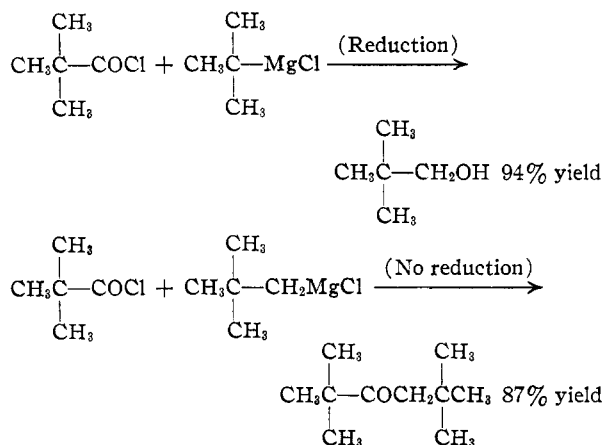# Grignard Reactions. XXI.[1] The Synthesis of Aliphatic Ketones[2]

BY WILLIAM C. PERCIVAL,[4] ROMEO B. WAGNER[3] AND NEWELL C. COOK
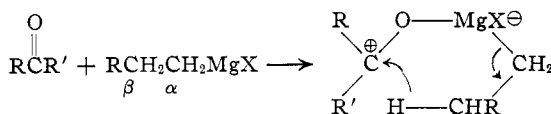
RECEIVED FEBRUARY 24, 1953

The reaction of a Grignard reagent with an acyl halide to produce a ketone in good yield has been studied by effecting varied conditions of temperature, catalyst and molar ratios of reactants. Results show that it is now possible to prepare straight chain and highly branched aliphatic ketones in good yields, only small amounts of reduction products being formed. Chemical evidence indicates that this reaction most probably takes place through an ionic mechanism.

Introduction

The great majority of work on the reaction of an acyl halide with a Grignard reagent has dealt with the reduction reaction in which aldehydes and secondary alcohols are formed. Gilman[5] and Kharasch[6] studied the reducing action of alkyl and aryl Grignard reagents, and Whitmore[7] conducted a large number of similar experiments with aliphatic compounds. Whitmore and George[8] showed that at least one hydrogen on the β-carbon of the Grignard reagent is necessary for reduction to occur.

$$\begin{array}{c} CH_3 \\ | \\ CH_3C-COCl \\ | \\ CH_3 \end{array} + \begin{array}{c} CH_3 \\ | \\ CH_3C-MgCl \\ | \\ CH_3 \end{array} \xrightarrow{\text{(Reduction)}}$$

$$\begin{array}{c} CH_3 \\ | \\ CH_3C-CH_2OH \quad 94\% \text{ yield} \\ | \\ CH_3 \end{array}$$

$$\begin{array}{c} CH_3 \\ | \\ CH_3C-COCl \\ | \\ CH_3 \end{array} + \begin{array}{c} CH_3 \\ | \\ CH_3C-CH_2MgCl \\ | \\ CH_3 \end{array} \xrightarrow{\text{(No reduction)}}$$

$$\begin{array}{cc} CH_3 & CH_3 \\ | & | \\ CH_3C-COCH_2CCH_3 \quad 87\% \text{ yield} \\ | & | \\ CH_3 & CH_3 \end{array}$$

The formation of a six-membered ring was postulated for the transfer of the hydride ion in the reduction of ketones or acyl halides[9]

$$\begin{array}{cc} O \\ \| \\ RCR' + RCH_2CH_2MgX \\ \beta \quad \alpha \end{array} \longrightarrow \begin{array}{c} R \quad O\text{---}MgX^{\ominus} \\ \diagdown \overset{\oplus}{C} \diagup \quad \diagup CH_2 \\ \diagup \diagdown \quad \diagdown \diagup \\ R' \quad H\text{---}CHR \end{array}$$

where R′ = alkyl or halogen. Mosher and La Combe[10] present convincing evidence in favor of

(1) For Paper XX, see N. C. Cook and W. C. Percival, THIS JOURNAL, **71**, 4141 (1949).

(2) From the Ph.D. thesis submitted by W. C. Percival to the Graduate School of The Pennsylvania State College, June, 1951.

(3) Hercules Powder Company, Wilmington, Delaware.

(4) Allied Chemical and Dye Fellow, 1950-1951.

(5) H. Gilman, R. E. Fothergill and H. H. Parker, *Rec. trav. chim.*, **48**, 748 (1929); H. Gilman and M. L. Mayhue, *ibid.*, **51**, 47 (1932).

