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POLYMETALLOPHILIC ORGANIC COMPOUNDS
II. ORGANOMAGNESIUM INTERMEDIATES OF 2-ALKYL-2-(CHLOROMETHYL)-1,3-DICHLOROPROPANES

EDWARD L. McCAFFERY AND SHALABY W. SHALABY
Chemistry Department, Lowell Technological Institute, Lowell, Massachusetts (U.S.A.)

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In the first paper of this series[1] it was reported that 2-methyl-2-(chloromethyl)-1,3-dichloropropane, (Ia), reacts with magnesium to form the Grignard reagent of 3-methyl-3-butenyl chloride, (IVa). It was suggested that the reactions which preceded the formation of (IVa) included an intramolecular coupling to give (IIa), the combination of (IIa) with additional magnesium to yield the Grignard reagent (IIIa), and the anionic* rearrangement of (IIIa). The study reported here is a summary of our work intended to demonstrate (1) that the reaction of trimetallophilic systems of the neopentyl type with magnesium gives rise to the same rearrangement, and (2) that 1-methyl-1-(chloromethyl)cyclopropane, (IIa), the prototype of the system being reported, is indeed an intermediate which exists prior to the rearrangement of (Ia).

(I) (II) (III) (IV)

$a, R = CH_3;\ b, R = C_2H_5;\ c, R = n\text{-}C_3H_7$

Our postulations appear to agree substantially with the other reports**[,2–10] concerning the rearrangement of cyclopropyl carbanions.

RESULTS AND DISCUSSION

The hydrolysis of the reaction product of 2-ethyl-2-(chloromethyl)-1,3-dichloropropane, (Ib), (formed by the reaction of the corresponding triol with thionyl chloride and pyridine) with two equivalents of magnesium in tetrahydrofuran produced a mixture of three hydrocarbons, the major component (94%) of which was 2-ethyl-1-butene, (VIb). Hydrocarbon (VIb) was identified by comparing its boiling point, refractive index and IR spectrum with established literature data; the yield of the hydrocarbon was estimated from vapor phase chromatographic analysis (VPC) of the volatile products in the hydrolyzate.

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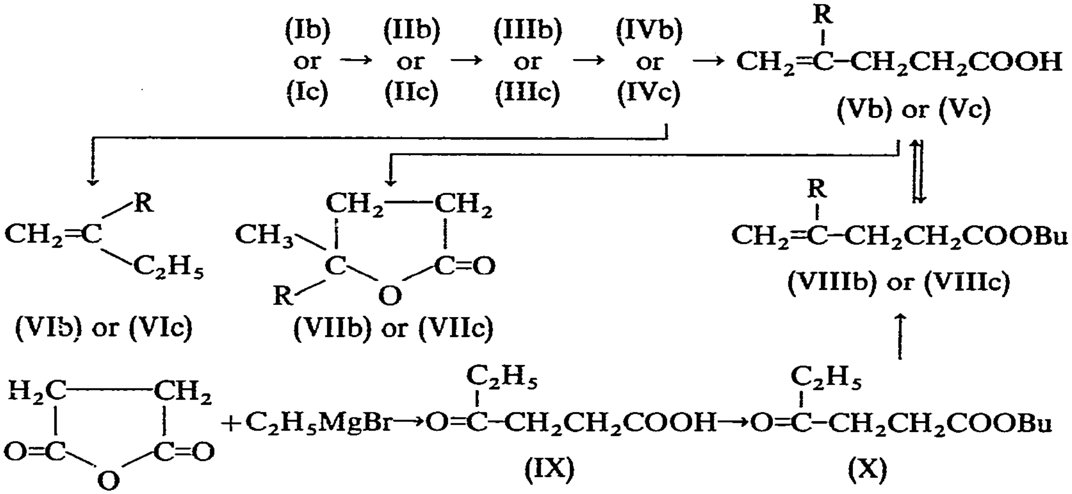
* Although the anionic nature of the Grignard reagent is adopted in this paper, nevertheless, a free radical participation has not been excluded [see G. M. WHITESIDES, F. KAPLAN AND J. D. ROBERTS, *J. Am. Chem. Soc.*, 87 (1965) 2854 and references therein]. Investigation on the structural aspects of the Grignard reagent are being conducted in this laboratory and will be published shortly.

