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GEMINAL DIMETALLIC COMPOUNDS

REACTIVITY OF METHYLENE MAGNESIUM HALIDES AND RELATED COMPOUNDS. A GENERAL CARBONYL OLEFINATION REACTION

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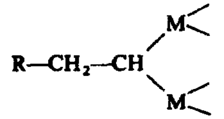
Abstract—The reaction of 1,1-dihalo-alkanes with magnesium and magnesium amalgam has been studied. Methylene bromide and iodide yield, under suitable conditions, a stable solution of methylene magnesium halide which easily olefinates aldehydes and ketones affording the corresponding methylenic olefins in good yields. Other alkylidene halides, under the conditions studied, do not give any stable geminal dimagnesium compound although geminal species are probably present during the *in situ* reaction between alkylidene halides, carbonyl compounds and magnesium amalgam. A general carbonyl olefination scheme taking into account the majority of the known reactions of this kind is proposed.

The chemistry of *gem*-dimetallic compounds is a field which has received only slight attention. Organometallic compounds having two metal atoms bonded to the same C atom have not been generally available, although the first compound of this class, methylene mercuric iodide was synthesized more than eighty years ago.[1]

Apart from early, unlikely appearing syntheses, recently reported gem-dimetallic compounds include methylene dilithium[2, 3] and methylene magnesium,[3] methylene magnesium halides,[4] some diphosphorus,[5] α-metallosilicon,[6] disilicon compounds[6] and di-trialkylstannylmethane.[7] Other compounds of this kind are the gem-diboron[8, 9] and dialuminum compounds[10] arising from dihydroboration and dihydroalumination of terminal acetylenes.

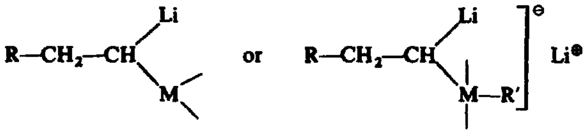
These last two methods afford a class of compounds of general formula:



$$R{-}CH_2{-}CH(M{<})_2$$

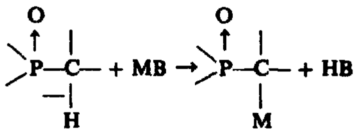
(M = B or Al: R = alkyl or aryl)

which can be converted into new gem-organometallic derivatives by transmetalation. In such a way, ethylene dimercuric chloride was obtained by action of mercuric chloride on the corresponding 1,1-ethylidene-diboronic acid.[11] Moreover, the treatment of gem-diboron[12] and dialuminum compounds[13] with lithium alkyls gives highly active mixed lithium–boron and lithium–aluminium compounds of general formula



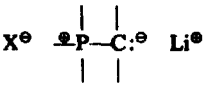
(M = B or Al; R and R' = alkyl).

The very important class of α-metallated PO compounds belongs also to the geminal organometallic compounds.[14] These are easily obtained by metalation of a CH group in a position α to a PO function as present for instance in compounds such as phosphine oxides, phosphinates and phosphonates.



(M = Na, K, Li)

Another interesting group of geminal dimetallic compounds includes the lithium halide adducts to the phosphorus ylides arising from the treatment of a phosphonium salt with lithium alkyls. Although the intimate nature of these compounds, commonly used in the "Wittig reaction", is not yet clear, there are arguments in favour of an α-lithium phosphonium salt structure:

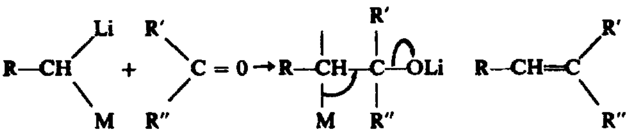


$$X^{\ominus}\ {}^{\oplus}\!\!\overset{|}{\underset{|}{P}}\!-\!\overset{|}{\underset{|}{C}}\!:^{\ominus}\ Li^{\oplus}$$

