# 188. *Some Reactions of Geranylmagnesium Chloride.*

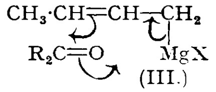
By D. Barnard and L. Bateman.

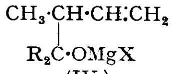
The predominantly primary allylic halide, geranyl chloride (V; X = Cl), is converted by the action of carbon dioxide or ethyl chloroformate on its Grignard derivative into the tertiary allylic acid (VI; X = $CO_2H$). The main by-product of these reactions is a hydrocarbon mixture derived from the combination of two geranyl fragments. This mixture, which is obtainable in better yield by direct methods, contains a higher proportion of *digeranyl* (VIII), relative to iso*digeranyl* (VII) than found in the corresponding product from related systems. The significance of this finding to the mechanism of the coupling process is discussed.

Little progress has been made in understanding the anomalous behaviour of allylic type Grignard reagents, but the recent extensive study of the butenyl derivatives by Young and his associates (reported in a series of papers, *J. Amer. Chem. Soc.*, 1936—1946) has done much to enlarge empirical knowledge. The findings and conclusions of these workers may be briefly summarised thus. In the absence of direct evidence, arguments based on certain reactivity characteristics of benzylmagnesium halides are generalised and are considered to indicate that the Grignard complex prepared from a primary allylic halide (I; X = halogen) itself possesses the primary (I) rather than the isomeric secondary allylic structure (II). No reaction is known, however, whereby replacement of the magnesium halide component yields a substantially pure crotonyl derivative (I). On treatment with water or oxygen, mixtures of isomeric butenes or butenols are obtained, respectively, and coupling reactions likewise give heterogeneous products. On the other hand, reactions with carbonyl compounds lead almost exclusively to the $\Delta^1$-olefinic derivatives (IV), the initial interaction of the two reagents being postulated as (III; $R_2CO$ representing an aldehyde, a ketone, or carbon dioxide). This somewhat unusual behaviour may not only introduce complications in synthetic work, but also lead to erroneous conclusions concerning the structure of allylic halides deduced from such reactions (cf. Bateman, Cunneen and Koch, *Nature*, 1949, **164**, 242; following paper). Lack of diagnostic value is accentuated by the observation (Roberts and Young, *J. Amer. Chem. Soc.*, 1945, **67**, 148) that

$CH_3\cdot CH{:}CH\cdot CH_2X$
(I.)

$CH_3\cdot CHX\cdot CH{:}CH_2$
(II.)


(III.)



$$\begin{array}{l} CH_3\cdot CH\cdot CH{:}CH_2 \\ \quad\;\;\; | \\ R_2C\cdot OMgX \end{array}$$

(IV.)

carboxylation of the Grignard compound prepared from 1-methylallyl chloride (II; $X = Cl$) gives the same acid (II; $X = CO_2H$) as is obtained by submitting the crotyl halide (I; $X = Br$) to the same procedure.

For reasons arising out of the difficulty experienced in preparing homogeranic acid (V; $X = CO_2H$) by standard methods (see the preceding paper), we investigated transformations of the

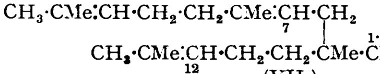
$CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2X$ (V.)

$CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMeX{\cdot}CH{:}CH_2$ (VI.)

Grignard derivatives of geranyl chloride (V and VI; $X = Cl$; containing *ca.* 80% of V, as usually isolated, cf. preceding paper). By infra-red spectroscopy (Barnard, Bateman, Harding, Koch, Sheppard, and Sutherland, *J.*, 1950, 915), structural changes analogous to those observed in the butenyl series were readily followed.

