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Alkylation of Ferrocene with α-Aryl Alcohols[1]

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A smooth condensation reaction can be achieved between ferrocene and secondary and tertiary aryl- and aryl-alkylcarbinols to give the corresponding aralkylferrocene derivatives in good to excellent yields. The condensations are conducted in the melt phase, using strong Lewis acids as catalysts at concentrations substantially lower than for usual Friedel–Crafts reactions. The principal formation of either the mono- or disubstituted derivative is determined by the reactant ratio. Reduced reactivity and yield trends are observed with decreasingly aryl-substituted carbinols. Relatively inert behavior is found for *t*-butyl alcohol and other aliphatic alcohols or deactivated monoaryl-alkylcarbinols under these reaction conditions.

Introduction

As part of a general investigation of the self-condensation reactions of ferrocenylcarbinols leading to polymeric products,[2] it became of interest to undertake the related study of the formation of aralkylferrocene derivatives *via* condensation reactions of benzenoid carbinols with the ferrocene nucleus. To date only three ferrocene derivatives bearing aralkyl substituents have been described in the literature: triphenylmethylferrocene,[3] 1,1′-dibenzhydrylferrocene[4–6] and 1,1′-di-(2-phenyl-2-propyl)-ferrocene.[6] None of these was prepared by direct substitution on the ferrocene rings, their syntheses all following multi-step reaction courses with low-to-moderate over-all yields. The lack of data on direct substitution reactions in ferrocene chemistry is not surprising in view of the unfavorable course of the Friedel–Crafts reaction with ferrocene using alkyl or aryl halides as compared to acid chlorides and anhydrides. While the latter reactants give rapid, high-yield reactions with ferrocene, the former were first considered as unfeasible in this use[7,8] until more successful attempts were reported by Nesmeyanov and co-workers.[9–11] However, even here, mixtures of several alkylation products were obtained requiring difficult separation methods, and the yields of the individual substitution products were low, making this procedure rather unsatisfactory for preparative purposes.

It has now been found that under the proper reaction conditions, secondary and tertiary α-aralkylferrocene derivatives can be prepared by direct substitution in good to excellent yields. This work is described in the present paper.

Results and Discussion

Synthesis of the above-mentioned aralkylferrocene compounds was brought about by condensing ferrocene with the correspondingly substituted carbinols in the melt phase. As catalysts, strong Lewis acids were used, anhydrous aluminum chloride being the most suitable compound. The concentrations required ranged from 3 to 20%[12] and, hence, were substantially lower than commonly applied in Friedel–Crafts reactions. In general, the reaction was found to be favored by increased temperature, but to minimize side reactions and risk of partial decomposition, the syntheses were conducted at the lowest temperatures required to obtain a homogeneous melt of the reactants (usually 100–140°). For work-up, the reaction products were extracted with appropriate solvents and further isolated and purified by chromatography or recrystallization.

With the proper choice of the reactant ratio, the conversion could be directed toward the principal formation of the monosubstituted or disubstituted derivative. For the former, an excess of ferrocene proved necessary since, at equimolar reactant ratio, a tendency toward the simultaneous formation of disubstituted products was always observed.

The structural assignments of the condensation products were based on elemental and infrared analysis. Wherever feasible, they were corroborated by comparison with compounds reported in the literature. Infrared analysis was also applied to determine or corroborate the substitution scheme in the di-substituted derivatives, utilizing the fact that two strong bands near 9 and 10 μ are characteristic of the presence of at least one unsubstituted ring in the ferrocene molecule.[13] This criterion, commonly referred to as the "9–10 μ rule," has been successfully applied by numerous authors in discriminating between homo- and heteroannular substitution.[4a,14–17] However, apparent exceptions are known involving certain heteroannularly disubstituted compounds which exhibit one or both of the 9 μ and 10 μ bands.[18] Therefore,

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(2) In preparation.

(3) A. N. Nesmeyanov and E. G. Perevalova, *Doklady Akad. Nauk S.S.S.R.*, **119**, 288 (1958).

(4) (a) P. L. Pauson, *J. Am. Chem. Soc.*, **76**, 2187 (1954); (b) R. B. Woodward and E. Csendes, reported by P. L. Pauson, ref. 4a.

(5) A. N. Nesmeyanov, E. G. Perevalova and Z. A. Beinoravichute, *Doklady Akad. Nauk S.S.S.R.*, **112**, 439 (1957).

(6) R. C. Koestler and W. F. Little, *Chemistry & Industry*, 1589 (1958).

(7) R. Riemschneider and D. Helm, *Ber.*, **89**, 155 (1956).

(8) See, for instance, V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955); P. L. Pauson, *Quart. Revs.* (*London*), **9**, 391 (1955).

(9) A. N. Nesmeyanov and N. S. Kochetkova, *Doklady Akad. Nauk S.S.S.R.*, **109**, 543 (1956).

(10) A. N. Nesmeyanov and N. S. Kochetkova, *ibid.*, **114**, 800 (1957).

(11) A. N. Nesmeyanov and N. S. Kochetkova, *ibid.*, **117**, 92 (1957).

(12) Unless otherwise stated, throughout this paper, the percentage of catalyst is always based on the weight of the carbinol component.

(13) M. Rosenblum, Ph.D. Thesis, Harvard University, 1953.

(14) M. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 900 (1957); **22**, 903 (1957).

(15) K. L. Rinehart, Jr., R. J. Curby, Jr., and P. E. Sokol, *J. Am. Chem. Soc.*, **79**, 3420 (1957).

(16) M. Rosenblum and R. B. Woodward, *ibid.*, **80**, 5446 (1958); M. Rosenblum, *Chemistry & Industry*, 953 (1958).

(17) M. Rosenblum, *J. Am. Chem. Soc.*, **81**, 4530 (1959).