However, we have to bear in mind, that, in such compounds, the carbon–lithium bond is, in general,[15] strongly ionic, the ylide carbon and the Li atom probably forming a contact or a solvent-separated ion pair.[16]

Apart from the α-metalated PO compounds and the lithium or sodium halogenide adducts of the phosphorus ylides, which are known to olefinate the CO group (the Horner and, to some extent, the Wittig reactions), the reported results of the synthetic value of gem-organometallic compounds have been discouraging. It is reported, for instance, that methylene dilithium and methylene magnesium are very insoluble, pyrophoric materials which react only with water to give methane.[3] The reactivity of the methylene di-Grignard reagents prepared in ether from the corresponding methylene dihalides and Mg was found to be exceptionally low. No reaction was, in fact, observed with benzaldehyde or acid halides even at reflux temperature although on treatment with water methane was evolved.[4]

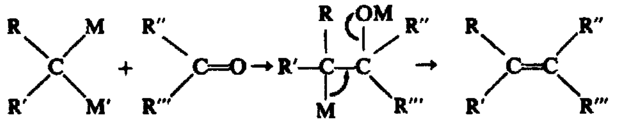
On the other hand, although gem-organodiboron derivatives do not react with carbonyl compounds, at least under normal conditions, the above-mentioned transmetalation products with Bu-Li, easily react with benzaldehyde and ketones yielding olefins probably in accordance with an addition–elimination sequence:[17]



(M = B or —B—R Li: X = Br or I   R = alkyl or aryl

*The results of this investigation allow us to deduce that the olefination of a carbonyl group is not limited to the well-known phosphorus containing reagents, but is a reaction typical of all gem-dimetallic compounds containing at least one carbon–metal bond capable of adding to a carbonyl group.**

A reagent of this kind is expected to add first to a CO bond forming a β-substituted organometallic compound which then eliminates, more or less easily, the heteroatoms to give an olefin:



M and M' = metals.

The type of mechanism involved in the elimination, its rate and stereochemistry and the possible side reactions depend on the nature of the metal and on the reaction conditions.

A few examples of "Wittig-like" reactions of geminal organometallic compounds are now known, which are in agreement with the above-formulated mechanism. It has been observed that geminal dialuminium compounds being more reactive than the corresponding boron analogs can olefinate aldehydes and ketones, although in low yield, without transmetalation. In this case, however, extensive reduction of the carbonyl compounds to the corresponding alcohols occurred.[18]

Geminal dizinc derivatives have been observed to olefinate aldehydes,[19] although a case of a hydroxyl-assisted methylenation of a ketone is now known.[20]

Recently, olefination reactions using geminal lithium–silicon compound have been reported.[21]

Continuing our investigations in this field the possibility of obtaining geminal dimagnesium compounds presented interesting aspects. As a first approach to this class of compounds, the reaction of methylene bromide and iodide with Mg in ethereal solvents was chosen. This reaction has been investigated in the past by several groups of workers but with poor results. In fact, it has been found that methylene bromide and iodide react vigorously with Mg turnings in ether under the usual conditions of the Grignard reaction leading to the formation of two liquid phases. Both of these are completely unreactive towards carbonyl compounds, although on treatment

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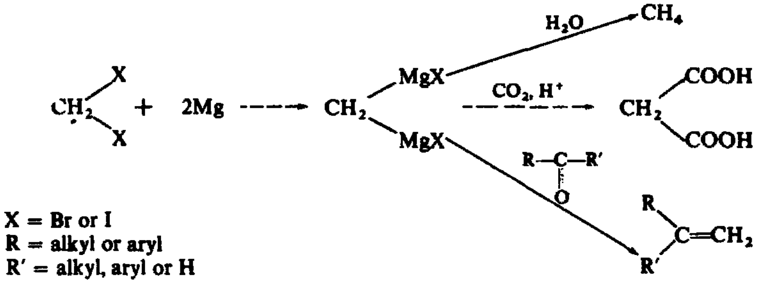
* We define here, purely formally, that a metal is any element less electronegative than carbon.