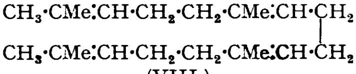
Carboxylation of the Grignard complex gave in 30% yield an acid of appreciably lower boiling point and refractive index than homogeranic acid (V; $X = CO_2H$). Strong infra-red absorption at 908 and 990 cm.$^{-1}$, in agreement with ozonolysis data, identifies the acid as iso*homogeranic acid* (VI; $X = CO_2H$). iso*Homogeranamide* (VI; $X = CO{\cdot}NH_2$), prepared *via* the *acid chloride* (VI; $X = COCl$), differed from its isomer (V; $X = CO{\cdot}NH_2$) (*J.*, 1950, 915) in being a non-crystallisable oil (as is the *p*-bromophenacyl ester), but the rather difficultly crystallisable *anilide*, m. p. 49—50°, may be used for characterisation. Similarly, the addition of the Grignard complex in ether to an ethereal solution of ethyl chloroformate at $-10°$ produced an ester which was not easily purified but which on hydrolysis also yielded *iso*homogeranic acid. Insofar as the isolation and physical examination of the products permitted, no evidence of the formation of the isomeric homogeranic acid in these reactions was obtained. These results show (i) that allylic rearrangement from the primary to the tertiary structure occurs with a facility comparable to that of the corresponding primary–secondary change in similar reactions, and (ii) that chloroformic ester is a reagent of non-carbonyl function which adds at the $\gamma$-carbon atom of the allylic system.

The principal by-product from both the *iso*homogeranic acid preparations was a high-boiling hydrocarbon mixture, separable by efficient fractionation into components boiling at 171·3—171·9°/12 mm. and 178·9—179·2°/11 mm., respectively, which were present in the proportion of *ca.* 2 : 1. No crystalline derivatives of either could be prepared, but analyses, infra-red spectra, and ozonolyses establish beyond doubt that the lower- and higher-boiling fractions are respectively iso*digeranyl* (VII) and *digeranyl* (VIII).



$$\begin{array}{l} CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}\underset{7}{C}H{\cdot}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ \quad CH_3{\cdot}CMe{:}\underset{12}{C}H{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{\cdot}\overset{1\cdot}{C}H{:}CH_2 \end{array}$$

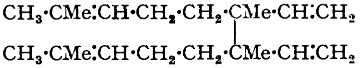
(VII.)



$$\begin{array}{l} CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2 \end{array}$$

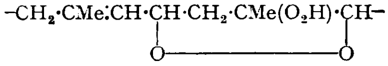
(VIII.)

Ozonolysis of the latter gave succinic acid (92%), but no formaldehyde; the former gave a crystalline acid which analysis indicates to be 2-methylbutane-1 : 2 : 4-tricarboxylic acid and which is clearly the product of oxidative scission at the 7-, 12-, and 1′-double bonds. Consistently, the latter olefin exhibited no marked infra-red absorption at 908 and 990 cm.$^{-1}$ characteristic of the presence of $CHR{:}CH_2$ groups, whereas the former did so with an intensity which virtually establishes its identity as (VII) rather than the related isomer (IX) on this evidence alone.



$$\begin{array}{l} CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{\cdot}CH{:}CH_2 \\ \qquad\qquad\qquad\qquad\qquad\quad | \\ CH_3{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{\cdot}CH{:}CH_2 \end{array}$$

(IX.)

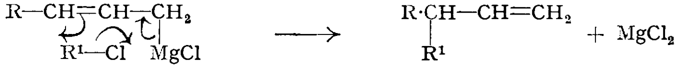


$$\begin{array}{l} -CH_2{\cdot}CMe{:}CH{\cdot}CH{\cdot}CH_2{\cdot}CMe(O_2H){\cdot}CH- \\ \qquad\qquad\qquad\;\; | \qquad\qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad\;\; O \text{---------------------} O \end{array}$$

(X.)

Hydrocarbon mixtures of similar composition were subsequently prepared in yields of the order of 70% by coupling geranylmagnesium chloride over silver bromide and by treating geranyl chloride directly over magnesium; (IX) was not detected. Digeranyl is the lower homologue of the naturally occuring triterpene, squalene, and has proved to be a valuable low-molecular model for studying polyisoprene reactivity. The departure from regular head-to-tail isoprene union throughout the molecule is of minor consequence in this connection. For example its oxidation characteristics closely simulate those exhibited by the long-chain polyisoprenes, gutta-percha and natural rubber hydrocarbons, both kinetically (unpublished work by Bolland and by Bateman, Bolland, and Gee) and in the unusual nature of the peroxide unit (X) in the primary product (Bolland and Hughes, this vol., p. 492; and unpublished).