** For a general discussion, see ref. 2.

Carboxylation of the Grignard reagent, (IVb), gave 4-ethyl-4-pentenoic acid, (Vb). The identity of (Vb) was established by conventional analysis and by alternate synthesis. The butyl ester, (VIIIb), formed from the reaction of (Vb) with butanol was found to be identical with the product formed from a Wittig reaction of butyl homolevulinate (X)*; in addition, saponification of (VIIIb), formed from the Wittig reaction, gave (Vb). Heating (Vb) with *p*-toluenesulfonic acid gave γ-ethyl-γ-valeroactone, (VIIb).

Under conditions similar to those used for the reaction of (Ib) with magnesium, 2-n-propyl-2-(chloromethyl)-1,3-dichloropropane, (Ic), was reacted with magnesium and the reaction product was hydrolyzed to give a hydrocarbon mixture composed primarily (95%) of 2-ethyl-1-pentene, (VIc). Carboxylation of (IVc) yielded 4-n-propyl-4-pentenoic acid, (Vc). Compound (Vc), like (Vb), lactonized when heated in the presence of *p*-toleuenesulfonic acid; γ-n-propyl-γ-valerolactone,(VIIc), was produced.



From the data presented for the reaction of magnesium with tetrahydrofuran solutions of (Ib) and (Ic) and from that previously reported[1] for (Ia), one is led to conclude (1) that the length of the alkyl group has no influence upon the course of the reaction of 2-alkyl-2-(chloromethyl)-1,3-dichloropropanes, and (2) therefore, that the mechanism for the rearrangement of (Ia) should be applicable to (Ib) and (Ic).

Since a common reaction path for the formation of system (IV) from the polymetallophilic system (I) was indicated, it was decided to initiate a more detailed study of the intermediates involved in these reactions in order to better understand the mechanism for the rearrangement. Compound (IIa), which was the most important intermediate proposed, was prepared from the corresponding alcohol[11,12] which, in turn, had been prepared by the reduction of 1-methyl-1-carbomethoxycyclopropane, (XI), with lithium aluminum hydride[13]. Compound (XI) was obtained by heating the pyrazoline which resulted from the reaction of diazomethane with methyl methacrylate.

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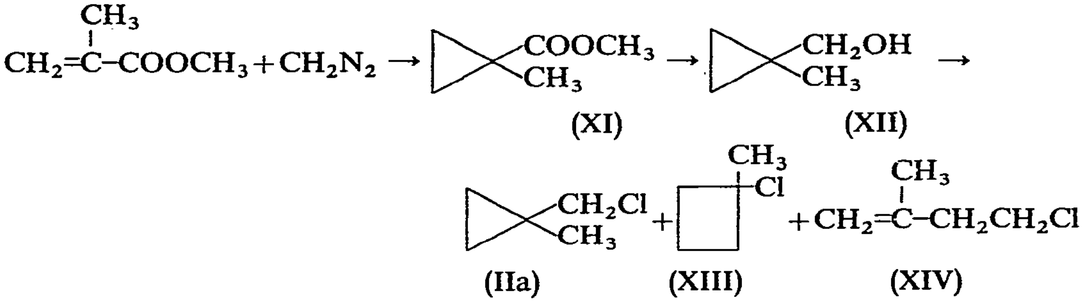
* The parent, homolevulinic acid (IX), was synthesized by reaction of ethylmagnesium bromide with succinic anhydride.



The mixture of products which was obtained by treatment of an ether solution of (XII) with thionyl chloride and tri-n-butylamine was separated into three components on a VPC column. The peaks of the chromatogram, arranged in increasing order of their retention times, were assigned as 1-methyl-1-(chloromethyl)cyclopropane, (IIa), 1-methylcyclobutyl chloride, (XIII), and 3-methyl-3-butenyl chloride, (XIV), from the evidence presented below. From the areas under the peaks of the chromatogram, it was possible to ascertain that the ratio of the components of the mixture was 6 : 3 : 1, respectively.

Unfortunately, we were not able to separate (IIa); even after careful fractionation of the mixture which did remove all of the (XIV), (IIa) was contaminated in every instance with (XIII). However, we believe that the subsequent evidence which is presented will show that, although some (XIII) is present in each reaction mixture, the quantity of reaction product due to (XIII) is predictable, and that the postulation of (IIa) as an intermediate in the Grignard rearrangement is justified.

