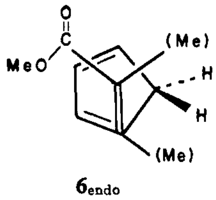
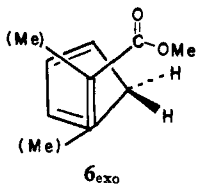


6$_{\text{endo}}$



6$_{\text{exo}}$

from the phenyl and methyl substituents, which are well removed from the reaction centers, the most obvious difference in **1** and cyclopentadiene is the absence of the out-of-plane methylene hydrogens in **1**. In the reactions of **1**, secondary orbital interactions between the carbonyl carbon and carbon 3 of the cyclopentadienone lead to stabilization of the endo transition state in all cases, while with cyclopentadiene, the methyl substituents interfere sterically with the methylene hydrogens, leading to greater amounts of exo adducts upon substitution by methyl. In the asymmetric transition states, **6**, an α-methyl experiences more steric repulsion than a β-methyl substituent.

The ester methyl can assume a conformation in the transition state such that no steric interference with the cyclopentadiene methylene hydrogens occurs. The possibility that dipolar repulsion between the carbonyls of the dienophile and **1** leads to endo adducts in all cases appears unlikely, since such effects do not overcome the "ortho" regioselectivity in Diels–Alder reactions of acrylic acid with vinylacrylic acid and similar compounds.[6]

These results, together with numerous studies of the reactions of nonconjugated dienophiles in the Diels–Alder reaction,[1,7] attest to the close proximity of addends in Diels–Alder transition states. Volume of activation measurements indicate that the transition state is smaller than the adduct,[8] such that substituents projecting out of the addend planes will experience mutual van der Waals repulsion rather than attraction due to dispersion (London) forces. At the same time, dipole orientation and induction forces can be important if highly polar groups are present in the addends.[2]

Acknowledgment. Financial support of this work by the Petroleum Research Fund, administered by the American Chemical Society, and by the Research Corporation is gratefully acknowledged.

(6) J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **6**, 16 (1967); A. S. Onishchenko, "Diene Synthesis," Israel Program for Scientific Translations, Jerusalem, 1964, p 22 ff and references therein.

(7) K. N. Houk and R. B. Woodward, *J. Amer. Chem. Soc.*, **92**, 4143, 4145 (1970); R. W. LaRochelle and B. M. Trost, *Chem. Commun.*, 1353 (1970); J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

(8) R. A. Grieger and C. A. Eckert, *J. Amer. Chem. Soc.*, **92**, 7149 (1970), and references therein.

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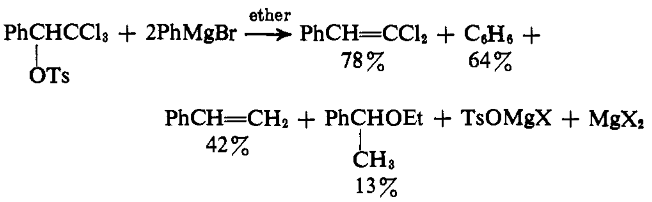
The Reaction of (Trichloromethyl)carbinyl Tosylates with Grignard Reagents

Sir:

We have studied reactions of Grignard reagents with tosylates of aryl-, alkyl-, and alkynyl(trichloromethyl)-carbinols and have observed a reaction without precedent. Two molecules of the Grignard reagent react with one molecule of the tosylate; both a tosylate and a chloro group are eliminated from the tosylcarbinol to form a *gem*-dichloroalkene.



$$\underset{\mathrm{OTs}}{\mathrm{PhCHCCl_3}} + 2\mathrm{PhMgBr} \xrightarrow{\text{ether}} \underset{78\%}{\mathrm{PhCH{=}CCl_2}} + \underset{64\%}{\mathrm{C_6H_6}} +$$

$$\underset{42\%}{\mathrm{PhCH{=}CH_2}} + \underset{\substack{\mathrm{CH_3}\\ 13\%}}{\mathrm{PhCHOEt}} + \mathrm{TsOMgX} + \mathrm{MgX_2}$$

Alkyl tosylates are known to react with Grignard reagents to form alkyl halides as well as hydrocarbons; these are nucleophilic displacement reactions.[1] The new reaction we have observed involves the neighboring trichloromethyl group, but it is not a simple halogen–metal interchange reaction of the type we have observed in another case[2] because chlorobenzene is not formed.