The formation of the relatively high proportion of (VIII) to (VII) compared with the proportions of the related isomers derived from crotonyl and cinnamyl halides—where the forms corresponding to (VII) predominate to the extent of about 8 : 1 and 4 : 1 respectively—is an interesting feature bearing on the mechanism of the coupling process. Koch (*J.*, 1948, 1111) recently commented on the differences found in the crotonyl and the cinnamyl systems and has suggested that the factor responsible is increased resonance stabilisation of the 3-phenylallyl as compared with the 3-methylallyl grouping. The present finding with a system intermediate in such electronic character between the above groups obviously renders any simple explanation in these terms inadequate. If we assume with Young and Roberts (*J. Amer. Chem. Soc.*, 1946, **68**, 1472) that the Grignard complex possesses an essentially covalent primary allylic structure,* the structural course of the reaction with a simple alkyl halide (*J.*, 1950, 941), just as with ethyl chloroformate and with chloromethyl *n*-butyl ether (Young, Roberts, and Wax, *J. Amer. Chem. Soc.*, 1945, **67**, 841), requires that a " chelated " transition complex similar to that envisaged for carbonyl-compound interaction (Johnson, *J. Amer. Chem. Soc.*, 1933, **55**, 3029; Young and Roberts, *loc. cit.*) promotes combination thus : †



Analogous functioning by an allyl halide can clearly account for a substantial proportion of the unsymmetrical coupled product (as VII) (cf. Johnson in Gilman, " Organic Chemistry," Wiley and Sons, New York, 2nd edn., 1943, p. 1881). However, several independent phenomena—*e.g.*, electro-chemical behaviour indicative of an ionised salt-like structure (Evans and Pearson, *J. Amer. Chem. Soc.*, 1942, **64**, 2865), or the profound influence of extraneous metallic compounds, notably cobaltous chloride, on the course of Grignard reactions, probably caused by initiation of free-radical processes (Kharasch *et al.*; for a summary see *Ann. Reports*, 1944, 195; cf., however, Wilds and McCormack, *J. Org. Chem.*, 1949, **1**, 45), and the small variations in reaction conditions and in the structure of the addenda which determine whether benzylmagnesium halides yield normal or abnormal (*o*-tolyl) products (Austin and Johnson, *ibid.*, 1932, **54**, 647)—clearly signify that Grignard reagents possess diverse reactivity potentialities which are not distinctly separated energetically. Hence, the liberation of allylic free radicals or anions, and their participation in reactions occurring concurrently with the " chelation " process are to be expected. Any tendency exhibited in this respect by the 3-methylallyl system will be enhanced in the 3-phenylallyl and 3 : 3-dialkylallyl systems owing to the increased facility for radical or ionic dissociation afforded by the greater resonance energies of the hydrocarbon fragments thus produced. Since processes involving free allylic ions (see, *e.g.*, Catchpole, Hughes, and Ingold, *J.*, 1948, 8; Campbell and Young, *J. Amer. Chem. Soc.*, 1947, **69**, 688, 3066) or radicals (Bolland and Koch, *J.*, 1945, 445; cf. *J.*, 1950, 941) invariably lead to mixtures of isomeric products, the increased heterogeneity of the hydrocarbon dimers derived from cinnamyl and geranyl halides is understandable. In comparing the last two systems among themselves, however, account must be taken of an important difference in location of the reactivity focus in the respective hydrocarbon radicals or ions. In contrast to the situation prevailing in covalent compounds—where the primary allylic isomer ($\mathrm{CHR{:}CH{\cdot}CH_2X}$) is much the more favoured thermodynamically—experiment shows (Birch, *Faraday Soc. Discussion*, 1947, **2**, 246, where other references are given), and theory readily interprets (de la Mare, Hughes, and Ingold, *J.*, 1948, **17**), that the charge in a 3-arylallyl anion is sited predominantly at $\mathrm{C_{(\gamma)}}$ ($\mathrm{Ar{\cdot}\overset{-}{C}H{\cdot}C{:}CH_2}$), whereas in a 3-alkylallyl anion it is at $\mathrm{C_{(\alpha)}}$ $\mathrm{Alk{\cdot}(CH{:}CH{\cdot}\overset{-}{C}H_2)}$. Accepting that $\mathrm{C_{(\gamma)}{-}C_{(\gamma)}}$ combination is repressed by special factors which cannot now be discussed, it is clear that this distinction—which undoubtedly exists equally in the free-radical analogues—is in accord with the experimental observations concerning the variations in $\mathrm{C_{(\alpha)}{-}C_{(\alpha)}}$ and $\mathrm{C_{(\gamma)}{-}C_{(\alpha)}}$ coupling in the geranyl and cinnamyl systems.