Compound (XIV) was identified by comparison of its retention time during VPC with the retention time of an authentic sample of (XIV) obtained as a product from the reaction of (IVa) with chlorine.

Nuclear magnetic resonance (NMR) spectra of various mixtures of (IIa) and (XIII), although rather complex, supported the VPC assignment for these compounds. The peaks for the CH_3, CH_2Cl and cyclopropane ring protons in the NMR spectra of (IIa) at τ 8.80, τ 6.65 and τ 9.50, respectively [12,14-17], and the peak for the CH_3 protons in (XIII) at τ 8.30[14-17] were sharp and well defined. The quantities of (IIa) and (XIII) in each of the mixtures analyzed as determined from the integration of the peak areas either by NMR or VPC analysis were identical.

Further support for the contention that (XIII) is 1-methylcyclobutyl chloride may be obtained from the "internal return mechanism" of Roberts and others[2,12,18-26]. According to their arguments, one would expect that treatment of (IIa) with Lucas reagent should result in the partial isomerization to (XIII). Treatment of the 6 : 3 : 1 mixture of isomers with even small amounts of Lucas reagent confirmed our expectation, and suggested a possible explanation of why we were unable to separate (IIa) and (XIII) by distillation.

With the identity of the components of the chloride mixture reasonably well established, the mixture was reacted with magnesium in tetrahydrofuran to determine if (VIa) could be formed from (IIa). In each of four separate runs a three-component hydrocarbon mixture was indicated after VPC analysis of the volatile products from the hydrolyzate. The two least retained peaks of the chromatogram were identified as (XV) and (VIa) by comparing their retention times with authentic samples. The identity of the third peak was deduced in the following way: One of the components of the chloride mixture which gave rise to the hydrocarbon mixture in question was (XIII) which has been shown[3,19] to resist rearrangement under anionic conditions. Therefore, some methylcyclobutane should be formed by the hydrolysis of the Grignard reagent of (XIII). Since there is only one unassigned peak in the hydrocarbon chromatogram, it should be (XVI). The assignment of the peaks in this manner places the compounds in the chromatogram in the order of their boiling points. Further support for the identity of (XVI) can be derived from NMR.

The NMR spectra of a number of hydrocarbon mixtures of different composition were examined and were compared with the spectra of pure samples of (XV) and (VIa). It was observed that in each case a change in the amount of (XVI) in the mixture altered the area under the peaks of the spectrum between τ 7.80 and τ 8.30; this behavior is typical of the few cyclobutane systems that have been reported[12,14–17]. In addition, the change in peak area predicted by NMR agrees quantitatively with the compositions predicted by VPC.

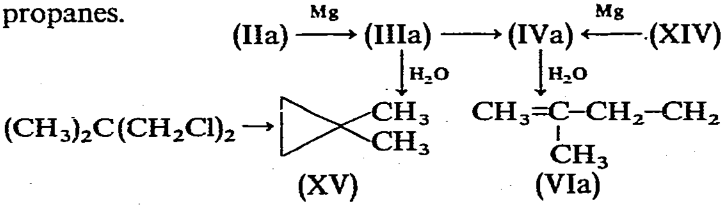
A rather good correspondence between the composition of the hydrocarbon mixtures obtained from mixtures of chlorides of quite different composition and the composition of the hydrocarbon mixtures that would be predicted from the following assumptions: (1) the amount of (XV) produced from a mixture of (IIa), (XIII) and (XIV) should be small since it can only be formed from (IIa), (2) (VIa) should be formed in 90% yield (see next paragraph) from (IIa), with a small quantity also formed from (XIV), and (3) since (XIII) does not rearrange, it should be converted quantitatively to (XVI) while an additional 10% of (IIIa) should isomerize to methylcyclobutylmagnesium chloride which will produce (XVI) upon hydrolysis; is shown in Table 1.