(18) For instance, 1,1′-ferrocene-diacetodithiomorpholide is reported by Rinehart (ref. 15) to exhibit bands at 1111 and 1006 cm.$^{-1}$ (9.00 and 9.94 μ). We have found many ferrocenyl ethers and alcohols to absorb in the region from 1100 to 1150 cm.$^{-1}$ (C–O stretching mode),

the rule is commonly interpreted in a negative sense, to the effect that absence of both bands clearly indicates substitution on both rings. From our spectroscopic data on numerous ferrocene compounds, we have even found it safe to conclude that sufficient evidence is given for heteroannular substitution by the absence of the 9 μ band alone, with the 10 μ band restricted to weak-to-medium intensity. The disubstituted derivatives reported in this paper failed to absorb at 9 μ and, hence, were assigned a heteroannular structure.[19] Expectedly, all monoderivatives showed the two strong bands in the mentioned region. Further infrared data in support of the assigned structures will be summarized in a later paragraph.

Condensation with Triphenylcarbinol.—Of all the condensations investigated in this work, triphenylcarbinol proved to react in the smoothest manner, the over-all crude yields averaging 80–98% of theory. Thus, in a typical run with 3.5% aluminum chloride[12] catalyzing the reaction and at a molar reactant ratio of 1:1, triphenylmethylferrocene (I)[20] and 1,1′-di-(triphenylmethyl)-ferrocene (II)[21] were obtained in nearly equal amounts. By employing a 2:1 molar ratio of carbinol to ferrocene, the disubstituted derivative II could be isolated in 85–97% yield, whereas a 1:3 ratio gave rise to the formation of nearly the same high percentage of the monoderivative I. However, in the latter case and even with a larger excess of ferrocene, small amounts of II were isolated in addition, bringing the total yield up to the same range.

For comparison, a run was conducted under typical Friedel–Crafts conditions, *i.e.*, in methylene chloride solution with equimolar amounts of catalyst and alcohol and molar ratio of carbinol to ferrocene of 2:1. Under these conditions, the total yield of disubstituted ferrocene (no monoderivative was formed) was poorer (*ca.* 50%) and, in addition to the main reaction product, small amounts of material were formed whose analysis showed aralkyl:ferrocene ratios greater than two, indicating that under these conditions less controllable substitution occurred. It has not yet been ascertained to what extent these polysubstituted products actually represent structures with higher degrees of substitution on the ferrocene nucleus. Isomeric structures may be possible, comprising more complex substituent groups resulting from self-condensation of the aromatic carbinol. Such substituents, however, should contain disubstituted phenyl nuclei, the presence of which could not be evidenced by infrared analysis in this nor in any of the subsequent instances.

Other experiments were run with triphenylmethyl chloride in lieu of the carbinol. The yields were 35–40% of compound II (no monoderivative), regardless of the procedure applied, *i.e.*, either in the melt phase or in methylene chloride solution. Here again, a mixture of polysubstituted products, with approximately 4–6 substituents per ferrocene nucleus, was obtained in a small percentage.

Condensation with Benzhydrol.—Considering the marked tendency of benzhydrol to engage in side reactions such as ether formation, decreased yields of substituted ferrocenes were to be anticipated with this component. In fact, the maximum yield of 1,1′-dibenzhydrylferrocene (III) obtained was approximately 55%, at a carbinol:ferrocene molar ratio of 2.2:1. A small proportion of polysubstituted compounds with an average of four substituents per ferrocene ring was formed simultaneously. Aluminum chloride catalyst was employed at 9%. Smaller concentrations were found to favor increasingly the formation of the ether, with the latter reaction occurring exclusively when only 1% aluminum chloride was present. The same effect was observed with weaker catalysts such as $ZnCl_2$ or $SnCl_4$, the former resulting solely in ether formation while, with stannic chloride, at least a small amount (18.5%) of III was obtained.

The tendency toward preferential formation of di- or polysubstituted ferrocenes observed with triphenylcarbinol appears to be still more pronounced with benzhydrol. Thus, even with ferrocene in large excess (carbinol:ferrocene molar ratio 1:2) only III, but no monoderivative, was isolated. Common Friedel–Crafts conditions, *i.e.*, equimolar amounts of carbinol and catalyst and use of an additional solvent, apparently favor the formation of still higher substituted compounds. For example, a 2.2:1 ratio of carbinol to ferrocene, the solvent being dioxane and the catalyst stannic chloride, gave a 43% yield of the disubstituted derivative III, while in addition roughly 10% yield of higher substituted ferrocenes was obtained. With methylene chloride as solvent and aluminum chloride as catalyst, at a 3:1 carbinol:ferrocene molar ratio, almost no III was isolated. Instead, the reaction product (71.5% yield; calculated for hexa-compound) constituted a mixture of polybenzhydrylferrocenes averaging 6–7 substituent groups per molecule, as shown by elemental analysis of individual fractions. A crude separation of the components was accomplished by chromatography on alumina with no attempts made for further purification[22]

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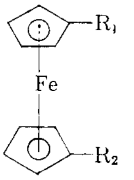
and acetyl derivatives are known to behave similarly giving rise to possible interference with the 9–10 μ rule (see, for instance, M. Rosenblum and R. B. Woodward, ref. 16). While in most cases these bands are located on the lower wave-length side of the 9 μ band, a typical instance of interference is illustrated by 1,1′-di-(1-hydroxyethyl)-ferrocene, which exhibits strong bands at 9.07 and 9.96 μ (see also following reference).

(19) In two cases (II and III), weak absorption was noticed in the vicinity of 10 μ. This band, which we also found in the spectrum of a great number of monosubstituted phenyl derivatives void of ferrocene, may be ascribed to the stretching mode (ν'_{13}) of the C–C bond connecting the benzene ring with the substituent. Some mixing must be expected with the more intense ring vibrational mode ν_{12} usually found in the 9.95–10.0 μ range.

(20) By interaction of diferrocenylmercury and triphenylmethyl chloride, A. N. Nesmeyanov and E. G. Perevalova, *Doklady Akad. Nauk S.S.S.R.*, **119**, 288 (1958), prepared a compound, to which structure I was assigned. This product differs in m.p. from ours by 10 degrees.

(21) By treating diphenylfulvene with phenyllithium and allowing the reaction product to react with $FeCl_2$, Koestler and Little (ref. 6) obtained a compound, m.p. 174–175°, believed to be 1,1′-bis-(triphenylmethyl)-ferrocene. However, no elemental analytical data corroborating this assignment could be obtained. Also, the reaction of diphenylfulvene and phenyllithium has been reported by Ziegler and Shafer (*Ann.*, **511**, 101 (1934)) to proceed abnormally, failing to yield the expected triphenylmethylcyclopentadiene product. Thus, in view also of our own unambiguous product, this assignment is clearly incorrect.