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* Two arguments additional to those advanced by Young and Roberts in support of this assumption warrant consideration. First, reactions of carbonyl compounds with the sodium derivative of allylbenzene in liquid ammonia, *i.e.*, conditions where carbanions certainly participate in the reaction, yield isomeric product mixtures (Campbell and Young, *J. Amer. Chem. Soc.*, 1944, **69**, 3066), in contrast to the remarkably homogeneous secondary allylic products obtained from the corresponding Grignard reactions. Secondly, the formation of structurally analogous carbinols and acids from crotonyl- and cinnamyl-magnesium halides (Gilman and Harris, *J. Amer. Chem. Soc.*, 1931, **53**, 3541) suggests strongly that these two Grignard reagents possess a common basic structure. For reasons outlined later in this paper, covalent attachment of the MgX group to the hydrocarbon component must be inferred, since in dissociated or pseudo-dissociated formulations the location of the principal reactivity centre at different points in the two hydrocarbon units should be reflected in dissimilarities of the product.

† An interpretation of the factors directing R- to the $\gamma$- rather than to the $\alpha$-carbon atoms is given later (*J.*, 1950, 941).

## EXPERIMENTAL.

*Geranyl Chloride.*—The commonly isolated isomeric mixture (cf. preceding paper) containing approx. 80% of the primary geranyl chloride (V; X = Cl) and 20% of the tertiary linalyl chloride (VI; X = Cl) has been used in the present work.

*Geranylmagnesium Chloride.*—The reaction leading to this Grignard reagent is difficult to start and can be markedly inefficient. The following was found to be the most satisfactory procedure. Magnesium turnings (12·5 g.) were covered with anhydrous ether (500 ml.), and 9 g. of geranyl chloride and a crystal of iodine added. A 15% solution of geranyl chloride in ether (2 ml.), vigorously reacting with a small amount of magnesium previously activated by heating with iodine, was added; on gently warming, the main reaction then started. More ether (500 ml.) was added immediately, and geranyl chloride (79 g.) dropped in at a rate sufficient to keep the mixture warm but not refluxing (2—4 hours). An atmosphere of dry nitrogen was maintained in the apparatus throughout these operations. Even in such conditions, much of the geranyl chloride participates in coupling reactions, as shown by the turbidity of the reaction mixture and by the use of less than the theoretical amount of magnesium.

iso*Homogeranic Acid.*—A rapid stream of dry carbon dioxide was passed for 2 hours into an ethereal solution of geranylmagnesium chloride, prepared as described above and maintained at −30°. The resulting mixture was cautiously treated with ice-cold 25% sulphuric acid (150 ml.), and the ethereal layer separated and extracted with 2N-sodium hydroxide. iso*Homogeranic* (3 : 7-*dimethylocta*-1 : 6-*diene*-3-*carboxylic*) *acid* (25·5 g.), thus extracted was isolated in the usual way and had b. p. 99—100°/0·05 mm., $n_D^{20}$ 1·4668 (Found: C, 72·6; H, 10·0%; equiv., 182·4. $C_{11}H_{18}O_2$ requires C, 72·5; H, 10·0%; equiv., 182·0).

iso*Homogeranamide.*—Thionyl chloride (3·5 ml.) was added slowly with stirring to *iso*homogeranic acid (5·8 g.) in ether (10 ml.) and pyridine (2·6 g.). The mixture was finally refluxed for 30 minutes, then cooled, diluted with ether (30 ml.), and filtered. Fractionation of the filtrate gave the *chloride* (5 g.) as a colourless oil, b. p. 49—51°/0·1 mm., $n_D^{20}$ 1·4754. This was added dropwise with stirring to ethanol (35 ml.) cooled to 0° and saturated with dry ammonia. After evaporation of the solvent under reduced pressure, the residue was extracted with ether. Fractionation of the extracts yielded iso*homogeranamide* as an oil (4·4 g.), b. p. 103—105°/0·05 mm., $n_D^{20}$ 1·4920 (Found: C, 72·9; H, 10·7; N, 7·9. $C_{11}H_{19}ON$ requires C, 72·9; H, 10·6; N, 7·8%). The infra-red spectrum of this amide exhibits strong bands at 916 and 1000 cm.$^{-1}$ indicative of the $CHR{:}CH_2$ grouping.