For the Grignard reagent, we have used *n*-butylmagnesium bromide, phenylmagnesium bromide, and benzylmagnesium bromide. With phenyl(trichloromethyl)carbinyl tosylate, all give β,β-dichlorostyrene in yields of 56–78%. With *n*-butylmagnesium bromide, 2-ethoxyhexane was the ether obtained as a by-product (29% yield); with benzylmagnesium bromide, no ether was obtained but bibenzyl was formed quantitatively.

p-Methoxyphenyl(trichloromethyl)carbinyl tosylate and *p*-bromophenyl(trichloromethyl)carbinyl tosylate react with *n*-butylmagnesium bromide in the same manner. β,β-Dichloro-*p*-methoxystyrene and *p*-bromo-β,β-dichlorostyrene are obtained in yields of 64 and 78%, respectively.

Four aliphatic trichloromethylcarbinyl tosylates have been studied. With ethyl(trichloromethyl)carbinyl tosylate and *n*-butylmagnesium bromide, 1,1-dichloro-1-butene was obtained in 33% yield, together with 8% of 2-ethoxyhexane and 5% each of *n*-butyl chloride and octane. Oddly enough, a primary tosylate, β,β,β-trichloroethyl tosylate, formed no 1,1-dichloroethylene.

With the tosylate of 1,1,1-trichloro-3-nonyn-2-ol and *n*-butylmagnesium bromide, 1,1-dichloro-1-nonen-3-yne was obtained in 73% yield. However, if an acetylenic hydrogen is present as in the tosylate of 1,1,1-trichloro-3-butyn-2-ol, the reaction fails; a mixture is obtained which appears to be free of alkynyl groups.

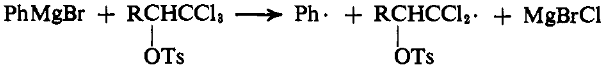
The reaction of phenyl(trichloromethyl)carbinyl tosylate with *n*-butylmagnesium bromide was carried out by adding, over a 3-hr period, 750 ml (0.52 mol) of 0.68 *M* Grignard reagent, prepared in the usual way, to 95 g (0.25 mol) of the tosylate, mp 129–130°, suspended in 1 l. of ether. The mixture was stirred mechanically and began to reflux gently soon after the dropwise addition of the Grignard reagent was started. The mixture was allowed to stand overnight and then decomposed by adding dilute hydrochloric acid. The ether layer was washed with water, dried, and distilled. 2-Ethoxyhexane (28% yield) was isolated by glpc from the 24-g forerun which distilled between 100 and 125°. The β,β-dichlorostyrene, 31 g (72% yield), bp 99–100° (12 mm), was shown to be identical with an authentic sample by ir and nmr. In the other cases also, all

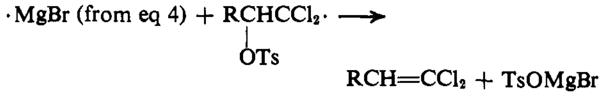
(1) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, New York, N. Y., 1954, p 1278.

(2) W. Reeve and L. W. Fine, *J. Amer. Chem. Soc.*, **86**, 880 (1964).

products were isolated by distillation or glpc and identified by ir, nmr, and elemental analyses.

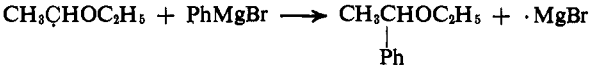
The mechanism of the reaction is puzzling; we tentatively propose the following

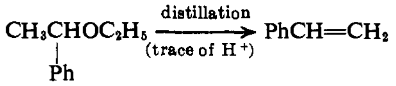

$$PhMgBr + RCH(OTs)CCl_3 \longrightarrow Ph\cdot + RCH(OTs)CCl_2\cdot + MgBrCl \quad (1)$$


$$\cdot MgBr \text{ (from eq 4)} + RCH(OTs)CCl_2\cdot \longrightarrow RCH{=}CCl_2 + TsOMgBr \quad (2)$$

and the observed by-products arise from

$$Ph\cdot + C_2H_5OC_2H_5 \longrightarrow C_6H_6 + CH_3\dot{C}HOC_2H_5 \quad (3)$$


$$CH_3\dot{C}HOC_2H_5 + PhMgBr \longrightarrow CH_3CH(Ph)OC_2H_5 + \cdot MgBr \quad (4)$$


$$CH_3CH(Ph)OC_2H_5 \xrightarrow[\text{(trace of H}^+)]{\text{distillation}} PhCH{=}CH_2 \quad (5)$$

Most Grignard reactions occur by a polar, "ionic" mechanism (although ionic dissociation is not a prerequisite) but certain radical reactions are well known.[3] The nature of the by-products in the case of the reaction of the Grignard reagent with the tosylate of the (trichloromethyl)carbinol strongly suggests a free-radical mechanism. A homolytic cleavage of the Grignard reagent is required to obtain the radicals to form the α-substituted diethyl ethers. Two ·MgBr radicals serve as reducing agents to supply two electrons to the tosylate, probably through the d orbitals of the chlorine atoms, which causes the tosylate anion to be expelled. With benzylmagnesium bromide, the relatively stable benzyl radical[4] formed in eq 1 reacts with the Grignard reagent to form bibenzyl rather than attacking the solvent as in the other cases (eq 3).