I, $R_1 = (C_6H_5)_3C-$, $R_2 = H-$
II, $R_1 = R_2 = (C_6H_5)_3C-$
III, $R_1 = R_2 = (C_6H_5)_2CH-$
IV, $R_1 = R_2 = C_6H_5(CH_3)C-$
VI, $R_1 = CH_3(C_6H_5)_2C-$, $R_2 = H-$
VII, $R_1 = R_2 = CH_3(C_6H_5)_2C-$
VIII, $R_1 = (CH_3)_3C-$, $R_2 = H-$

Condensation with 2-Phenylpropane-2-ol.—This carbinol is known to split off readily one mole of water to form the corresponding isopropenylbenzene. This dehydration may take place upon heating with $KHSO_4$, acetic anhydride or even by distillation of the carbinol itself.[23] Accordingly, the occurrence of side reactions consuming part of the reactant could be anticipated, as well as further reaction of the olefin thus formed with ferrocene to give the expected 2-phenyl-2-propyl compounds.

Condensed with ferrocene at a molar ratio of 2.5:1 and 10% aluminum chloride as catalyst, the carbinol dehydrated in high conversion as shown by the amount of water released during the reaction. However, only part of the resulting isopropenylbenzene reacted with ferrocene to form 1,1′-di-(2-phenyl-2-propyl)-ferrocene (IV), in a 20% yield, while the rest of the olefin remained unreacted or underwent self-polymerization. To circumvent premature hydrolysis of the aluminum chloride, it was convenient to run the condensation in two stages. This procedure was accomplished by first heating the reactants for one hour with zinc chloride principally to effect dehydration, followed by the addition of 3.7% aluminum chloride, whereupon the proper substitution reaction proceeded to give IV in a 50–60% yield. When conducted with the mild catalyst $ZnCl_2$ alone, the reaction yielded only a small amount of IV, the main portion of the reaction mixture consisting of both the dehydration product and unreacted ferrocene.

In the course of the above reaction catalyzed solely by aluminum chloride, a second ferrocene compound (V) was separated in a few per cent. yield from IV by fractional crystallization. Both elemental and infrared analyses are consistent with the structure of a homoannular isomer of IV, either singly substituted with a self-condensed dimeric carbinol or, less probably, 1,2- or 1,3-di-(2-phenyl-2-propyl)-substituted. Further characterization of the compound was not undertaken at this time.

Condensation with 1,1-Diphenylethene.—As a further verification of the condensation reaction of ferrocene with olefinic intermediates, as illustrated in the previous example, a condensation reaction was carried out under these same reaction conditions using an unsaturated hydrocarbon as the starting material. As such an olefin, 1,1-diphenylethene was employed in lieu of the corresponding alcohol, 1,1-diphenylethanol. With 25% aluminum chloride as the catalyst, condensation occurred in the expected way. Again, formation of the disubstituted compound prevailed over that of the monoderivative. A typical run with a slight molar excess of ferrocene yielded *ca.* 60% of crude product, consisting of approximately two-thirds of 1,1′-di-(1,1-diphenylethyl)-ferrocene (VII) and one-third of the corresponding monocompound VI. To increase the proportion of the latter, a considerable excess of ferrocene had to be employed. With zinc chloride as the catalyst, no reaction took place even under such extreme conditions as heating in a sealed tube at 175°.

Condensations with *sec*-Aryl-alkyl- and *prim*-Arylcarbinols.—To provide comparisons of the relative reactivities of the *t*-aryl-, *t*-aryl-alkyl-, and *sec*-diarylcarbinols of the preceding sections with *sec*-aryl-aralkyl- and *prim*-arylcarbinol examples, 1,2-diphenylethanol and *p*-methoxybenzyl alcohol were treated with ferrocene under similar conditions. Both alcohols exhibited relatively inert behavior, with crude over-all yields below 20%. By elemental analysis the crude oils, after separation from unreacted starting materials, were found to constitute essentially the expected substituted ferrocenes. However, no further attempts were made to isolate and purify these condensation products because of the comparatively poor yields obtained.

As expected, nitro-deactivated examples, 1-(*p*-nitrophenyl)-ethanol and *p*-nitrobenzyl alcohol, were even more inert and yielded no reaction products. As temperatures exceeded 120–130°, water formation with simultaneous decomposition of the ferrocene nucleus leading to partially insoluble residues was observed, the balance of the ferrocene remaining unreacted.

Condensations with *t*-Butyl Alcohol.—To complete the comparisons of representative alcohol types in their reactivity with ferrocene, analogous condensations with purely aliphatic alcohols were also attempted. No substantial reaction was found to occur with primary aliphatic alcohols. Nesmeyanov and Kochetkova[11] have reported the condensation of ferrocene with *t*-butyl alcohol under normal Friedel–Crafts conditions, obtaining yields of 10% each of mono- and di-(*t*-butyl)-ferrocene. Under the experimental conditions employed in the present work, no reaction took place and the ferrocene was recovered almost quantitatively. Likewise, the ferrocene remained essentially unreacted in a sealed tube at 130°, and not until $ZnCl_2$ was employed as an additional condensing agent and the temperature maintained at 170°, could condensation be enforced. However, the yields of substituted ferrocenes did not exceed those reported by Nesmeyanov and Kochetkova.

A more efficacious catalyst proved to be BF_3 and also the polyphosphoric acid–$AlCl_3$ system. In both instances, the crude over-all yields in-

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(22) The spectrum of a representative polysubstituted fraction exhibited the weak band at 9.97 μ discussed in ref. 19 and, at the same time, a very small peak was shown at 9.01 μ. Rather than suggesting the possibility of a slight portion of homoannular substitution, we believe this band also to be associated with phenyl vibrations (combination $\nu_{11} + \nu_{16A}$) enhanced by the accumulation of phenyl moieties (*cf.* C. Y. Liang and S. Krimm, *J. Polymer Sci.*, **27**, 241 (1958)). We have found such absorption of very low intensity with many aromatic compounds such as toluene, ethylbenzene, biphenyl, diphenylmethane, triphenylmethane, etc. In contrast, J. K. Wilmshorst and H. J. Bernstein, *Can. J. Chem.*, **35**, 911 (1957), ascribe this band in the toluene spectrum to ν_8.