iso*Homogerananilide.*—*iso*Homogeranoyl chloride (2·6 g.) was added slowly to an ice-cold solution of re-distilled aniline (1·84 g.) in ether (5 ml.). After further dilution with ether (20 ml.), the filtered solution was washed with dilute hydrochloric acid, sodium hydroxide solution, and water, dried ($K_2CO_3$), and freed from solvent. The residual oil crystallised slowly on storage at 0°. Fractional elution from alumina using light petroleum (b. p. 40—60°), followed by sublimation at 0·05 mm., yielded the pure *anilide*, m. p. 50·5—51° (Found: C, 79·2; H, 8·7; N, 5·7. $C_{17}H_{23}ON$ requires C, 79·3; H, 9·0; N, 5·5%).

*Ozonolysis of* iso*Homogeranic Acid.*—The acid (1·2 g.) in glacial acetic acid (12 ml.) was treated with a slow stream of ozonised oxygen for 3 hours at room temperature. The resulting solution was dropped slowly into boiling water (100 ml.) containing suspended zinc dust (7 g.), and the volatile distillate passed into a solution of dimedon (2 g.) in aqueous ethanol. The formaldehyde–dimedon compound separated (0·30 g.), m. p. 187—188°, mixed m. p. with an authentic specimen, 188—188·5°.

*Reaction of Ethyl Chloroformate with Geranylmagnesium Chloride.*—The Grignard reagent prepared from geranyl chloride (106 g.) in ether (1250 ml.) was added slowly with stirring to freshly distilled ethyl chloroformate (67 g.) in ether (250 ml.) at −10°. After the addition was complete, the mixture was kept for 1 hour at room temperature and then acidified (dilute sulphuric acid), and the product in the ethereal layer recovered in the usual way. On distillation, two main fractions were collected: b. p. 100—114°/12 mm. (25 g.), and b. p. 108—118°/0·05 mm. (30 g.). The former was hydrolysed by refluxing it with potassium hydroxide (10 g.) in ethanol (200 ml.) for 4 hours. Pure *iso*homogeranic acid, b. p. 89—90°/0·01 mm., $n_D^{20}$ 1·4669 (15 g.) was obtained. The derived chloride and amide were identical with the corresponding compounds prepared as described previously.

*By-products from the Above Reactions of Geranylmagnesium Chloride.*—In all the above Grignard reactions, a considerable amount of a high-boiling hydrocarbon by-product was produced, having b. p. 134—139°/0·5 mm., $n_D^{20}$ 1·4820—1·4838. Analytical data indicated that the *substance* originated in the coupling of two molecules of the Grignard reagent (Found, lower-boiling fraction: C, 87·5; H, 12·4%; *M*, 276. Higher-boiling fraction: C, 87·6; H, 12·4%; *M*, 280. $C_{20}H_{34}$ requires C, 87·5; H, 12·5%; *M*, 274).

*Coupling Reaction of Geranylmagnesium Chloride in the Presence of Silver Bromide.*—Finely ground and vacuum-dried silver bromide (155 g.) was added slowly to a vigorously stirred Grignard solution prepared from geranyl chloride (170 g.) and magnesium (24 g.) in ether (600 ml.) and maintained at 0°. Reaction was made evident by the formation of metallic silver, and completed by refluxing the mixture for 1 hour. After cooling and acidification with dilute sulphuric acid, the ethereal layer was separated and worked up in the usual way. A small portion of the product was freed from volatile material by being kept at $10^{-5}$ mm. in contact with a trap cooled in liquid air, and then distilled at 40°/$10^{-5}$ mm. in a pot-type molecular still, and then had $n_D^{20}$ 1·4828. This sample showed no change in infra-red spectrum and had almost the same *n* (1·4832) after being heated at 175° in a vacuum for 135 minutes, thus proving the absence of isomerisation [*e.g.*, from (IX) to (VIII)] under normal fractionation conditions which might mask the true composition of the coupled product. The bulk of the material was distilled from sodium (b. p. 132—137°/0·5 mm.; 102 g.), and then carefully fractionated through a Fenske-type column packed with glass helices (11 theoretical plates); later fractionations were carried out using a column packed with gauze rings (22 theoretical plates) with similar results. Separation into two homogeneous fractions was achieved with very little fore-run and residue; an intermediate mixture of the two fractions provided the major loss.