(6) M. S. Kharasch and S. Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

(7) F. C. Whitmore and co-workers, THIS JOURNAL, **63**, 643 (1941).

(8) F. C. Whitmore and R. S. George, *ibid.*, **64**, 1239 (1942); also, R. S. George, Ph.D. Thesis, The Pennsylvania State College, 1943, copy available through the University Microfilm Service, Ann Arbor, Michigan.

(9) F. C. Whitmore, paper presented before the Atlantic City Meeting of the American Chemical Society, September, 1941.

(10) H. S. Mosher and E. La Combe, THIS JOURNAL, **72**, 3994, 4991 (1950).

the six-membered ring complex of the transition state for the reduction of ketones by Grignard reagents and it seems likely that a similar mechanism holds for the reduction of acyl halides.

The addition reaction of Grignard reagents to such carbonyl systems is not so thoroughly understood. Alexander[11] considers the process to proceed by an attraction of the polarized carbonyl group for the ionized Grignard reagent. Swain[12] pictures the addition reaction to ketones as taking place through a six-membered ring complex involving two moles of Grignard reagent (or one mole of the Lewis acid, magnesium bromide and one mole of reagent).

Discussion

Synthesis of Straight Chain Ketones.—In continuation of previous work,[1] cuprous chloride and a number of other anhydrous metallic halides were tested for catalytic activity in the reaction of acetyl chloride and n-butylmagnesium chloride to produce 2-hexanone. Ferric chloride was found to be superior to aluminum chloride, cuprous chloride, zinc chloride, manganese chloride, cobaltous chloride and magnesium bromide, the yields ranging from 13% with $CoCl_2$ to 47% with $FeCl_3$ at a reaction temperature of 15° (Table II). Variation in the temperature from 34 to −65° in the presence of Cu_2Cl_2 increased the yield of product fourfold (Table III).[13] A 300% molar excess of acetyl chloride gave little change in the yield (Table IV). The reactions were complete in less than five minutes after the admixture of the Grignard reagent was complete at −65°. Hence, the optimum conditions for the production of straight chain ketones appear to be addition of one mole of Grignard reagent to one or more moles of the acyl chloride at −65° in the presence of a ferric chloride catalyst (1.5 g./mole acid chloride). The yield of 2-hexanone was in the range of 70–75% (based on Grignard reagent). With no catalyst, the yield of 2-hexanone was only 31%. Previous workers have obtained about 25% yields in comparable reactions.[14]

Synthesis of Highly Branched Ketones.—The temperature of reaction is not as critical as in the synthesis of straight chain ketones. As an ex-

(11) E. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 188.

(12) C. G. Swain, THIS JOURNAL, **73**, 870 (1951).

(13) It has been shown that in the reaction of acid anhydrides with Grignard reagents, a large increase in yield of ketone is obtained by lowering the temperature from −40 to −70°. See M. S. Newman and W. T. Booth, Jr., THIS JOURNAL, **67**, 154 (1945); also, *J. Org. Chem.*, **13**, 593 (1948).

(14) G. Vavon and J. Decembre, *Bull. soc. chim. France*, [5] **11**, 373 (1944).

TABLE I

Ketone[a]	B.p., °C.[b] (mm.)	°C.[c] n_D	°C.[d] d_4	Absolute[e] viscosity (centi- stokes)	Molar[f] refraction Theor. Found	Carbon,[g] % Theor. Found	Hydrogen,[g] % Theor. Found	Mol. wt.[h] Theor. Found
(I)	63 (4)	1.4443 (20°) 1.4404 (30°) 1.4369 (40°)	0.8604 (20°) 0.8531 (30°) 0.8458 (40°)	4.699 (20°) 3.744 (30°) 3.060 (40°)	57.88 56.94	78.09 78.19	12.8 13.0	184 184
(II)	113 (13)	1.4521 (20°) 1.4483 (30°) 1.4447 (40°)	0.8727 (20°) 0.8656 (30°) 0.8586 (40°)	6.102 (20°) 4.731 (30°) 3.797 (40°)	62.51 61.34	78.65 78.72	12.9 13.2	198 199
(III)	83.5 (4)	1.4575 (20°) 1.4541 (30°) 1.4504 (40°)	0.8815 (20°) 0.8747 (30°) 0.8676 (40°)	8.923 (20°) 6.645 (30°) 5.153 (40°)	67.14 65.66	78.75 79.18	12.6 13.2	212 212

