allylic chlorine atoms and gives a good yield of 1,2,3,4-tetrachlorocyclopentadiene (II).



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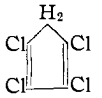

II

1,2,3,4-Tetrachlorocyclopentadiene is a colorless solid melting at 62–63°.[3] It dimerizes on heating turns dark on exposure to light and air and gives off phosgene under the influence of ozone. 1,2,3,4-Tetrachlorocyclopentadiene can be kept for several weeks at room temperature in well-filled brown bottles. With aqueous or alcoholic sodium hydroxide or with aqueous sodium carbonate, 1,2,3,4-tetrachlorocyclopentadiene rapidly gives a blue-green color which changes to black. It does not react with alcoholic silver nitrate in the cold, whereas hexachlorocyclopentadiene gives an immediate precipitate with the same reagent.

Attempts to condense II with aromatic alde-

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[1] In part from the Ph.D. Thesis of R K. Meyers, Purdue University, February, 1950.

[2] In part from the Ph.D. Thesis of C. F. Baranauckas, Purdue University, February, 1948.

[3] R. Riemschneider, who investigated the reduction of hexachlorocyclopentadiene with zinc and hydrochloric acid, reports a crystalline product, m.p. 62°, with the structure 1,2,3,4 tetrachloro-5-(2',3',4',5'-tetrachlorocyclopentadienyl)-cyclopentadiene [*Z. Naturforsch.*, **6B**, 463 (1951); and *Chimie and industrie*, **64**, 698 (1950)]. In view of the present work, it is considered highly probable that the compound was actually 1,2,3,4-tetrachlorocyclopentadiene.