iso*Digeranyl* (50 g.) (2 : 6 : 9 : 13-*tetramethyl*-9-*vinyltetradeca*-2 : 6 : 12-*triene*) had b. p. 171·3—171·9°/12 mm., $n_D^{20}$ 1·4821 (Found: C, 87·4; H, 12·6%; *M*, 277. $C_{20}H_{34}$ requires C, 87·5; H, 12·5%;

*M*, 274). The infra-red spectrum reveals the presence of the unsaturated grouping $CH_2{:}CHR$ in addition to the grouping $CHR{:}CR_2$ (see preceding paper). *Ozonolysis.* A slow stream of ozonised oxygen was bubbled through a solution of the hydrocarbon (2 g.) in carbon tetrachloride (20 ml.) at −15° for 4 hours. Removal of the solvent left a semi-crystalline ozonide, which was dissolved in aqueous (50%) acetic acid (20 ml.), 30% hydrogen peroxide was added (10 ml.), and the solution boiled under reflux for 1·5 hours. After the solution had been made alkaline and extracted with ether, the re-acidified solution was extracted with ether to yield an oil which was dissolved in the minimum quantity of light petroleum (b. p. 60—80°) and kept at −5° for several days. Lustrous sheaves of crystals, which separated in small yield, had m. p. 126—127° after high-vacuum sublimation and recrystallisation from light petroleum (Found: C, 47·3; H, 6·1. $C_8H_{12}O_6$ requires C, 47·1; H, 5·9%).

*Digeranyl* (2 : 6 : 11 : 15-*tetramethylhexadeca*-2 : 6 : 10 : 14-*tetraene*) (24 g.) had b. p. 178·9—179·2°/11 m., $n_D^{20}$ 1·4837 (Found: C, 87·3; H, 12·5%; *M*, 277; ⊨, 4·05 by microhydrogenation. $C_{20}H_{34}$ requires C, 87·5; H, 12·5%; *M*, 274; ⊨, 4·00). The infra-red spectrum shows the olefinic unsaturation to be solely of the type $CHR{:}CR_2$ (see preceding paper). *Ozonolysis.* (i) Ozonised oxygen was passed slowly through a solution of digeranyl (0·5 g.) in glacial acetic acid (15 ml.) for 3 hours. The resulting solution was dropped into boiling water (100 ml.) containing zinc dust (7 g.), and the distillate passed into an ice-cold saturated solution of dimedon in aqueous ethanol. No formaldehyde derivative was obtained. (ii) Digeranyl (1·51 g.) in anhydrous carbon tetrachloride (30 ml.) was ozonised at −20° for 4·5 hours. After decomposition of the ozonide in boiling aqueous acetic acid containing hydrogen peroxide as described above and destruction of excess of peroxide by the addition of silver oxide, the solution was freed from soluble or colloidal silver compound with dilute hydrochloric acid, filtered, and concentrated under reduced pressure to *ca.* 2 ml. The succinic acid which separated was sublimed at 0·1 mm. and had m. p. and mixed m. p. 184—185° (Found: C, 41·0; H, 5·2%; equiv., 60. Calc. for $C_4H_6O_4$: C, 40·6; H, 5·1%; equiv., 59). Yield, 0·595 g. (91·5% theoretical).

*Coupling Reaction of Geranyl Chloride over Magnesium.*—Geranyl chloride (210 g.) was converted into the Grignard reagent in the usual manner, using, however, only half the theoretical quantity of magnesium. The product on isolation consisted largely of the digeranyl hydrocarbons (101 g.). Fractionation yielded pure digeranyl (27 g.) and *iso*digeranyl (52 g.).

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