with water methane is evolved. This fact was interpreted as proof of the formation of a geminal dimagnesium species, although the lack of reactivity towards carbonyls remained unexplained.[4]

On treatment of methylene bromide or iodide with Mg turnings or, even better, with Mg/Hg at room temperature in ether–benzene, a clear, stable solution of an organomagnesium derivative is produced, which reacts with aldehydes and ketones to give the corresponding methylenic olefins in accordance with the above-illustrated scheme. The geminal dimetallic nature of the Grignard reagent has been confirmed by carbonation which gives malonic acid in substantial yields:



The NMR spectrum in ether–benzene (1 : 1) of the reagent obtained from methylene iodide shows two signals. A minor, very small one at low field and of variable intensity can be attributed to a trace of MeMgI. Comparison of the spectrum, in benzene–ether (1 : 1) and toluene–ether (1 : 1) solutions, of an authentic sample of MeMgI with that of our impurity, showed similar chemical shifts, the very small differences being due to small variations in concentration and polarity of the two solutions.

The principal signal occurs at 2·32 δ i.e. ca. 1 ppm higher than that of MeMgI confirming the dimetallic character of the principal product. This behaviour is in accord with that of bridged Me groups as against that of the external ones in $(Me_3Al)_2$.[22]

As the temperature is decreased this signal broadens and at −38° splits into three components with δ 2·17, 2·25 and 2·47 respectively.

This low temperature splitting is probably due to different forms of the dimetallic compound, e.g. dimer–monomer or perhaps to others that at room temperature exchange reciprocally in a shorter time than that required for NMR resonance.

The preparation of the reagent is carried out by adding a 1:1 ether–benzene solution of methylene bromide or iodide to an excess of Mg turnings covered by a small quantity of ether as in the case of a Grignard reagent. Addition of a crystal of iodide facilitates the commencement of the reaction. The use of a well-stirred Mg/Hg (0·5–3 % Mg)* affords, in general, better and more reproducible results. With Mg/Hg, a clear 0·5–0·8 molar solution of the di-Grignard reagent in 50–60 % yield relative to the methylene halide, is easily obtained. The solution of the di-Grignard compound is remarkably stable, the titre being practically unchanged after storing at 0° for several weeks or after boiling at reflux for 15 min.

The methylene magnesium halide does not exhibit carbenoidic character as no reaction is observed on treating the reagent with 1-octene or cyclohexene under a variety of conditions including boiling at reflux for 20 min.

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* The concentration of the Mg/Hg does not appear to be critical.

The methylenation of carbonyl compounds is achieved by mixing, at room temperature under nitrogen or argon, a benzene or benzene–ether solution of the aldehyde or ketone with an equimolar quantity of the reagent. The reaction is complete in a few minutes and the yields are usually good (Table 1). For preparative purposes, however, it is more convenient to prepare the reagent *in situ*. In this case an ether solution containing equimolar amounts of methylene bromide or iodide and the carbonyl compound, is added at room temperature to an excess of a well stirred magnesium amalgam or, less conveniently, to Mg turnings. If necessary the reaction mixture can be boiled at reflux for a few minutes to complete the process.

Some experimental results are summarized in Table 1.

TABLE 1. OLEFINS OBTAINED FROM THE REACTION OF METHYLENE IODIDE AND MAGNESIUM WITH CARBONYL COMPOUNDS

Carbonyl compound	Olefin obtained	Yield %
Dodecanal	1-Tridecene	65[a], 60[b]
Benzaldehyde	Styrene	70[a]
p-Chlorobenzaldehyde	*p*-Chlorostyrene	80[a]
6-Undecanone	1,1-Di-n-amyl-ethylene	30[b]
Cyclohexanone	Methylenecyclohexane	68[a], 63[e]
Benzophenone	1,1-Diphenylethylene	40[a], 30[b]
5α-Cholestan-3-one	3-Methylene-5α-cholestane	67[a], 35[b], 22[d], 52[e]
Cholest-4-en-3-one	3-Methylene-cholest-4-ene	70[a], 33[b]
Pregn-5-en-3β-ol-20-one	Pregn-5-en-3β-ol-20-methylene	80[a, c]
Androst-5-en-3β-ol-17-one	Androst-5-en-3β-ol-17-methylene	45[a, c]

[a] With magnesium amalgam: Method A.