(23) K. Matsubaba and H. W. Perkin, *J. Chem. Soc.*, **87**, 671 (1905); A. Klages, *Ber.*, **35**, 2639 (1902).

creased to approximately 60%. However, even with an equimolar reactant ratio, essentially polysubstituted derivatives averaging three substituent groups were formed, with the monoderivative (*t*-butylferrocene, VIII) constituting only a small portion of the condensation product. Increased ferrocene:carbinol ratios should result in improved yields of the mono- and dibutyl compounds.

Comparative Reactivities.—The series of alkylation reactions of the aromatic ferrocene ring under the experimental conditions described above outlines a fairly wide range of reactivities for the representative carbinol types investigated. Triphenylcarbinol reacted most readily, leading to almost quantitative conversion. Decreased reactivity was exhibited by benzhydrol together with a greater tendency to side reactions. This was observed to be even more the case with 2-phenylpropane-2-ol. With such *sec*-aryl-aralkyl- and *prim*-arylcarbinols as 1,2-diphenylethanol and *p*-methoxybenzyl alcohol, only very limited conversion was achieved to the desired products. Finally, considerable change in the reaction conditions was necessary for the purely aliphatic *t*-butyl alcohol to give reasonable yields.

From this sequence, the importance of the contribution of the α-aryl substituents toward increased bond polarization in the carbinol–aluminum chloride complex is evident, falling off from the triphenylmethyl example, with its maximum charge stabilization, as phenyls are successively substituted by alkyl groups and hydrogen. Smoot and Brown[24] have pointed out the gradual progression in the Friedel–Crafts reaction from a displacement to an ionization mechanism as the carbonium ion character of the transition state increases with α-substitution. The increased contribution to bond ionization in the case of triphenylcarbinol is apparent over other examples in the present work and may therefore suggest the predominance of an ionic mechanism. However, no conclusive evidence on this point can be given without a thorough kinetic analysis. The corresponding rate ratios calculated for both a displacement and an ionization mechanism on the basis of the reactant and catalyst concentrations employed in the present series of experiments were too narrow to allow for a clear differentiation between the two limiting mechanisms.

Infrared Correlations.—Besides a great number of well-known and assignable bands of ferrocene and the corresponding substituents (monosubstituted benzene ring, methyl, *t*-CH, *t*-butyl), the aralkyl compounds here described exhibited in their infrared spectra several characteristic absorptions of known or unknown origin.[25] For instance, weak bands were shown near 7.22 and 7.60 μ as well as in the vicinity of 7.85 μ.[26] Absorption of weak-to-medium intensity was also exhibited near 8.15 μ. This band has been observed with all of 25 ferrocene derivatives[27] examined in this Laboratory having a tetrahedral carbon atom linking the ferrocene ring with the remainder of the substituent.[28] Two bands typical of substituted ferrocenes were noticed in the 9.60–9.80 μ range (superimposed by the strong phenyl absorption due to the ν_{18A} in-plane bending mode) as was a variable-intensity band in the 10.7–10.9 μ region. Absorption of usually weak intensity occurred in the neighborhood of 11 μ[29] and also near 11.25 μ (in VI shifted to 11.05 μ). With compounds containing methyl groups, perturbance by the well-known methyl vibration occurring in this range was observable (notably with IV).

Experimental[30]

Starting Materials.—The ferrocene used in these reactions was prepared by the diethylamine method described by Wilkinson.[31] Without decreasing the yields, it was possible to reduce the amounts of tetrahydrofuran and diethylamine by roughly 25%, which proved useful for large batches. It appeared to be feasible, also, to extract the residue resulting from evaporation of the excess diethylamine with water, thus removing the amine hydrochloride formed during the reaction and facilitating the subsequent extraction with benzene (better than the suggested petroleum ether). In addition, the purity of the ferrocene was enhanced, giving upon one recrystallization from hexane a product of m.p. 175–176°.

The carbinols and halides used were commercial reagent grade compounds and were employed without further purification. Anhydrous aluminum chloride was directly used, but the very hygroscopic zinc chloride required heating for 2 hours above the melting point for complete dehydration. Before each use, the approximate amount needed

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[24] C. R. Smoot and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 6249 (1956).

[25] Owing to limited solubility of several derivatives in CCl_4 and CS_2, the spectra were recorded from KBr pellets (spectrum of VII from a Nujol mull). *t*-Butylferrocene was employed as a capillary film.

[26] We have found bands of variable, mostly very low intensity near the first two positions in the spectra of numerous phenyl derivatives. While the absorption at 7.22 μ may be assigned to a combination vibration, possibly $\nu_6 + \nu_{16A}$ (see, however, R. R. Randle and D. H. Whiffen, "Molecular Spectroscopy," Institute of Petroleum, London, 1955), the band near 7.60 μ may be due to a deformation mode (ν'_8; in some cases, additional absorption at 7.55 μ was found, probably due to ν_{14}). The band near 7.85 μ also appears to be associated with a phenyl vibration; comparison, in intensity and position, with ν_{10A} in the 11.70 μ region suggests a combination band ($\nu_{10A} + \nu_{16A}$). An additional phenyl band in the vicinity of 8 μ was occasionally noticed (*e.g.*, with III, IV, VI) for which we find no assignment. Randle and Whiffen, referred to above, and also J. C. Hawkes and A. J. Neale, *Spectrochim. Acta*, **16**, 633 (1960), observed a band in the 8 μ range with monoalkylbenzenes, ascribing it to a CH in-plane deformation mode. It should be noted that ferrocene and its derivatives show very weak absorption in the same position.

[27] Among these, ferrocenylcarbinols and their respective inter- and intramolecular ethers were found to absorb in the mentioned region with strongly enhanced intensity. 1,2-Di-(hydroxyethyl)-ferrocene (D. S. Trifan, J. L. Weinmann and L. P. Kuhn, *J. Am. Chem. Soc.*, **79**, 6566 (1957)) is exceptional, lacking absorption between 8.10 and 8.20 μ, possibly by shift and superposition on its strong 8.0 μ band.