[a] No derivatives could be synthesized, presumably because of steric factors. [b] Uncorrected (taken from column head temperature). [c] Measured on a five-place Valentine refractometer. [d] Measured in standard pycnometers. [e] Measured in Cannon type E viscosimeters. [f] The failure of the observed molar refractions to show close agreement with the calculated values is not surprising with molecules which show great steric hindrance. This fact has been noted on several occasions in this Laboratory, particularly with the tetramethyl hexanes and hexenes.[17] [g] Analyses run at the Clark Microanalytical Laboratory, Urbana, Illinois. [h] Determined cryoscopically in benzene.

ample, 2,5-dimethyl-3-hexanone was synthesized in 88% yield from isobutylmagnesium chloride and isobutyryl chloride with FeCl₃ as catalyst and a reaction temperature of 5°.

Other work was completed before the activity of ferric chloride was discovered. The early reactions were performed at the reflux temperature of the ethereal solutions in the presence of cuprous chloride. Three highly branched ketones were synthesized in 45–47% yield as follows: 2,2,4,4,5,5-hexamethyl-3-hexanone (I) from triptylmagnesium chloride (1,1,2,2 - tetramethylpropylmagnesium chloride) (IV) and trimethylacetyl chloride; 2,2,-3,3,5,5-hexamethyl-4-heptanone (II) from IV and 2,2-dimethylbutanoyl chloride; and 2,2,3,3,5,5,6-heptamethyl-4-heptanone (III) from IV and 2,2,3-trimethylbutanoyl chloride. The attempted synthesis of 2,2,3,3,5,5,6,6-octamethyl-4-heptanone from IV and 2,2,3,3-tetramethylbutanoyl chloride was unsuccessful because of a poor yield of the Grignard reagent and great difficulty in isolating the high melting product. The physical properties of these compounds are given in Table I.

The synthesis of hexamethylacetone was repeated with a ferric chloride catalyst. An 84% yield of fractionated product was obtained. The best yields obtained heretofore with the cuprous chloride catalyst were 70–75%.

The use of the organo-cadmium compound offers a generally more involved and less satisfactory route to highly branched ketones.[15] Generally, the alkyl organic radical of the Grignard reagent must be primary in order for the synthesis of ketones by the cadmium compound to be successful.[16]

Possible Mechanism.—In the syntheses described here, in particular those for the production of the highly branched ketones, the reaction conditions without catalyst are favorable for the reduction reaction. However, the presence of small amounts of ferric chloride results in addition prod-

ucts almost exclusively and any mechanism must account for this fact.

A free-radical mechanism has been proposed by Kharasch[17a] for similar aromatic reactions in the presence of cobaltous chloride and other metallic halides including ferric chloride. A thorough search of the products from the present reactions performed under the optimum conditions showed no trace of disproportionation or coupling products. Also, water is necessary to liberate the ketone at the end of the reaction. It would be expected that, if the reaction were of a free-radical nature, the ketone would be liberated during the reaction and not bound in a stable complex. The stability of the complex was illustrated in several experiments in which the reaction complex was heated for several days with no liberation of ketonic product. The fact that the ketone cannot be coördinated after formation was demonstrated in an experiment in which the heating of a mixture of 2-hexanone, magnesium chloride and ether permitted a quantitative recovery of the ketone. Therefore, it does not seem likely that ferric chloride is present as a free-radical type catalyst but instead as a Lewis acid in an ionic reaction.

The proposed mechanism is
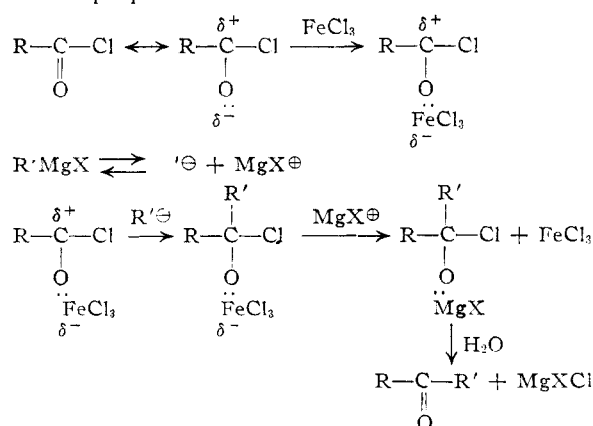
(15) R. Heilmann and G. de Gaudemaris, Compt. rend., **233**, 874 (1951).

(16) J. Cason, Chem. Revs., **40**, 15 (1947).

(17) C. J. Stehman, N. C. Cook, W. C. Percival and F. C. Whitmore, This Journal, **72**, 4163 (1950).