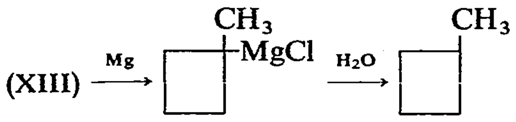
TABLE 1

RELATION BETWEEN THE HYDROCARBONS PRODUCED FROM THE GRIGNARD REACTION OF THE CHLORIDE MIXTURES

Run	*Chlorides in the mixture (%)*			*Hydrocarbons in the mixture (%)*			
				Calculated		*Observed*	
	(II-a)	*(XIII)*	*(XIV)*	*(VIa)*	*(XVI)*	*(VIa)*	*(XVI)*
1	59	35	6	59	41	45	42
2	62	30	8	64	36	58	36
3	31	66	3	31	69	35	62
4	60	30	10	64	36	63	36

When (Ia) was treated with magnesium and tetrahydrofuran and subsequently hydrolyzed, the products of the hydrolysis were identified by VPC analysis as 89% of (VIa), 9% of (XVI) and 2% of (XV). When compound (IIa) was reacted in a similar manner, precisely the same products were formed. It would appear that (II) is an intermediate in the Grignard reaction of 2-alkyl-2-(chloromethyl)-1,3-dichloropropanes.





(XVI)

EXPERIMENTAL

Preparation of 2-ethyl-2-(chloromethyl)-1,3-dichloropropane, (Ib)

2-Ethyl-2-(chloromethyl)-1,3-dichloropropane was prepared in 80% yield from 2-ethyl-2-(hydroxymethyl)-1,3-propanediol* (m.p. 58–60°) by treatment of the triol with thionyl chloride and pyridine following the same procedure as previously reported for the preparation of pentaerythrityl chloride[27]. The reaction product recrystallized from methanol gave colorless crystals, m.p. 42–43° [lit.[28] m.p. 43–44°]. The IR spectrum of (Ib) was similar to that of (Ia)[1].

Preparation of 4-oxohexanoic acid (or homolevulinic acid), (IX), and its n-butyl ester, (X)

Homolevulinic acid was prepared by the addition of ethylmagnesium bromide [made from 55.7 g (0.51 mole) ethyl bromide and 12 g (0.5 mole) magnesium in 200 ml ether] to a suspension of succinic anhydride (50 g, 0.5 mole) in 200 ml of anhydrous ether[29]. The homolevulinic acid obtained by this method (13 g, 20% yield) boiled at 114–116° (2.5 mm) and melted at 37–38° after recrystallization from ether/petroleum ether [lit.[30] m.p. 36–37°; lit.[31] b.p. 115° (2 mm)]. The semicarbazone derivative of the acid melted at 162–164° (lit.[31] m.p. 164–164.2°). The IR spectrum of (IX) was similar to that of levulinic acid.

The n-butyl homolevulinate, (X), was prepared from (IX) and an excess of n-butanol by a trap reflux procedure using benzene as the entrainer and *p*-toluenesulfonic acid as the catalyst. The ester, a colorless liquid, was obtained in 67% yield; b.p. 101–103.5° (3.5 mm); n_D^{25} 1.4292–1.4300 [lit.[31] b.p. 115–117° (9 mm); n_D^{25} 1.4296].

Preparation of 4-ethyl-4-pentenoic acid, (Vb), and its n-butyl ester, (VIIIb)

4-Ethyl-4-pentenoic acid, (Vb), was prepared by the carboxylation of the Grignard reagent (IVb) [formed by the reaction of (Ib) (94.8 g, 0.5 mole) with magnesium (24 g, 1.0 mole) in tetrahydrofuran] following the procedure used for the preparation of 4-methyl-4-pentenoic acid[1]. The reaction product was distilled to give 47.5 g (74% yield) of a colorless liquid, b.p. 98–99° (3.9 mm); n_D^{25} 1.4430. Compound (Vb) appeared to contain unsaturation both from its IR spectrum[32] (1650 cm^{-1}) and from its ability to decolorize bromine in acetic acid. (Found: C, 65.35 $C_7H_{12}O_2$ calcd.: C, 65.63%.) The IR spectrum of (Vb) was similar to that of 4-methyl-4-pentenoic acid[1].

