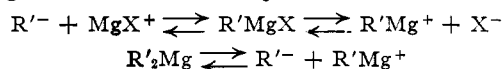


It is realized that the simple ionization of the Grignard reagent to R'^- and MgX^+ is an oversimplification of the facts and accordingly R^- is meant to imply the carbanion or its equivalent. From kinetic data on the reaction of methylmagnesium bromide on acetone, Aston and Bernard¹⁸ demonstrated that the rate controlling step in the reaction is the disruption of $(CH_3)_2Mg \cdot MgX_2$ into its molecular species. Evans and Pearson¹⁹ showed that electrolysis and transference studies of Grignard reagents indicated the equilibrium reactions



Chemical evidence which substantiates the presence of R'^- and X^- is found in the reaction of a Grignard reagent with ethylene oxide.²⁰ In view of the lack of complete evidence, the simple ionization as pictured by Alexander¹¹ is deemed applicable for this discussion.

In the optimum conditions described for the synthesis of straight chain or highly branched ketones, the Grignard reagent is added to the acyl halide which contains a large excess of uncomplexed molecules for every molecule which has coordinated with the ferric chloride. Consequently, the failure to produce significant amounts of reduction products can only be ascribed to the comparative rates of the addition and reduction reaction. According to this proposed ionic mechanism the presence of the catalyst should have a retarding effect on the reduction reaction and should increase the rate of the addition reaction, as has been observed. The effect of both an electrophilic and a nucleophilic reagent on reaction rates has been discussed by Swain.²¹

The work of Entemann and Johnson²² supports the premise that addition to the carbonyl linkage of the acyl chloride is an integral part of the reaction.

Experimental

The fractionating columns were of the total-condensation, variable take-off type, packed with $3/16$ -in. single-turn glass helices. The dimensions of the packed section (cm.) for column I and column II are 70×1.5 and 90×2.2 , respectively.

For runs involving cuprous chloride, a 7-l., water-jacketed, copper vessel (11 in. \times 8 in.) stirred with an off-center propeller driven by a $1/4$ -h.p. motor was employed. For runs using ferric chloride or other catalysts, a 3-l. flask equipped with a mercury-sealed stirrer, reflux condenser, dropping funnel, nitrogen-inlet tube and thermometer well was used. For low temperature runs, the flask was maintained in a Dry Ice and methanol-bath or a water-ice-bath.

The Grignard reagents were synthesized in large preparations and were stored in glass carboys under a nitrogen atmosphere. Only clear filtered reagent was used. Representative yields of reagents are as follows: from *n*-butyl chloride, 92%; from *t*-butyl chloride, 86%; from isobutyl bromide, 90%; from *t*-amyl chloride, 78%; and from triptyl chloride, 61%.

Acetyl chloride (Eimer and Amend) was purified by frac-

tionation through column I (b.p. 51°). The remaining acyl halides were synthesized from the appropriate acid and thionyl chloride: *n*-butyryl chloride, b.p. 101.5° , 58% yield; isobutyryl chloride, b.p. 92° , 75% yield; 2,2-dimethylbutanoyl chloride, b.p. 132.5° , no yield calculated; and 2,2,3-trimethylbutanoyl chloride, b.p. 153° , 65% yield. The preparation of trimethylacetyl chloride has been previously described in detail.¹

The metallic halide catalysts were rendered anhydrous. The solvent was ethyl ether (Mallinckrodt, Analytical Reagent).

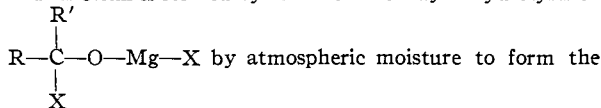
Two runs which are illustrative of preferred syntheses are described below and can be considered typical of the numerous experiments run under a wide variety of conditions.

Preparation of 2-Hexanone.—Into a 3-l. flask was charged 471 g. (6 moles) of distilled acetyl chloride, 1.0 l. of ethyl ether and 3 g. of ferric chloride. The flask was cooled to -70° in a Dry Ice-methanol-bath while maintaining the contents of the flask under a nitrogen atmosphere. Over a five-hour period two moles of *n*-butylmagnesium chloride (approximately 3 *M*) was added.