[b] With Mg turnings: Method B.

[c] Three moles of CH_2I_2 and six moles of Mg employed per mole of carbonyl compound.

[d] Method A: THF as solvent.

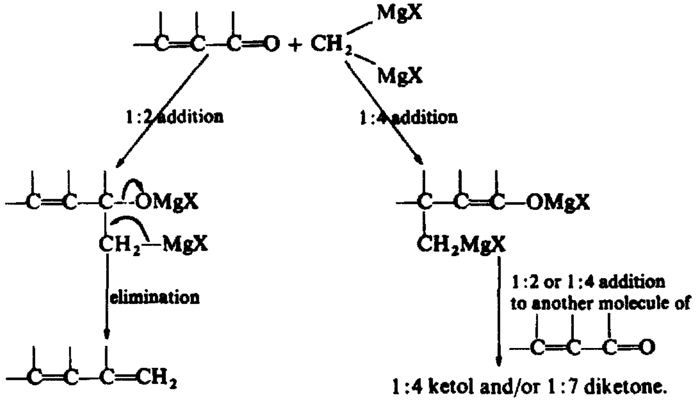
[e] Method A: CH_2Br_2 instead of CH_2I_2.

The yields indicated refer to the *in situ* procedure with Mg/Hg (Method A) and Mg turnings (Method B) respectively. With the use of preformed methylene magnesium halide the yields are generally better and the reaction is cleaner. This latter procedure is, however, less practical if a large scale reaction is performed.

Product identification was achieved either by direct comparison with the authentic material or by spectroscopical, mass spectral and elemental analysis.

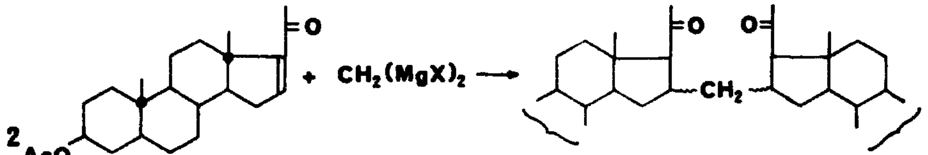
As shown in Table 1 the reaction seems to have a wide range of applicability. Saturated aliphatic and aromatic aldehydes and ketones including steroids can be employed. Very recently a successful application of this reaction on alkaloids has been also reported.[23]

As expected on the basis of the well-known behaviour of Grignard reagents, the reaction of methylene magnesium halides on α,β-unsaturated compounds is, in part, anomalous. In fact, the first attack of the reagent on the carbonyl compound can be a 1:2 or a 1:4 addition. In the first case, elimination of the heteroatoms with consequent formation of the corresponding methylenic olefins is to be expected. In the second case, the 1:4 addition leads to the formation of an intermediate organometallic compound from which the metal atoms cannot be eliminated, as it is in effect a normal Grignard reagent.



This intermediate can add 1:2 or 1:4 to another molecule of the unsaturated carbonyl compound leading, after hydrolysis, to a 1:4 ketol or a 1:7 diketone respectively. The type of addition in the first and, probably, in the second step of the reaction depends on the structure of the unsaturated carbonyl compound. Only a few α,β-unsaturated compounds have been studied to date. The reactions of two of these which are in accord with the above-illustrated reaction scheme will be discussed.