n-Butyl 4-ethyl-4-pentenoate, (VIIIb), was prepared (*a*) from (Vb) and an excess of n-butanol by a trap reflux procedure using benzene as the entrainer and *p*-toluenesulfonic acid as the catalyst. Compound (VIIIb) was obtained in 94.5% yield as a colorless liquid, b.p. 85–86° (3.5 mm); n_D^{25} 1.4341–1.4343. The IR spectrum indicated the characteristic bands for the ester carbonyl and the unsaturation[32] (1740 cm^{-1} and 1650 cm^{-1}). (*b*) Reaction of a benzene solution of methylenetriphenyl-

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* Donated by the Celanese Chemical Company, Chestnut Hill, Massachusetts.

phosphorane, prepared from 5.0 g (1.24×10^{-2} mole) of triphenylmethylphosphonium iodide and 0.285 g (1.24×10^{-2} mole) sodium in 5 ml liquid ammonia with (X) (2.3 g, 1.24×10^{-2} mole) using a procedure previously reported[1] produced compound (VIIIb) in 44% yield, b.p. 84–87° (3.5 mm); n_D^{25} 1.4342–1.4340. The identity of the product was further established by the comparison of its IR spectrum and its retention time determined by VPC[33] (six foot column packed with 10% carbowax on a 60–80 mesh Diatoport W.) with (VIIIb) prepared by method (*a*). Saponification of (VIIIb) (made by *b*) gave (Vb).

Preparation of 2-ethyl-1-butene, (VIb)

2-Ethyl-1-butene was prepared by hydrolysis of a cooled solution of (IVb) [from Compound (Ib) (45.7 g, 0.24 mole) plus magnesium (11.5 g, 0.48 mole) in tetrahydrofuran] as described above. The volatile products were distilled and analyzed by VPC (six foot column packed with 10% diisodecyl phthalate on a 60–80 mesh Diatoport W.) This analysis indicated the presence of three peaks A, B and C besides the one from tetrahydrofuran. The weight of the hydrocarbon mixture (18.39 g, 91% yield) was calculated from the weight of the analyzed distillate. Of the three peaks, A, B and C (arranged in order of their increasing retention times) peak B was due to a hydrocarbon which represented about 94% of the total hydrocarbon mixture*. This major hydrocarbon was isolated in a pure state by fractional distillation as a colorless liquid: b.p. 64–64.5°; n_D^{25} 1.3940–1.3943 (lit.[34] b.p. 65–70°; n_D^{25} 1.3950; lit.[35] b.p. 64.68°; n_D^{25} 1.3938). The identity of this product was further established from its IR spectrum[36] and a positive test for unsaturation with bromine in CCl_4.

Preparation of γ-ethyl-γ-valerolactone, (VIIb)

γ-Ethyl-γ-valerolactone was prepared by heating (Vb) (6.4 g, 0.05 mole) with *p*-toluenesulfonic acid (0.5 g) at 130° to make the two phases compatible, then for one additional hour at 110°. After the reaction mixture had stood overnight it was mixed with water and extracted with ether. The ether layer was extracted with a dilute sodium bicarbonate solution, washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated from the dried solution and the residue was distilled to give 4.2 g (66%) of a colorless liquid, b.p. 70–71.5° (1.7 mm); n_D^{25} 1.4400 [lit.[37] b.p. 105–106° (18 mm); $n_D^{13.7}$ 1.4432; lit.[38] b.p. 76–78° (5 mm)]. The IR spectrum of (VIIb) indicated a carbonyl stretching frequency for the lactone[32] at 1775 cm^{-1}.

Preparation of 2-n-propyl-2-(chloromethyl)-1,3-dichloropropane, (Ic)

2-n-Propyl-2-(chloromethyl)-1,3-dichloropropane was prepared from 2-n-propyl-2-(hydroxymethyl)-1,3-propanediol (m.p. 101–102°) under the same reaction conditions used in the preparation of (Ib). The crude reaction product was distilled to give a pale yellow liquid (75% yield), b.p. 93–94° (2.4 mm); n_D^{25} 1.4803–1.4805. The purity of the product was confirmed by VPC (using a carbowax column). The identity of (Ic) was established both from the similarity of the IR spectrum of (Ic) to those of (Ia) and (Ib), and from elemental analysis. (Found: Cl, 52.66, $C_7H_{13}Cl_3$ calcd.: Cl, 52.33%.)

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* A and B comprised about 1% and 5% of the total area of the peaks.