Approximately five minutes after the addition of the Grignard reagent was complete, the reaction mixture was poured onto ice and agitated thoroughly. The light yellow solid which was present dissolved without difficulty. The solution was neutralized with sodium carbonate, and the combined water and ether layers were steam distilled. The water layer from the distillate was separated from the product layer and extracted with three 200-ml. aliquots of ethyl ether. The extracts were added to the main product layer. After the solvent had been removed through column I, the product was precisely fractionated through column II. Approximately 10 g. of material was collected over the first 81° temperature rise; the complexity of this material defied separation and identification. At 126° 2-hexanone, 142 g. (1.44 moles, 72% yield), was obtained. It formed a 2,4-dinitrophenylhydrazone, m.p. $107-108^\circ$. A mixture with an authentic sample of 2-hexanone 2,4-dinitrophenylhydrazone, m.p. 108° , showed no depression. It also furnished a semicarbazone, m.p. and mixed m.p. with an authentic sample of 2-hexanone semicarbazone, 125° . The refractive index, n_D^{20} , was 1.4001; literature values b.p. 127^{23} and n_D^{20} 1.4002.²⁴

After a second 10-g. fraction boiling over a 36° range, 28 g. of an olefin was obtained, tentatively identified as 5-methyl-4-nonene, b.p. 162° (730 mm.) and n_D^{20} 1.4288. Literature values for this compound are b.p. 68° (24 mm., calculated as 165° at 760 mm.) and n_D^{20} 1.4288.²⁵

This olefin is formed by either of two ways: hydrolysis of



ketone which subsequently reacts with the Grignard reagent, or by direct coupling of this compound to produce the tertiary alcohol complex. Dehydration of the alcohol during fractionation would give 5-methyl-4-nonene.

The material balance is 190 g. or 95% recovery.

The effect of the various catalysts is shown in Table II. All reactions were run using comparable technique in reaction conditions.

TABLE II

Catalyst ^a	Addition temp., °C.	Yield of 2-hexanone, %	Catalyst ^a	Addition temp., °C.	Yield of 2-hexanone, %
Cu_2Cl_2	34	12	$MnCl_2$	15	19
$CoCl_2$	34	4	$ZnCl_2$	15	15
Cu_2Cl_2	15	25	$CoCl_2$	15	13
$FeCl_3$	15	47	$AlCl_3^b$	15	0
$AlCl_3$	15	34	$MgBr_2^b$	-65	.. ^c

^a Anhydrous catalyst, 1.5 g./mole acyl halide. ^b 1 Mole catalyst/mole acyl halide. ^c The product from this run underwent extensive decomposition before fractionation.

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The increase in yield with lowered temperature is shown in Table III. The catalyst concentration was 1.5 g./mole of acetyl chloride.

TABLE III

Addition temp., °C.	Catalyst	Yield of 2-hexanone, %	Addition temp., °C.	Catalyst	Yield of 2-hexanone, %
34	Cu ₂ Cl ₂	12	34	CoCl ₂	4
15	Cu ₂ Cl ₂	25	15	CoCl ₂	13
5	Cu ₂ Cl ₂	37	15	FeCl ₃	47
-30	Cu ₂ Cl ₂	41	-65	FeCl ₃	72
-65	Cu ₂ Cl ₂	48	-65	None	31

TABLE IV

RCOCl/RMgX (moles/mole)	Addition temp., °C.	Catalyst, g./mole RCOCl	Yield ^a of 2-hexanone, %
1/1	5	1.5 Cu ₂ Cl ₂	37
3/1	5	1.5 Cu ₂ Cl ₂	39
1/1	15	1.5 FeCl ₃	47
3/1	15	1.5 FeCl ₃	50
3/1	-65	1.5 FeCl ₃	72
3/1	-65	None	31
3/1	-65	10.0 FeCl ₃	68

^a The small variance in yield between comparable reactions is presumably the reproducibility of a single reaction.

The effect of varying ratio of reactants is shown in Table IV.

The fact that the reaction proceeds instantaneously was shown in three reactions using FeCl₃ at -65° (Table V).

TABLE V

Period of RMgX addition, hr.	Additional stirring time at -65°	Heating period at 100°	Yield of 2-hexanone, %
5	12 (hr.)	3 (days)	72
5	12 (hr.)	0	66
5	5 (min.)	0	71

The time of addition is apparently limited only by the efficiency of heat transfer during this very exothermic reaction.