[28] By contrast, mono- or polyphenylferrocenes fail to give bands in this region, as do acetyl-, benzoyl- and 1,1′-diacetylferrocene. However, expectedly, they do absorb when additional methyl or ethyl groups are present as substituents on the ferrocene moiety. Contrary to the quoted carbonyl compounds, the homoannular 1,2-diacetylferrocene (ref. 27) does exhibit a strong band in the mentioned region, although slightly shifted to lower wave lengths (8.08 μ). Methyl 1,1′-ferrocenyldicarboxylate was found to absorb, although very weakly, at 8.17 μ. The latter two examples may indicate that the findings described above regarding the appearance of the band near 8.15 μ do not constitute a rule.

[29] A strong contribution by the ν_{17B} (out-of-plane deformation) phenyl vibration may be expected in this range. See also the interesting observations in the 11 μ range on variously substituted acetylferrocenes reported by Rosenblum and Woodward (ref. 16 and 17).

[30] All melting points are uncorrected. Infrared spectra were recorded from KBr pellets, using a Perkin-Elmer model 21 double beam spectrometer equipped with rock salt optics (exceptions: ref. 25). Elemental analyses performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, N. Y., and G. I. Robertson, Jr., Florham Park, N. J.

[31] G. Wilkinson, *Org. Syntheses*, **36**, 34 (1956).

was preheated at above 100° and powdered at this temperature in a preheated mortar under dry nitrogen.

Triphenylmethylferrocene (I) and 1,1'-Di-(triphenylmethyl)-ferrocene (II). (a) In the Melt Phase (Carbinol:Ferrocene Molar Ratio 1:3).—The well-ground mixture of 4.29 g. of ferrocene, 2.0 g. of triphenylcarbinol and 0.1 g. of (5%) anhydrous $AlCl_3$ was placed into a 50-ml. round-bottom flask equipped with a mechanical stirrer. Two side-necks originating from the upper portion of the bulb were utilized in passing a slow current of dry nitrogen over the mixture throughout the condensation. The flask was heated for 1 hour with stirring in an oil-bath maintained at 140°. The brownish melt, solidified upon removal of the heat source, was ground and extracted with 50 ml. of hot methanol to remove traces of catalyst and unreacted carbinol, as well as part of the excess ferrocene. The remaining crystalline residue constituting essentially a mixture of ferrocene and monosubstituted compound, with traces of the disubstituted compound present, was stepwise dissolved, with cautious heating, in a total of 80 ml. of cyclohexane. By this method of incomplete solution, the monoderivative was at last entirely dissolved, while the disubstituted product remained in the least-soluble residue and could be purified by recrystallization from benzene (see description of this derivative under section b). The combined cyclohexane solutions were chromatographed on activated alumina (Alcoa, grade F-20) packed in a 2.5 × 70 cm. column and wetted with low-boiling petroleum ether. Development of the chromatogram was carried out, first, with 50 ml. of cyclohexane–petroleum ether (1:1) and subsequently with petroleum ether alone. Clear-cut separation occurred, with an orange-yellow band of substitution products remaining at the upper part of the column, while the orange ferrocene zone slowly migrated to the bottom. After removal of a very thin, brownish top layer containing *ca.* 0.1 g. of higher substituted ferrocene compounds, the orange-yellow upper zone was exhaustively extracted with boiling benzene and the extract evaporated to dryness. The crystalline residue was washed with hot methanol to remove traces of unreacted carbinol still present at this point, whereupon 2.55 g. (77.5%)[32] of the crude triphenylmethylferrocene (I) were obtained. Recrystallization from benzene yielded 2.35 g. (71.5%), as orange-yellow needles, m.p. 188–190° (lit.[3] 179–181°). By repeated recrystallization, the compound was obtained in analytical purity, m.p. 190–190.5°. The compound is very soluble in benzene, but only very slightly soluble in alcohol, by which it is precipitated from concentrated benzene solution.

Anal. Calcd. for $C_{29}H_{24}Fe$ (I): C, 81.31; H, 5.65; Fe, 13.04. Found: C, 81.28; H, 5.68; Fe, 12.67.

The disubstituted compound, in the above procedure, was isolated in a yield of 0.3 g. (11.6%).

(b) In the Melt Phase (Carbinol:Ferrocene Molar Ratio 1.5:1).—A reactant mixture in the above ratio, catalyzed by 3.5% anhydrous $AlCl_3$, was treated in the manner described under (a). However, due to a gradual solidification of the melt, stirring was possible only for the first half hour. The crude reaction product was first washed with hot methanol and then extracted exhaustively with boiling benzene. After standing overnight, a portion of the 1,1'-di-(triphenylmethyl)-ferrocene (II) had crystallized from the extract. Two more fractions of crude II were obtained from the concentrated mother liquor, thus amounting to a total yield of 95%. Precipitation from concentrated benzene solution by the addition of methanol and recrystallization from benzene–cyclohexane gave the compound as fine, orange needles, m.p. 286°, soluble in benzene and very slightly soluble in alcohol.

Anal. Calcd. for $C_{48}H_{38}Fe$ (II): C, 85.96; H, 5.71; Fe, 8.33. Found: C, 85.40; H, 5.69; Fe, 8.37.

From the last residue obtained by evaporating the benzene mother liquor to dryness, traces of the monoderivative were isolated (2%). Separation from some unreacted ferrocene present at this point was effected by precipitation from hot benzene solution by the addition of methanol.

(c) In the Melt Phase (Carbinol:Ferrocene Molar Ratio 1:1).—An equimolar mixture of ferrocene and carbinol with 3.5% $AlCl_3$ was treated as in run a. The condensation products, after chromatographic separation from unreacted ferrocene in the manner described above, were separated from one another by fractional crystallization from benzene. The diderivative, less soluble than the monoderivative, was isolated first; crude yields: I, 50.0%; II, 35.9%.

(d) In the Melt Phase, with Triphenylmethyl Chloride (Chloride:Ferrocene Molar Ratio 2:1).—A mixture of 2.0 g. of ferrocene, 5.98 g. of triphenylmethyl chloride and 0.2 g. of $AlCl_3$ was finely powdered and heated for 1 hour, in the previously described manner, at 130°. Melting began at slightly above 100° with evolution of HCl. The reaction mixture was worked up as described under (b) to give crude II in an over-all yield of 2.9 g. (40%; this figure includes a small portion obtained, along with ferrocene, by $SnCl_2$ reduction of the water extract of the black, tarry residue remaining from benzene extraction).