Preparation of 4-n-propyl-4-pentenoic acid, (Vc)

4-n-Propyl-4-pentenoic acid (Vc) was prepared by the carboxylation of the Grignard reagent (IVc) [formed from 30.5 g (0.15 mole) of (Ic) and 7.2 g magnesium (0.3 mole) in tetrahydrofuran] following the procedure used in preparing (Vb). The crude product was distilled to give 15.8 g (75% yield) of a colorless liquid, b.p. 106–107° (2.8 mm); n_D^{25} 1.4442. The identity of (Vc) was established both from the similarity of its IR spectrum (with the characteristic unsaturation absorption band at 1650 cm^{-1}) to those of (Vb) and 4-methyl-4-pentenoic acid[1] and from the carbon analysis. (Found: C, 67.82. $C_8H_{14}O_2$ calcd.: C, 67.60%.) The product was also found to decolorize bromine in acetic acid.

Preparation of 2-ethyl-1-pentene, (VIc)

2-Ethyl-1-pentene was prepared by the hydrolysis of the Grignard reagent of (Ic) [made from 12.2 g (0.06 mole) of (Ic) and 2.9 g magnesium (0.12 mole) in tetrahydrofuran] under the same conditions described above for (VIb). The organic phase in the hydrolyzate was separated and was shown (by VPC using a diisodecyl phthalate column) to contain a mixture of hydrocarbons responsible for two peaks, A and B. Peak A with the shorter retention time comprises 95% of the mixture as indicated by the total area under the two peaks. The hydrolyzate was acidified with dilute hydrochloric acid. The organic layer of the hydrolyzate was separated, extracted three times with 10-ml portions of water and was dried over anhydrous sodium sulfate. The tetrahydrofuran solution of the hydrocarbon was fractionally distilled and compound (VIc) was obtained (85%) as a colorless liquid, b.p. 93–95°; n_D^{20} 1.4050–1.4053 (lit.[39] b.p. 93.9–94.3°; n_D^{20} 1.4050). The identity of (VIc) was further confirmed both by its IR spectrum [with the characteristic unsaturation band at 1650 cm^{-1} similar to that of (VIb)] and by its ability to decolorize a solution of bromine in CCl_4.

Preparation of γ-n-propyl-γ-valerolactone, (VIIc)

γ-n-Propyl-γ-valerolactone was prepared from (Vc) (6.2 g, 0.044 mole) by treatment with *p*-toluenesulfonic acid (0.5 g) under the same conditions used for the preparation of (VIIb). Compound (VIIc) was obtained in 74% yield as a colorless liquid, b.p. 85–86° (2.3 mm); n_D^{25} 1.4422–1.4425. The product failed to decolorize bromine in acetic acid. The IR spectrum indicated a carbonyl stretching frequency for the lactone at 1775 cm^{-1} and was similar to the spectrum of (VIIb).

Preparation of n-butyl 4-n-propyl-4-pentenoate, (VIIIc)

n-Butyl 4-n-propyl-4-pentenoate, (VIIIc), was prepared from (Vc) and n-butanol under the same conditions described for the preparation of (VIIIb). Compound (VIIIc) was obtained in 81% yield as a colorless liquid, b.p. 92–93° (2.5 mm); n_D^{25} 1.4348. The IR spectrum of (VIIIc) was similar to those of (VIIIb) and n-butyl 4-methyl-4-pentenoate[1]. The spectrum has characteristic IR bands both for the ester carbonyl and for the unsaturation[32] (1650 cm^{-1} and 1745 cm^{-1} respectively). Carbon analysis (Found: C, 72.44. $C_{12}H_{22}O_2$, calcd.: C,72.76%), and the ability of the compound to decolorize bromine in acetic acid were used to support the assignment of the structure.

Preparation of 2-methyl-2-(chloromethyl)-1,3-dichloropropane, (Ia)

2-Methyl-2-(chloromethyl)-1,3-dichloropropane, (Ia), was prepared as previously described[1].