Cholest-4-en-3-one reacts to give good yields of the expected methylenic olefin (1:2 addition followed by elimination) whereas 3β-acetoxy-5α-pregn-16-en-20-one gives only traces of the methylenic olefin, the chief product (30% of the theoretical yield) being a 1:7 diketone arising from two successive 1:4 additions of the reagent to two molecules of the starting α,β-unsaturated carbonyl compound.

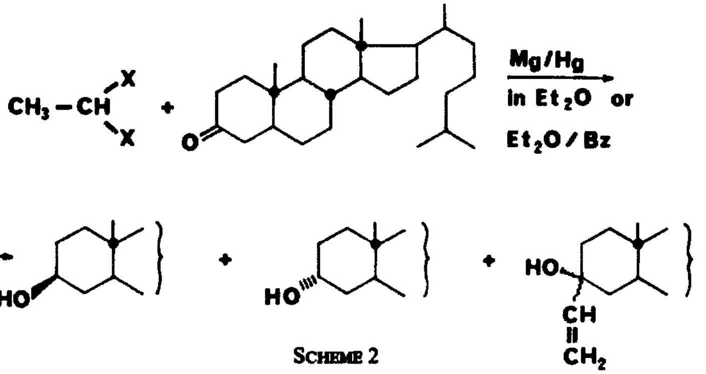


SCHEME 1

At this point the possibility of obtaining other di-Grignard reagents by reaction of Mg or Mg/Hg with 1,1-alkyl-dibromides or diiodides appeared interesting. However 1,1-dibromo- and di-iodoethane, 1,1-dibromoneopentane and benzylidene bromide on treatment with Mg turnings or Mg/Hg in ether or ether–benzene solution under different conditions did not show any evidence, either chemical or spectroscopical, of the formation of a geminal dimetallic species, although in all cases the starting material disappeared completely.

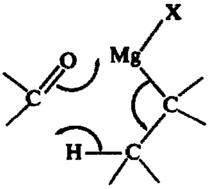
The products formed during this reaction are at present under investigation. Bearing in mind that the dimetallic species eventually formed decompose rapidly, we tried to capture it immediately after its formation *in situ* by treatment of an equimolar ether or ether–benzene solution of geminal dihalogenide and cholest-5α-3-one or benzaldehyde with Mg/Hg at 0°.

With this procedure, ethylidene bromide or iodide and cholestan-5α-3-one gave only traces of the ethylenic olefin expected; it was found that the bulk of the reaction mixture was constituted by three products in approximately equal amounts: 5α-cholestan-3β-ol, 5α-cholestan-3α-ol and a substance, $C_{29}H_{50}O$, to which, on the basis of its chemical and spectroscopical behaviour, could be attributed the structure of 3ξ-vinyl-3ξ-hydroxy-5α-cholestane.



Scheme 2

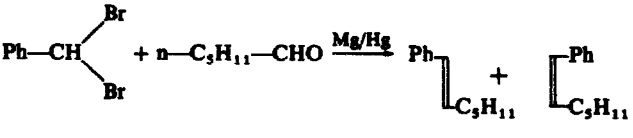
The extensive reduction of the CO group is not exceptional, such a reaction always taking place if the Grignard reagent is sterically hindered. For this type of reduction a mechanism involving the transfer in a cyclic 6-membered transition state of a hydride ion in the position β to the metal has been proposed:[24]



In our case, if the reduction is brought about by the expected di-Grignard species, the hydride transfer is coupled with the formation of a molecule of vinyl magnesium halide, which can obviously react with another molecule of cholest-5α-an-3-one to give the isolated 3ξ-vinyl-3ξ-hydroxy-5α-cholestane.

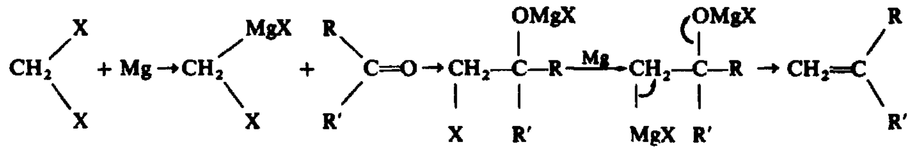
The formation of this compound as well as the other above-mentioned products may, therefore, be explained as resulting from the reaction of a geminal dimetallic intermediate.