(e) Friedel-Crafts Procedure, with Triphenylmethyl Chloride (Molar Ratio Chloride:Ferrocene:Catalyst 2:1:2).—In a 250-ml. three-neck round-bottom flask equipped in the usual manner with stirrer, reflux condenser ($CaCl_2$ tube) and a nitrogen inlet, were placed 2.87 g. of $AlCl_3$ and 70 ml. of dry methylene chloride. To this mixture a solution of 2.0 g. of ferrocene and 5.98 g. of triphenylmethyl chloride in 70 ml. of methylene chloride was added dropwise with rapid stirring, whereupon the green color of the complex appeared immediately. The exothermic reaction, resulting in gentle reflux, was allowed to cease and stirring continued for 12 hours at room temperature. Upon addition of ice-water, the mixture was worked up by extraction with chloroform, thorough washing of the extract with water and evaporation to near dryness. From the residue, after washing with hot methanol, the disubstituted ferrocene compound (3.02 g., 41.8%) was isolated by chromatography, as described under (a).

The small, brownish top layer of the column was extracted with benzene to give 0.6 g. of polysubstituted ferrocene by precipitation with methanol. The yellow-brown material was infusible up to 300°.

Anal. Calcd. for $C_{105}H_{80}Fe$ (pentasubstituted compound): C, 90.23; H, 5.77; Fe, 4.00. Found: C, 89.81; H, 5.63; Fe, 4.31.

With triphenylcarbinol employed in place of the chloride in the same molar concentration, the total crude yield of II amounted to 3.8 g. (52.8%). In addition, approximately 0.5 g. of polysubstituted material was isolated, but not further investigated.

1,1'-Dibenzhydrylferrocene (III) and Polybenzhydrylferrocenes. (a) In the Melt Phase (Molar Ratio Carbinol:Ferrocene 1:2).—The thoroughly ground mixture of 4.0 g. of ferrocene, 1.98 g. of benzhydrol and 0.2 g. of $AlCl_3$ was heated, in the usual manner, for 2 hours at 130–140°. The melt was dissolved in cyclohexane and chromatographed as described above for the triphenylmethyl compounds, to separate the reaction product from unreacted ferrocene. Upon extraction of the upper, yellow zone with benzene, evaporation of the extract to dryness, solution in dimethylformamide and addition of 5 ml. of methanol to the hot, concentrated solution, 1.26 g. (45%) 1,1'-dibenzhydrylferrocene (III) crystallized as orange-yellow needles, m.p. 160–161°. Recrystallization in the same manner raised the m.p. to 164.5–165° (lit.[4a] 162–163°).

Anal. Calcd. for $C_{36}H_{30}Fe$ (III): C, 83.39; H, 5.83; Fe, 10.77. Found: C, 82.83; H, 5.87; Fe, 10.56.

From the mother liquor, besides additional III (included in above yield), 0.3 g. of crude dibenzhydryl ether was deposited after adding excess methanol, m.p. 110° (from hexane); no depression on admixture with authentic sample.

(b) In the Melt Phase (Molar Ratio Carbinol:Ferrocene 2.2:1).—Ferrocene (2.42 g.), 5.27 g. of benzhydrol and 0.47 g. (9%) of $AlCl_3$ were thoroughly ground and heated for 1 hour at 120–130° in the previously described manner. Chromatography on alumina from benzene solution resulted in separation of higher substituted compounds present in the first, small forerun fraction from which they were isolated by evaporation to dryness and precipitation from concentrated dimethylformamide solution by methanol (0.2 g.) as a tan, fine-crystalline powder, melting range 80–130°.

Anal. Calcd. for $C_{62}H_{50}Fe$ (tetrasubstituted compound): C, 87.51; H, 5.92. Found: C, 87.23; H, 5.71.

The main benzene eluate was evaporated to dryness and the resulting residue triturated with hot, low-boiling

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(32) Unless otherwise stated, all yield calculations are based on weight of carbinol or chloride reactant.

petroleum ether (for removal of admixed dibenzhydryl ether), to give 3.7 g. (54.8%)[33] of crude 1,1′-dibenzhydrylferrocene (III), m.p. 162° (from dimethylformamide–methanol).

With $SnCl_4$ (5%) in lieu of $AlCl_3$, the crude yield of III did not exceed 18.5%.[33]

(c) **Friedel–Crafts Procedure (Molar Ratio Carbinol:-Ferrocene:$AlCl_3$ 3:1:2.5).**—Starting materials and catalyst were treated in the above-stated molar ratio following procedure e of the preceding section (triphenylcarbinol condensation). From the organic phase, by evaporation to dryness and thorough washing of the residue with hot methanol, a crude mixture of polybenzhydrylferrocenes was obtained. By chromatography on alumina from benzene solution and collecting the eluate in four cuts, the mixture was crudely fractionated, the highest-substituted compounds concentrating in the first fractions. Further subfractionation was achieved by fractional precipitation by methanol from dimethylformamide solution of the individual evaporation residues, with the less soluble, higher substituted components enriched in the first precipitates. The total yield of tan-colored, fine-crystalline solid thus precipitated was 71.5% (calculated for hexa-compound). Some of the final fractions are listed, along with melting range and elemental composition, in Table I. The final mother liquor of the last chromatographic cut contained a mixture of essentially di- and trisubstituted material. Careful recrystallization from dimethylformamide–methanol gave III in nearly 10% yield, m.p. 158–160°.

By changing the molar ratio carbinol:ferrocene:catalyst ($SnCl_4$ in place of $AlCl_3$) to 2.2:1:2.2, with dioxane as solvent, the yield of III increased to 43%,[33] while that of polysubstituted ferrocenes was only 12% (based on tetracompound). In this run, the reaction product was worked up as in (b) above.