Preparation of methyl 1-methylcyclopropanecarboxylate, (XI)

Methyl 1-methylcyclopropanecarboxylate was prepared from diazomethane (generated from N-nitrosomethylurea) and methyl methacrylate[18] using a modification of the procedure of Siegel and Bergstrom[13]. The pyrazoline which was produced quantitatively (29 g) decomposed when heated to give (XI). This crude decomposition product (21 g) was fractionally distilled and the middle cut was refractionated to give in 51.5 % yield a material boiling at 124–125.5° (760 mm); n_D^{25} 1.4198– 1.4200 [lit.[18] b.p. 55.9–57.1° (60.4–65.6 mm); n_D^{25} 1.4192–1.4193].

Preparation of 1-methylcyclopropanemethanol, (XII)

1-Methylcyclopropanemethanol was prepared in 75% yield by reduction of methyl 1-methylcyclopropanecarboxylate with lithium aluminum hydride[13], b.p. 125–127° (750 mm); n_D^{25} 1.4292–1.4298 [lit.[18] b.p. 125.8–126.3° (739 mm); n_D^{25} 1.4290–1.4292]. The 3,5 dinitrobenzoate of (XII) melted at 88–90° (lit.[18] 88.9–90.7°) after recrystallization from benzene/cyclohexane. A strong band at 1025 cm^{-1} in the IR spectrum of (XII) indicated that a cyclopropane ring[32] was present.

Preparation of 1-methyl-1-(chloromethyl)cyclopropane, (IIa)

1-Methyl-1-(chloromethyl)cyclopropane was prepared by the treatment of an ether solution of 1-methylcyclopropanemethanol (3.6 g, 0.0418 mole) with thionyl chloride and tri-*n*-butylamine[11,12]. A mixture of isomeric chlorides was produced in 82% yield (3.6 g). Analysis of the mixture by VPC revealed that it was composed of three fractions which were presumed to be 1-methyl-1-(chloromethyl)cyclopropane, (IIa), 1-methylcyclobutyl chloride, (XIII), and 3-methyl-3-butenyl chloride, (XVI), in the ratio 6 : 3 : 1, respectively. The mixture was fractionally distilled and the fractions collected at temperatures between 83 and 88° (n_D^{25} 1.4150–1.4308) were found by VPC analysis to contain progressively larger amounts of the higher boiling isomers as previously assigned. A medium strength band at 1020 cm^{-1} and a weak band at 945 cm^{-1} in the IR spectrum of the mixture indicated a cyclopropane and a cyclobutane ring system were present[32].

The NMR spectra* indicated single peaks at τ 8.80, τ 9.50 and another at τ 6.65 which were assigned for the CH_3 group, the CH_2 group in the ring and the CH_2Cl group in (IIa), respectively[12,14–17]. In addition a complex portion of the spectra between τ 7.30 and τ 8.20 and a single peak at τ 8.30 were observed. The single peak was assigned for the CH_3 group and the multiplet between τ 7.30 and τ 8.20 for the CH_2 groups in (XIII)[12,14–17]. The total area under all peaks was measured and was compared with the areas of the peaks at τ 9.50, τ 8.80, τ 8.30 and τ 6.65. These measurements were used to calculate the percentage of (IIa) in the mixture. The NMR data were both qualitatively and quantitatively in agreement with the structural assignments made from the VPC analysis.

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* All the 60 Mc proton NMR spectra of the systems reported in this paper were taken on the A-60 high resolution spectrometer. The samples were examined in carbon tetrachloride with tetramethylsilane as the standard reference.

Preparation of 3-*methyl*-3-*butenyl chloride*, (*XIV*)

3-Methyl-3-butenyl chloride was prepared by bubbling purified chlorine (3.55 g, 0.1 mole) gas through a tetrahydrofuran solution of a freshly prepared sample of 3-methyl-3-butenylmagnesium chloride[1,40] [from 17.5 g (0.1 mole) of (Ia) plus 4.8 g (0.2 mole) of magnesium]. A mixture of chloro compounds was formed and a fraction representing only 5.5% of the yield was collected at 101–103° (761 mm). This fraction was identified as (XIV) on the basis of its physical properties: b.p. 101–103° (750 mm); n_D^{25} 1.4304–1.4308 [lit.[18] b.p. 101–102.7° (729 mm); n_D^{25} 1.4301–1.4305]. A weak band at 1650 cm^{-1} in its IR spectrum was indicative of the unsaturation[32].