In accordance with the proposed mechanism, the *in situ* reactions of benzylidene bromide and hexanal with Mg/Hg did not show any trace of the corresponding alcohol although the expected olefination product (*cis-trans* n-amyl-styrene) were isolated in poor yields (about 15 %).



trans-cis ≃ 1:1

The above reported experimental results do not rule out an alternative sequence involving the attack of an α-halo-alkyl Grignard reagent followed by a magnesium-induced elimination reaction.



Recently α-halomethyl-Grignards have been obtained by Villieras[25] as unstable substances (for instance the decomposition of I-CH_2MgCl in ether is rapid at −55°) which react in a normal way with carbonyl compounds to give the corresponding halohydrins.

On the other hand 1-phenyl-1-iodoethanol and the corresponding bromo derivative easily afford styrene on treatment with Mg/Hg under the conditions described above.

At the moment we cannot distinguish with certainty between these two routes and further work is being carried out to clarify the mechanism of reaction.

EXPERIMENTAL

General procedure for the synthesis of methylenic olefins

Method A: in situ *with magnesium amalgam.* In a 3-necked flask equipped with mechanical stirrer, reflux condenser and dropping funnel, Mg/Hg was prepared by stirring 200 g Hg and 600 g (25 m atoms) Mg turnings, under argon. To the well-stirred amalgam, 20 ml of dry ether was added, followed by a soln containing methylene iodide (11 mmoles) 0·9 ml and the appropriate carbonyl compound (10 mmoles) in 25–30 ml of dry ether during a period of 15 min at room temp. The mixture was allowed to remain at room temp for an additional hr, then poured into ice-water and extracted with ether. After washing with water, drying and evaporating, the products were isolated by chromatography on silica gel 0·05–0·2 mm (Merck). Only the methylene compounds were investigated.

Method B: in situ *with magnesium turnings.* 600 mg Mg turnings in 15 ml dry ether and a trace of I_2 were placed in a flask equipped with magnetic stirrer and reflux condenser under N_2. The soln of carbonyl compounds and methylene iodide (or bromide), in the same quantity as in method A, was added with stirring over 15 min. The reaction mixture was refluxed for 2 hr, worked up in the usual manner and the products isolated as in method A. The yields and modifications of these experiments are reported in Table 1. All products listed were identified by proton NMR, UV, IR, mass spectra, elemental analysis and by comparison with literature data or with the authentical materials.

1,1-*Di-n-amyl-ethylene.* This hydrocarbon was obtained in 30% yield (mg 475) from g 1·58 of 6-undecanone using method B. b.p. 110 (30 mm). (Found: C, 85·18; H, 14·56; mol. wt. (mass spectroscopy), 168. Calc for $C_{12}H_{24}$: C, 85·63; H, 14·37; mol. wt. 168); IR: 892, 1652 cm^{-1} (methylene). The NMR spectrum was in agreement with this structure.

Solution of methylene dimagnesium iodide. 25 ml of a benzene–ether 1:1 soln of 1·8 ml (22 mmoles) methylene iodide was added to an amalgam prepared as described (method A) from 200 g Hg and 1·2 g (50 matons) Mg covered with 25 ml benzene–ether (1:1). During the addition the temp was kept at 15°. After 30 min, stirring was stopped and the organic phase removed and centrifuged under argon. A 40 ml portion of the soln was poured onto solid CO_2. Acidification and continuous extraction with ether gave, after evaporation of the solvent, 540 mg of malonic acid m.p. 134° not depressed on mixing with an authentic sample. The remaining soln was tested for reactivity with 5α-cholestan-3-one. The hydrocarbon isolated, in a yield of about 80% relative to the ketone, was identical with 3-methylene-5α-cholestane obtained by method A.

