is used as the coupling agent. This side product is not formed when copper(II) valerate is utilized; however, the yield of dimer is not increased.

A representative procedure is the following conversion of ethyl propionate into diethyl 2,3-dimethylsuccinate. A dry 100-ml flask is equipped with magnetic stirrer, septum inlet, and mercury bubbler. The flask is flushed with nitrogen and 25 ml of a 1.0 *M* solution of lithium *N*-isopropylcyclohexylamide[5] in tetrahydrofuran is injected with a syringe. The flask is immersed in a Dry Ice–acetone bath and 2.6 g (25 mmol) of ethyl propionate is added dropwise. After 15 min, $CuBr_2$ (6.7 g, 20 mmol) is added all at once through a powder funnel. The solution is stirred for an additional 15 min and then allowed to reach room temperature. Hydrochloric acid (15 ml of 10% solution) is added together with 30 ml of pentane. The separated organic layer is dried with magnesium sulfate and subjected to vacuum distillation to obtain 2.1 g (75%) of diethyl 2,3-dimethylsuccinate, bp 106–109° (15 mm) (lit.[10] bp 108° (15 mm)).

The copper(II)-promoted coupling of ester enolates represents a highly convenient route to dialkyl succinate esters. Even in those cases where the yield of coupled product is relatively low, the major contaminant in the crude reaction mixture is unconverted starting ester and the dimer is readily obtained in a state of high purity by means of simple distillation. We are presently exploring the reaction of copper salts with other enolate anions, including those derived from other derivatives of carboxylic acids and from aldehydes and ketones.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(10) W. Hückel and H. Müller, *Chem. Ber.*, **64**, 1981 (1931).

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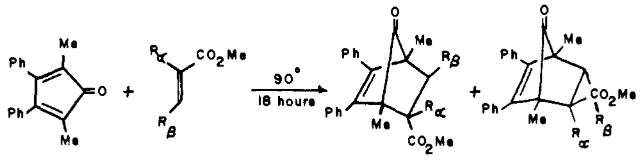
The Influence of Steric Interactions on Endo Stereoselectivity

Sir:

Of the numerous effects which potentially determine the difference in stability between exo and endo Diels–Alder transition states, only secondary orbital interactions between unsaturated centers and van der Waals repulsions between saturated centers appear to be of general significance,[1] except in the reactions of chlorinated dienes.[2] However, Kobuke, Fueno, and Furukawa have recently proposed that attractive van der Waals (dispersion) forces between methyl groups in the dienophile and unsaturated diene centers may play a role in the stabilization of Diels–Alder transition states.[3] We wish to report evidence which contravenes this explanation.

The reactions of 2,5-dimethyl-3,4-diphenylcyclopentadienone (**1**)[4] with three acrylic esters at 90° (Scheme I) lead to the kinetically controlled *endo–exo*-carbomethoxy Diels–Alder adduct mixtures shown in Table I. For comparison, Table I also shows the kinetically controlled adduct ratios obtained by Kobuke *et al.*,[3] in their studies of reactions of these dienophiles with cyclopentadiene.

Scheme I



1 **2** **3**$_{endo}$ **3**$_{exo}$

a, R_α = H; R_β = H
b, R_α = Me; R_β = H
c, R_α = H; R_β = Me

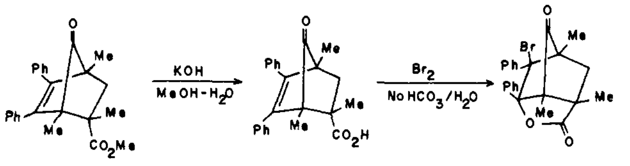
Table I. Adduct Ratios

Dienophile	*endo*-CO_2Me/*exo*-CO_2Me With **1** (90°)	With C_5H_6 (50°)[a]
Methyl acrylate (**2a**)	17.9	2.73
Methyl methacrylate (**2b**)	15.7	0.43
Methyl crotonate (**2c**)	12.2	1.05

[a] Reference 3.

The endo stereochemistry of the major methyl methacrylate adduct was shown by hydrolysis followed by bromination, which gave the bromolactone **5** (Scheme II).[5] The nmr spectrum of the crude methyl methacrylate reaction mixture contained, in addition to the resonances of **3b**$_{endo}$, resonances assigned to **3b**$_{exo}$. The ester methyl resonances which appear at 3.46 ppm for **3b**$_{endo}$ and 3.72 ppm for **3b**$_{exo}$ are especially noteworthy. For the reactions of **2a** and **2c**, these and other characteristic nmr resonances were used to identify the endo and exo adducts.[5]

Scheme II



3b$_{endo}$ **4** **5**

Kobuke, *et al.*, rationalized the variation in endo–exo ratios with these dienophiles and cyclopentadiene by suggesting that methyls in the dienophile can experience attractive van der Waals forces with sp^2 carbons in cyclopentadiene. In the asymmetric transition states, **6** leading to endo and exo adducts, an α-methyl substituent was suggested to experience a greater attractive interaction with C-2 of cyclopentadiene than a β-methyl substituent, due to the closer proximity of the former to C-2 of cyclopentadiene.[3]

This explanation cannot be valid, since the same effect should be realized in the reactions of **1**. Aside

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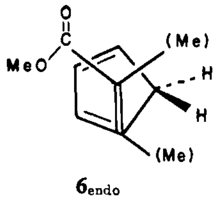
(1) K. N. Houk, *Tetrahedron Lett.*, 2621 (1970), and references therein.

(2) K. L. Williamson, Y. L. Hsu, R. Lacko, and C. H. Youn, *J. Amer. Chem. Soc.*, **91**, 6129 (1969); K. L. Williamson and Y. L. Hsu, *ibid.*, **92**, 7385 (1970).

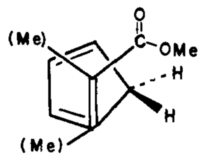
(3) Y. Kobuke, T. Fueno, and J. Furukawa, *ibid.*, **92**, 6548 (1970).

(4) C. F. H. Allen and J. A. Van Allan, *ibid.*, **64**, 1260 (1942).

(5) All new compounds, with the exception of the exo adducts, which were not isolated, gave elemental and spectral analyses compatible with the assigned structures: **2a**, mp 114–115° (lit.,[4] mp 115°); **2b**, mp 120.5–121°; **2c**, mp 121–124°; **4**, mp 211° dec; **5**, mp 161–162°.



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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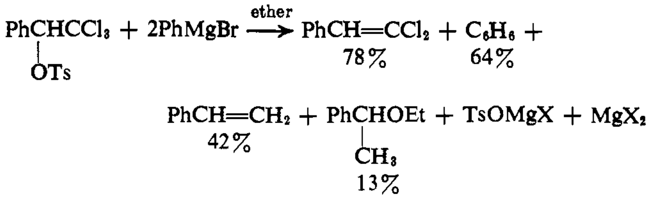
The Reaction of (Trichloromethyl)carbinyl Tosylates with Grignard Reagents

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.



$$\underset{\mathrm{OTs}}{\mathrm{PhCHCCl_3}} + \mathrm{2PhMgBr} \xrightarrow{\text{ether}} \underset{78\%}{\mathrm{PhCH{=}CCl_2}} + \underset{64\%}{\mathrm{C_6H_6}} + \underset{42\%}{\mathrm{PhCH{=}CH_2}} + \underset{13\%}{\underset{\mathrm{CH_3}}{\mathrm{PhCHOEt}}} + \mathrm{TsOMgX} + \mathrm{MgX_2}$$

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).