TABLE I

No. of sub-stit.	Melting range, °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Iron, % Calcd.	Iron, % Found
9	130–150	90.67	90.46	5.99	6.21	3.32	3.30
8	120–145	90.33	90.07	5.98	6.16	3.68	3.45
7	105–130	89.89	89.77	5.97	6.04		
6–7	90–120	89.61	89.55	5.97	6.22		
5–6	85–115	88.94	88.96	5.96	6.16	5.61	5.09

1,1′-Di-(2-phenyl-2-propyl)-ferrocene (IV). (a) **In the Melt Phase, with $AlCl_3$ as Catalyst (Molar Ratio Carbinol:-Ferrocene 2.5:1).**—To a thoroughly powdered mixture of 2.2 g. of ferrocene and 0.4 g. of $AlCl_3$ was added 4.02 g. 2-phenylpropane-2-ol. The mass, spontaneously warming up, was heated for 1 hour at 130–140° in the conventional manner. The reaction product was further purified by trituration with warm methanol, followed by chromatography on alumina. The benzene eluate was evaporated to dryness and the oily residue exhaustively extracted with a total of 80 ml. of boiling ethanol, from which 1.0 g. (20%[33]) of 1,1′-di(2-phenyl-2-propyl)-ferrocene (IV) crystallized on slow cooling as orange-yellow needles, m.p. after repeated recrystallization from hexane or ethanol 136–137° (lit.[6] 133.5–135°).

Anal. Calcd. for $C_{28}H_{30}Fe$ (IV): C, 79.62; H, 7.16; Fe, 13.22. Found: C, 79.76; H, 6.75; Fe, 13.37.

On concentration of the alcoholic mother liquor, small additional amounts of IV were collected (included in the above yield) followed by the isolation of 0.08 g. of an unidentified isomeric, but homoannular compound (V) appearing as fine, yellow needles, m.p. 179–180° (ethanol).

Anal. Calcd. for $C_{28}H_{30}Fe$ (V): C, 79.62; H, 7.16, Fe, 13.22. Found: C, 80.20; H, 6.68; Fe, 13.17.

(b) **In the Melt Phase, with $ZnCl_2$ and $AlCl_3$ as Catalysts (Molar Ratio Carbinol:Ferrocene 2:1).**—A powdered mixture of 2.2 g. of ferrocene and 1.1 g. of $ZnCl_2$ was heated with 3.22 g. of 2-phenylpropane-2-ol at 110–115° as described previously. After the brisk water formation had nearly ceased (approximately 1 hour), 0.12 g. (3.7%) of $AlCl_3$ was added and heating was continued for 1.5 hours at 120–125°. The brown hot melt was decanted from the tarry catalyst-containing bottom phase and solidified to a crystalline mass constituting crude IV. The catalyst phase was extracted with boiling water and cold methanol and the remaining residue taken up with boiling benzene to yield, upon evaporating to dryness, an additional small crop of orange-yellow crystals of IV. The combined portions, after washing with warm methanol and drying, weighed 3.0 g. (60%), m.p. 132–134° (from hexane–ethanol).

From the hexane–ethanol mother liquor, 0.1 g. of isomer V (m.p. 175°, on admixture with ferrocene strong depression) was isolated in the manner described under (a).

(1,1-Diphenylethyl)-ferrocene (VI) and 1,1′-Di-(1,1-diphenylethyl)-ferrocene (VII). In the Melt Phase (Molar Ratio Olefin:Ferrocene 1:1.1).—A finely powdered mixture of 2.5 g. of ferrocene and 0.55 g. (25%, based on olefin) of $AlCl_3$ was heated with 2.2 g. of 1,1-diphenylethene in the manner described for procedure a of the preceding example (IV). However, to obtain a uniform melt, the temperature had to be raised to 160–165°; also the catalyst was added in three portions, rather than at once, during the first 30 minutes. The residue from evaporation of the benzene eluate, 2.2 g. (61%[34]), constituted a crude mixture of VI and VII. The two components were separated by fractional extraction with boiling ethanol, the more soluble monoderivative, (1,1-diphenylethyl)-ferrocene (VI), being concentrated in the first extracts. It was finally obtained as fine, orange-yellow prisms (crude yield 0.67 g. or 15%, based on olefin), very soluble in dimethylformamide, benzene and hexane, slightly so in alcohol; m.p. 125–129°. Recrystallization from hexane–ethanol increased the m.p. to 131–132°.

Anal. Calcd. for $C_{24}H_{22}Fe$ (VI): C, 78.70; H, 6.05; Fe, 15.25. Found: C, 78.65; H, 6.18; Fe, 15.15.

From the extraction residues, 0.9 g. (27% yield, based on olefin) of crude 1,1′-di-(1,1-diphenylethyl)-ferrocene (VII) was collected, giving after repeated recrystallization from dimethylformamide, fine, light-orange needles, m.p. 210°, very soluble in benzene and dimethylformamide, slightly soluble in hexane, and very difficultly so in alcohol.

Anal. Calcd. for $C_{38}H_{34}Fe$ (VII): C, 83.51; H, 6.27; Fe, 10.22. Found: C, 82.77; H, 6.39; Fe, 10.02.

***t*-Butylferrocene and Poly-(*t*-butyl)-ferrocenes. In Polyphosphoric Acid, with $AlCl_3$ as Catalyst (Molar Ratio Carbinol:Ferrocene 1:1).**—Ferrocene (8.84 g.) was thoroughly powdered with 3.52 g. of $AlCl_3$ (100%) and heated under a nitrogen blanket with 80 g. of polyphosphoric acid in a 250-ml. three-neck, round-bottom flask equipped with stirrer and dropping funnel. When the temperature had risen to 100°, 3.52 g. of *t*-butyl alcohol was added dropwise, with stirring over a 30-minute period, and heating was then continued for 4 hours at 120°. The reaction mixture was extracted with hot water to remove polyphosphoric acid and catalyst. The crude condensation products were purified by passing their benzene solution (combined with the concentrated benzene washings of the aqueous phase) through a short column packed with alumina. The benzene eluate was evaporated under reduced pressure, followed by distillation *in vacuo*. From 7.76 g. (67.5%, calculated for monosubstituted compound) of the crude mixture, 2.5 g. (21.7%) of a major fraction were collected: orange-brown oil, boiling range at 5 mm. 105–112° (lit.[11] b.p. 103–105° (3 mm.) for *t*-butylferrocene).