Preparation of 1,3-*dichloro*-2,2-*dimethylpropane*

1,3-Dichloro-2,2-dimethylpropane was prepared from 2,2-dimethyl-1,3-propanediol (m.p. 127–129°) by treatment with thionyl chloride and pyridine[41]. The crude product was distilled to give the desired dichloro compound in 80% yield: b.p. 142–143° (755 mm); n_D^{25} 1.4462 [lit.[41] b.p. 144–145° (730 mm); n_D^{25} 1.4460].

Preparation of 1,1-*dimethylcyclopropane*, (*XV*)

1,1-Dimethylcyclopropane was formed by the reaction of 1,3-dichloro-2,2-dimethylpropane and magnesium in tetrahydrofuran. The product was collected in a trap, cooled in a dry ice/acetone bath; b.p. 20° (750 mm) [lit.[18] 19.9–20.0° (738 mm)]. The NMR spectra of (XV) indicated two sharp single peaks at τ 8.95 and τ 9.80 characteristic of the CH_3 group and the ring CH_2 group, respectively.

Isomerization by Lucas reagent

The treatment of 30 drops of the isomeric chloride mixture containing (IIa), (XIII) and (XIV) in the ratio 6:3:1 with 6 drops of Lucas reagent[3,12] resulted in a partial isomerization of (IIa) to (XIII). The change in the composition of the mixture over a period of 2 h was followed using VPC. At the end of this time the mixture contained more than 50% of (XIII) as estimated by measuring the area under the different peaks.

Hydrocarbon formation by hydrolysis of Grignard reagent

The Grignard reagent of (Ia) was made and hydrolyzed as previously reported in the preparation of 2-methyl-1-butene[1]. VPC analysis of the volatile products distilled from the hydrolyzate (collected in trap, cooled in a dry ice/acetone bath) revealed the presence of three hydrocarbon peaks: A (2%), B (89%), and C (9%) arranged in an increasing order of their retention times. Peaks A and B were identified as (XV) and (VIa) from a retention time comparison with authentic samples. The NMR spectra of both a pure sample of (XV) and (VIa) and a few hydrocarbon mixtures of variable composition were made and examined for qualitative and quantitative comparison with the VPC analyses. The assignment of Peak C as (XVI) was made on the basis of the reasons outlined in the discussion. The NMR spectra of a pure sample of (VIa) indicated the presence of a triplet at τ 8.95 and a singlet at τ 8.30, a quartet at τ 8.00 and a singlet at τ 5.35 which were assigned for the protons on C_4, the protons of the CH_3 on C_2, the protons of C_3 and the protons of C_1, respectively[14–17].

The Grignard reagent of several chloride mixtures of varying composition were made and were hydrolyzed under similar conditions used for (Ia). The approximate composition of the resulting hydrocarbons was determined by VPC. In all cases, a mixture of three hydrocarbons was obtained and was shown to contain the same components (differing amounts) as the hydrocarbon mixtures formed from the Grignard reagent of (Ia). The composition of these mixtures and the mixtures of their corresponding hydrocarbons are shown in Table 1.

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SUMMARY

The reactions of 2-ethyl- and 2-n-propyl-2-(chloromethyl)-1,3-dichloropropanes with magnesium in tetrahydrofuran were investigated. Hydrolysis of these Grignard reagents produced 2-ethyl-1-butene and 2-ethyl-1-pentene as the major product in the respective cases; carboxylation of the same organomagnesium compounds gave 4-ethyl- and 4-*n*-propyl-4-pentenoic acid, respectively. These products were consistent with the postulate that the reaction proceeds through formation and rearrangement of an alkyl chloromethyl cyclopropane as previously reported[1] for the methyl homolog. The identity of the proposed compounds was established both by conventional analysis and by alternate synthesis.

A quantitative analysis of the hydrolysis products of the reaction of 2-methyl-2-(chloromethyl)-1,3-dichloropropane with magnesium was carried out using vapor phase chromatography and nuclear magnetic resonance. The analysis revealed that in addition to the expected product, 2-methyl-1-butene, some 1,1-dimethylcyclopropane and methylcyclobutane was also formed. Strong support for the contention that 1-methyl-1-(chloromethyl)cyclopropane was an intermediate in this reaction was realized when it was demonstrated that hydrolysis of the Grignard reagent of this compound resulted in the formation of exactly the same products as were formed from hydrolysis of the parent compound.

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