(17a) M. S. Kharasch, W. Nudenberg and S. Archer, This Journal, **65**, 495 (1943).

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 Bernard[18] 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 Pearson[19] showed that electrolysis and transference studies of Grignard reagents indicated the equilibrium reactions

$$R'^- + MgX^+ \rightleftarrows R'MgX \rightleftarrows R'Mg^+ + X^-$$
$$R'_2Mg \rightleftarrows R'^- + R'Mg^+$$
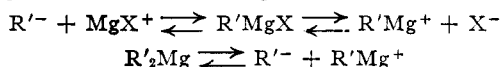
Chemical evidence which substantiates the presence of R'^- and X^- is found in the reaction of a Grignard reagent with ethylene oxide.[20] In view of the lack of complete evidence, the simple ionization as pictured by Alexander[11] is deemed applicable for this discussion.

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 coördinated 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 Johnson[22] 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 $^3/_{32}$-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 7-1., water-jacketed, copper vessel (11 in. × 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 3-1. 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-

(18) J. G. Aston and S. A. Bernard, *Nature*, **165**, 485 (1950).

(19) W. V. Evans and R. Pearson, THIS JOURNAL, **64**, 2864 (1942); W. V. Evans and F. H. Lee, *ibid.*, **56**, 654 (1934).

(20) N. G. Gaylord and E. I. Becker, *Chem. Revs.*, **49**, 525 (1951).

(21) For a leading reference, see C. G. Swain, THIS JOURNAL, **72**, 4578 (1950). An excellent summary is given by C. G. Swain, *Record of Chem. Progress*, **12**, 21 (1951).

(22) C. E. Entemann and J. R. Johnson, THIS JOURNAL, **55**, 2900 (1933).

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°. 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, $n^{20}D$, was 1.4001; literature values b.p. 127°[23] and $n^{20}D$ 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 $n^{20}D$ 1.4288. Literature values for this compound are b.p. 68° (24 mm.) (calculated as 165° at 760 mm.) and $n^{20}D$ 1.4288.[25]

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

$$R-\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}-O-Mg-X \text{ by atmospheric moisture to form the}$$

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.

(23) D. M. Cowan, G. H. Jerrery and A. I. Vogel, *J. Chem. Soc.*, 171 (1940).

(24) A. L. Henne and P. Hill, THIS JOURNAL, **65**, 753 (1943).

(25) M. Doss, "Physical Constants of Principal Hydrocarbons," 3rd Edition, The Texas Company, New York, N. Y., 1943, p. 32.

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-hexa-none, %	Addition temp., °C.	Catalyst	Yield of 2-hexa-none, %
34	Cu_2Cl_2	12	34	$CoCl_2$	4
15	Cu_2Cl_2	25	15	$CoCl_2$	13
5	Cu_2Cl_2	37	15	$FeCl_3$	47
−30	Cu_2Cl_2	41	−65	$FeCl_3$	72
−65	Cu_2Cl_2	48	−65	None	31

TABLE IV

RCOCl/RMgX (moles/mole)	Addition temp., °C.	Catalyst, g./mole RCOCl	Yield[a] of 2-hexa-none, %
1/1	5	1.5 Cu_2Cl_2	37
3/1	5	1.5 Cu_2Cl_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 $FeCl_3$ at −65° (Table V).

TABLE V

Period of RMgX addition, hr.	Additional stirring time at −65°	Heating period at 100°	Yield of 2-hexa-none, %
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°, $n^{20}D$ 1.4192. The yield is 84%. The identification of this product has been described.[1]

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

BY NORMAN KHARASCH AND ANTON J. HAVLIK[1]

2,4-Dinitrobenzenesulfenyl chloride, bromide and thiocyanate, 2-nitrobenzenesulfenyl chloride, *p*-toluenesulfenyl chloride and 2,4-dichlorobenzenesulfenyl 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-dinitrobenzenesulfenyl 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-nitrobenzenesulfenyl chloride, 2,4-dichlorobenzenesulfenyl chloride and *p*-toluenesulfenyl chloride, however, were

liquids. Since the four adducts resulting from 2-nitrobenzenesulfenyl chloride and 2,4-dichlorobenzenesulfenyl 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*-toluenesulfenyl 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*-toluenesulfenyl 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*-toluenesulfenyl 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]

(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).

(3) D. J. Cram, *ibid.*, **71**, 3884 (1949).

(4) L. M. Joshel, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 590 (1943).

(5) Infrared spectrograms in the 2 to 16μ 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*-toluenesulfenyl 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.