Preparation of Hexamethylacetone.—To a solution of 241 g. (2 moles) of trimethylacetyl chloride in 2 l. of ethyl ether was added 2 g. of ferric chloride, and the reactants were heated to reflux. During 2 hours, 2 moles of *t*-butylmagnesium chloride (approximately 3 *M*) was added. The reactants were stirred at reflux temperature for an additional hour and the mixture was then decomposed by the addition of a water-ice mixture. The layers were separated and the product was fractionated through column II to give 477 g., 1.68 moles, of hexamethylacetone, b.p. 152°, *n*_D²⁰ 1.4192. The yield is 84%. The identification of this product has been described.¹

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Derivatives of Sulfenic Acids. XI. Reactions of Sulfenyl Halides with the *cis*- and *trans*-2-Butenes

BY NORMAN KHARASCH AND ANTON J. HAVLIK¹

RECEIVED MARCH 20, 1953

2,4-Dinitrobenzenesulfonyl chloride, bromide and thiocyanate, 2-nitrobenzenesulfonyl chloride, *p*-toluenesulfonyl chloride and 2,4-dichlorobenzenesulfonyl chloride react with the *cis*- and *trans*-2-butenes to give excellent yields of the corresponding 1:1 adducts. On the basis of melting points, oxidations to different sulfones, refractive indices and infrared spectra, it is concluded that the products are diastereomeric racemates. The probable mode of formation of the adducts is briefly discussed.

While the reaction of sulfenyl halides with olefins is now well known,² the only example involving a *cis-trans* olefin pair is the characterization of the isomeric 2-phenyl-2-butenes, reported by Cram.³ In undertaking our work on this aspect of sulfenyl halide chemistry, it therefore seemed desirable to investigate, initially, the reactions of several sulfenyl halides with the simplest *cis-trans* olefin pair. Table I summarizes the results with six selected sulfenyl halides. The additions of the halides to the 2-butenes were carried out at room temperature, in dry ethylene chloride solutions, in a gas-addition apparatus similar to the one described by Joshel.⁴

The six adducts from 2,4-dinitrobenzenesulfonyl chloride, bromide and thiocyanate and the 2-butenes were excellent solid derivatives. The melting points of the corresponding adduct pairs differed between themselves, and mixtures of the isomeric adducts showed decided melting point depressions. The adducts from 2-nitrobenzenesulfonyl chloride, 2,4-dichlorobenzenesulfonyl chloride and *p*-toluenesulfonyl chloride, however, were

liquids. Since the four adducts resulting from 2-nitrobenzenesulfonyl chloride and 2,4-dichlorobenzenesulfonyl chloride were readily converted to corresponding pairs of sulfones, the isolations of the pure 1:1 adducts were not effected in these cases. For the 1:1 adducts from the 2-butenes and *p*-toluenesulfonyl chloride, however, isolations of the pure liquids were carried out, since conversion to a solid sulfone could be effected only for the adduct from the *trans*-2-butene. The adduct of *p*-toluenesulfonyl chloride and *cis*-2-butene did not yield a solid sulfone, even though identical conditions were used to carry out the oxidation as were used in the formation and isolation of the sulfone from the isomeric *trans* adduct. While this difference implied that the *p*-toluenesulfonyl chloride adducts were not identical, the variation in indices of refraction of the pure adducts, as well as the results of the infrared spectrograms (Fig. 1) definitely confirmed the implied difference.⁵

(5) Infrared spectrograms in the 2 to 16 μ region were also obtained for all the other 1:1 adducts or corresponding sulfones of Table I. While the differences between the *cis* and *trans* adducts of *p*-toluenesulfonyl chloride (Fig. 1) are more marked than those from any other pair of the products, the results in every case support the conclusion that the products stemming from *cis*-2-butene are different from the corresponding products resulting from *trans*-2-butene. The remaining spectra, together with those of the sulfenyl halides and several groups of related products stemming from the latter, will be described in a later paper.

(1) Atomic Energy Commission Predoctoral Fellow, University of Southern California, 1951-1953.

(2) N. Kharasch and C. M. Buess, *THIS JOURNAL*, **71**, 2724 (1949) and references cited therein. Cf. also *ibid.*, **74**, 3422 (1952).

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