The carbinols and their tosylates are easily prepared by standard methods, and the subsequent reactions of their tosylates with Grignard reagents provide an attractive synthetic route to the dichloro olefins.

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(3) Reference 1, pp 116 and 138.

(4) E. S. Huyser, "Free Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, p 69.

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A Standard Acidity Scale. The pK_a of Alcohols in the Gas Phase

Sir:

It has been realized for some time that the observed acid strength of uncharged acids in the condensed phase can be a strong function of the nature of the solvent. This has led to a number of acidity scales and acidity functions all of which are highly dependent on the specific solvent system.[1] Since the exact nature of solvation effects is quite complex and not generally understood it seems natural to avoid solvation when defining an acidity scale and adopt the acid strength in the gas phase as a standard. Recent experimental innovations have led to the first determinations of orders of acidity in the gas phase.[2,3] We report here the first quantitative measurements of differences in gas-phase acidities of uncharged acids which suggest that the adoption of the gas-phase acidity as a standard acidity may now indeed become practicable.

The technique employed for these measurements was the flowing afterglow technique[4] which has recently been applied to the study of negative ion-molecule reactions of interest in organic chemistry. Rate constants were measured for both the forward and reverse direction of proton transfer in reactions of type 1 proceeding in the gas phase at 300°K. The experimental results are summarized in Tables I and II. Proton transfer between the selected alcohol molecules and alkoxide ions was observed to be quite rapid, $k \geq 5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}, in both directions in all three cases (Table I). The values for the equilibrium constants, K, listed in Table I were deduced[5] from the experimental data recorded in a study of the tendency of acetylene to transfer a proton to the alkoxide ions (Table II).[6]

$$A^- + BH \rightleftarrows B^- + AH \qquad (1)$$

Table I. Thermochemical Data for the Acid-Base Equilibria between Selected Alcohols in the Gas Phase at 300°K

Acid-base equilibrium	K	$-\Delta G°_{300}$, kcal/mol	ΔpK_a
$CH_3O^- + C_2H_5OH \rightleftarrows C_2H_5O^- + CH_3OH$	3	0.7	0.5
$C_2H_5O^- + i\text{-}C_3H_7OH \rightleftarrows i\text{-}C_3H_7O^- + C_2H_5OH$	1×10	1.4	1
$i\text{-}C_3H_7O^- + tert\text{-}C_4H_9OH \rightleftarrows tert\text{-}C_4H_9O^- + i\text{-}C_3H_7OH$	≥ 0.3	≥ -0.7	≥ -0.5

Table II. Rate Constants for the Proton Transfer Reactions between Alkoxide Ions and Acetylene in the Gas Phase at 300°K

Alkoxide ion	k_f ($\times 10^9$ cm^3 mole-	k_r cule^{-1} sec^{-1})	$K \times 10^{-1}$	$-\Delta G°_{300}$, kcal/mol	ΔpK_a
CH_3O^-	1.3	0.05	3	2.1	1.5
$C_2H_5O^-$	1.1	0.1	1	1.4	1
$i\text{-}C_3H_7O^-$	0.52	0.5	0.1	0	0
$tert\text{-}C_4H_9O^-$	0.16	≥ 0.05	≤ 0.3	≤ 0.7	≤ 0.5

The thermodynamic equilibrium constant, K, for reaction 1 proceeding in the gas phase can be related

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(1) See, for example, D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 1.

(2) J. I. Brauman and L. K. Blair, *J. Amer. Chem. Soc.*, **92**, 5986 (1970).

(3) D. K. Bohme and L. B. Young, *ibid.*, **92**, 3301 (1970).

(4) E. E. Ferguson, *Advan. Electron. Electron Phys.*, 24, 1 (1968); E. E. Ferguson, F. C. Fehsenfeld, and A. L. Schmeltekopf, *Advan. At. Mol. Phys.*, **5**, 1 (1969). See ref 3 for details concerning the application of this technique to the organic chemistry of negative ions in the gas phase.

(5) The ratio of the rate constant for the forward direction of proton transfer, k_f, to the rate constant for the reverse direction, k_r, was taken to be equal to the thermodynamic equilibrium constant since the energy distributions of the respective reactants are expected to be Maxwell-Boltzmann. The standard free-energy change, $\Delta G°$, can then be computed by employing the relation $\Delta G° = -RT \ln K$.

(6) For information regarding the generation of alkoxy anions in the gas phase see: D. K. Bohme and L. B. Young, *J. Amer. Chem. Soc.*, **92**, 7354 (1970).