Anal. Calcd. for $C_{14}H_{18}Fe$ (VIII): C, 69.44; H, 7.49; Fe, 23.07. Found: C, 69.65; H, 7.80; Fe, 22.71.

A second main fraction containing higher substituted ferrocenes was obtained (2.4 g.) but not further examined, distilling at 160–180° (5 mm.).

With gaseous BF_3 as the catalyst in the absence of solvent, with a reaction time of 2 hours and at temperatures below 50–70°, 6.1 g. of crude condensation products were obtained aside from 3.5 g. unreacted ferrocene. The crude mixture was chromatographed on alumina from petroleum ether solution to give two main center cuts, from which, after vacuum stripping of the solvent, reddish-brown oils were isolated showing the analytical data listed below. The yield, respectively, was 1.5 g. (26.7%) and 1.3 g. (23.2%), both calculated for tri-compound.

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[33] Based on weight of ferrocene.

[34] Based on olefin, assuming a weight ratio VI to VII of 1:2.

Anal. Calcd. for $C_{22}H_{34}Fe$ (tributyl-compound): C, 74.57; H, 9.67; Fe, 15.76. Found: C, 74.13; H, 9.38; Fe, 15.82. Calcd. for $C_{20}H_{30}Fe$ (di-/tributyl-compound): C, 73.61; H, 9.27; Fe, 17.12. Found: C, 73.02; H, 8.71; Fe, 17.70.

From the next-to-last cut, besides 0.7 g. of ferrocene crystallizing from the concentrate, 0.5 g. (4.35%) of crude VIII was separated as a reddish oil (*Anal.* Found: C, 69.15; H, 7.25; Fe, 23.41). The final fraction gave only ferrocene (0.5 g.).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON 6, WISC.]

The Preparation and Characterization of the *cis*- and *trans*-Methylsilylcyclohexanes[1]

BY TERRY G. SELIN[2] AND ROBERT WEST

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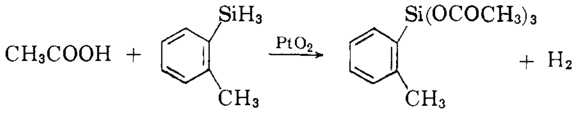
The pure *cis* and *trans* isomers of 1-methyl-2-silylcyclohexane, 1-methyl-3-silylcyclohexane and 1-methyl-4-silylcyclohexane have been prepared and characterized. Hydrogenation of the various tolyltriethoxysilanes over Raney nickel followed by lithium aluminum hydride reduction to the free silanes produced principally the *cis* isomers. The coupling of the 3- and 4-methylcyclohexyl Grignard reagents with silicon tetrachloride again followed by reduction to the silane yielded predominantly the diequatorial isomers. The methylsilylcyclohexanes were resolved and purified by means of preparative gas chromatography. Configurational assignments were made using the modified von Auwers–Skita rule, and were consistent with predictions based on the mode of synthesis. The Grignard reagents from 1- and 2-methylcyclohexyl halides did not couple with silicon tetrachloride but instead reacted to form olefins and Si–H-containing products. 1-Methylcyclohexylmagnesium chloride also reacted abnormally with tetraethoxysilane.

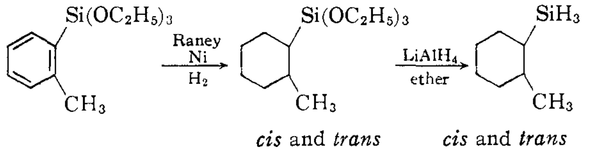
In the course of stereochemical studies concerning the addition of silanes to olefins it was necessary to prepare and identify the *cis* and *trans* isomers of 1,2-, 1,3- and 1,4-methylsilylcyclohexane (*i.e.*, 4-methylcyclohexylsilane). Normally, the syntheses would involve reactions known to be selective or stereospecific thus simplifying the configurational assignment. However, the relatively few methods by which silicon–carbon bonds can be formed limits the synthetic approach in the present case.

The heterogeneously catalyzed hydrogenation of olefins and substituted aromatic compounds frequently gives products corresponding to *cis* addition of hydrogen.[3,4] This is especially true for hydrogenation in the presence of platinum dioxide in acetic acid under mild conditions. Unfortunately, *o*-tolylsilane, triacetoxy-*o*-tolylsilane and triethoxy-*o*-tolylsilane could not be hydrogenated using platinum dioxide in acetic acid at moderate temperatures and pressures (*i.e.*, 30° and 60 p.s.i.g.). The addition of Adams catalyst to solutions of *o*-tolylsilane in acetic acid resulted in the rapid evolution of hydrogen and the formation of triacetoxy-*o*-tolylsilane



Similar reactions have recently been described utilizing chloroplatinic acid as a catalyst.[5]

Raney nickel in absolute ethanol at temperatures of 95–115° readily effected hydrogenation of triethoxy-*o*-tolylsilane. These conditions are similar to those used by Benkeser[6] in selectively hydrogenating trimethylsilylalkynes to the corresponding *cis*-olefins. The product, after reduction to the silane with lithium aluminum hydride, was resolved into two isomeric components by the use of vapor phase chromatography. The *m*- and *p*-tolyltriethoxysilanes were hydrogenated in the same way with two isomers arising in each instance. Samples of the isomers were collected from the gas chromatograph and characterized by their refractive indices, infrared spectra and combustion analyses.



Each set of isomers must necessarily be *cis–trans* pairs since the purity of the triethoxytolylsilanes was demonstrated by lithium aluminum hydride reduction to the tolylsilane followed by gas chromatographic analysis. The chromatogram of each tolylsilane was shown to be characteristic and illustrated the absence of the other isomers except in trace amounts.

A second synthetic approach was also utilized in the preparation of the 1,3- and 1,4-methylsilylcyclohexanes. Coupling of the appropriate Grignard reagent with silicon tetrachloride provided a mixture of the *cis*- and *trans*-methylcyclohexyltrichlorosilanes. The methylsilylcyclohexanes were obtained by lithium aluminum hydride reduction and the isomers were separated by gas chromatography. These isomers were present in different ratios, but were otherwise identical in all respects to those obtained by the hydrogenation route. The Grignard reagent from 2-methylcyclohexyl bromide did not react with silicon tetrachloride or tetraethoxysilane in the expected manner

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