The NMR spectrum at room temp of a 0·36M soln in ether–benzene (1:1) of methylene magnesium iodide determined on a Varian HA-100 instrument shows signals at higher fields than the protons of TMS: 1·56 δ (MeMgI impurity), 2·32 δ ($CH_2(MgI)_2$). At −38° the signal at 2·32 δ splits into three components with

2·17, 2·25 and 2·47 δ. A MeMgI soln in the same solvent mixture shows signals at 1·18 δ (concentration of the soln: 0·75M) or at 1·05 δ (concentration: 0·31M).

The titre of the soln was determined each time by measuring the volume of the gas evolved on reaction with water. This gas was shown by gaschromatography to consist of 97% of methane.

The yield of the reagent relative to the methylene magnesium iodide are in the order of 50–80% strongly dependent from the experimental conditions. In order to obtain the best results the solvents and the methylene iodide should be carefully dried and purified and any trace of moisture and oxygen is to be avoided.

In the same way ether–benzene solns of methylene magnesium bromide have been prepared.

Elimination of halohydrins. 1-Phenyl-2-iodoethanol[26] gave styrene in 45% yield by method A. The same hydrocarbon was also obtained from 1-phenyl-2-bromoethanol[27] (7% yield).

Reaction of cholestanone with ethylene bromide and magnesium amalgam. 3·85 g (10 mmoles) cholestanone and 1·1 ml (12 mmoles) $MeCHBr_2$ in ether soln were added to a Mg/Hg prepared as in method A. The reaction mixture was stirred at room temp for 8 hr, then poured into ice-water and worked up in the usual manner. From a chromatographic separation on silica gel the following products were isolated: 100 mg of a hydrocarbon of mol. wt. 398 (mass spectroscopy) which is probably the true olefination product; 880 mg of 3ξ-vinyl-3ξ-hydroxy-5α-cholestane m.p. 115–120°, $[\alpha]_D = +24°$ ($CHCl_3$), IR 3450 cm^{-1}. (Found: C, 83·63; H, 12·20; O, 4·60; mol. wt. 414–418 in benzene soln. Calc for $C_{29}H_{50}O$: C, 83·99; H, 12·15; O, 3·86%; mol. wt. 414·69), mass spectrum: peak at 396 (M − 18); NMR in accordance with the structure proposed; 700 mg of 5α-cholestan-3α-ol and 2·2 g of 5α-cholestan-3β-ol. The assigned structures of these two last compounds being confirmed by mixed m.p. and comparison of the IR spectra with the authentic compounds.

Reaction of 5α-pregn-16-en-3β-ol-20-one acetate and methylene magnesium iodide. 760 mg (2 mmoles) of the α,β-unsaturated ketone was added dropwise to 20 ml of an ether–benzene soln of 0·54M di-Grignard reagent. After reaction the product mixture was worked up, acetylated in pyridine with Ac_2O and chromatographed on silica gel. The principal product isolated (220 mg): m.p. 255–260° (dec); Calc mol. wt. 732, mass wt. 732, mol. wt. determined in benzene soln 723·5; $[\alpha]_D = +34·4$ ($CHCl_3$); IR, 1740 cm^{-1}, 1710 cm^{-1}. (Found: C, 75·70; H, 9·78; O, 13·58. $C_{47}H_{72}O_6$ requires: C, 77·00; H, 9·90; O, 13·10%). The product was saponified: IR 3400 cm^{-1}, 1690 cm^{-1}; Calc mol. wt. 648, mass wt. 648.

Reaction between benzylidene bromide and hexanal. The reaction was carried on by method A. Filtration through silica gel gave, in 15% yield, a 1:1 mixture of two hydrocarbons which were separated by means of preparative gas chromatography and identified by comparison with authentic samples of *cis* and *trans* 1-phenyl-hept-1-ene.

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