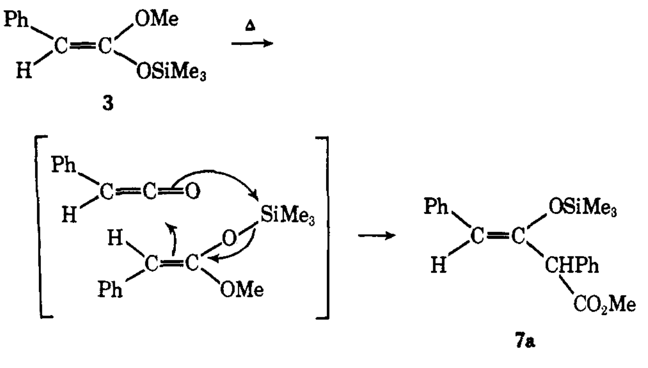
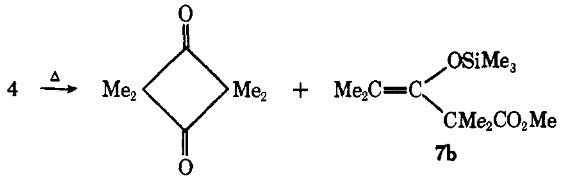


3

7a

methylketene dimer (tetramethyl-1,3-cyclobutadione, δ 1.28) and 80% ketene-ketene acetal addition product **7b**.



7b

Compounds **5** and **6** gave similar results.

The pyrolysis study of ketene bis(trialkylsilyl) acetals is currently in progress.

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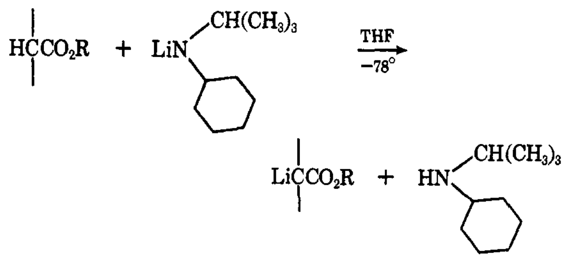
The Reaction of Ester Enolates with Copper(II) Salts. A Synthesis of Substituted Succinate Esters

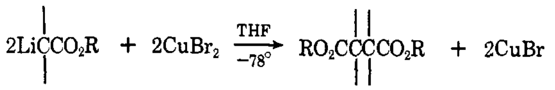
Sir:

The dimerization of carbon anions in the presence of copper salts is a well-established reaction of organic chemistry.[1] Nevertheless, there are relatively few examples of the copper-promoted dimerization of enolate anions.[2]

We wish to report that lithium ester enolates, prepared according to eq 1,[5] undergo a facile reaction with copper(II) salts to provide the corresponding dimerized esters in satisfactory yields (eq 2).



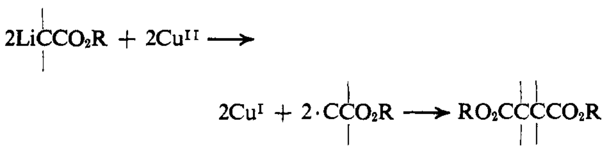
(1)



$$2\mathrm{Li}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{CO_2R} + 2\mathrm{CuBr_2} \xrightarrow[-78^\circ]{\mathrm{THF}} \mathrm{RO_2C}\overset{|\,|}{\underset{|\,|}{\mathrm{CC}}}\mathrm{CO_2R} + 2\mathrm{CuBr} \tag{2}$$

Addition of 1 equiv of copper(II) bromide to a tetrahydrofuran solution of lithio *tert*-butyl acetate maintained at a temperature of −78° results in a series of color changes starting with green and proceeding through deep red. At the end of 15 min, the reaction mixture is dark brown and becomes completely homogeneous on warming to room temperature. Work-up produces an 85% yield of di-*tert*-butyl succinate. Use of reduced amounts of the copper salt produces a corresponding reduction in the yield of product; consequently the stoichiometry of the reaction is as shown by eq 2.

A minor side product of the reaction is *tert*-butyl bromoacetate. However, the major path for the formation of the succinate ester does not involve coupling of the bromo ester with the ester enolate.[6] Addition of authentic *tert*-butyl bromoacetate to a solution of lithio *tert*-butyl acetate produces only negligible yields (10%) of di-*tert*-butyl succinate. Furthermore, the dimerization reaction proceeds equally well (95%) with the halogen-free copper salt, copper(II) valerate.[8] For the present, all of our data can be accommodated by a radical-coupling mechanism (eq 3).



$$2\mathrm{Li}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{CO_2R} + 2\mathrm{Cu^{II}} \longrightarrow 2\mathrm{Cu^{I}} + 2\cdot\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{CO_2R} \longrightarrow \mathrm{RO_2C}\overset{|\,|}{\underset{|\,|}{\mathrm{CC}}}\mathrm{CO_2R} \tag{3}$$

Results obtained with a variety of esters using either copper(II) bromide or copper(II) valerate are illustrated in Table I. The yield of dimer appears to decrease with increasing alkyl substitution adjacent to the carbonyl grouping of the ester (see entries for ethyl isobutyrate and ethyl isovalerate in Table I). This is attended with an increase in the production of the corresponding α-bromo ester when copper(II) bromide

Table I. Dimerization of Esters Using Copper(II) Salts

		—Yield, %[b]—	
Ester	Product[a]	$CuBr_2$	$Cu(O_2C_5H_9)_2$
tert-Butyl acetate	Di-*tert*-butyl succinate	85	95
Ethyl propionate	Diethyl 2,3-dimethylsuccinate	81	50
Ethyl hexanoate	Diethyl 2,3-di-*n*-butylsuccinate	63	
Ethyl isobutyrate	Diethyl tetramethylsuccinate	25	20
Ethyl isovalerate	Diethyl 2,3-diisopropylsuccinate	20	20
Ethyl phenylacetate	Diethyl 2,3-diphenylsuccinate	75	60

[a] Usually obtained as a mixture of stereoisomers. The identity of all products was verified by spectral analysis or by comparison with published physical properties. [b] Isolated yields based on starting ester.

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(1) *Cf.* T. Kauffmann and D. Berger, *Chem. Ber.*, **101**, 3022 (1968).

(2) The dimerization of the sodium enolate of acetophenone promoted by copper(II) chloride has been described by Kauffmann.[3] The formation of dimers as side products from the copper-catalyzed oxidation of α,β-unsaturated aldehydes and ketone enolates has been reported by Volger, *et al.*[4]

(3) T. Kauffman, *et al.*, *Angew. Chem., Int. Ed. Engl.*, **7**, 540 (1968).

(4) H. C. Volger, W. Brackman, and J. W. F. M. Lemmers, *Recl. Trav. Chem. Pays-Bas*, **84**, 1203 (1965).

(5) M. W. Rathke and A. Lindert, *J. Amer. Chem. Soc.*, **93**, 2318 (1971).

(6) The reaction of α-bromo esters with ester enolates has been described by Hauser.[7]

(7) B. E. Hudson and C. R. Hauser, *J. Amer. Chem. Soc.*, **63**, 3161 (1941).

(8) The preparation of copper(II) valerate was essentially that described by Lieben.[9]

(9) A. Lieben and A. Rossi, *Justus Liebigs Ann. Chem.*, **159**, 66 (1871).

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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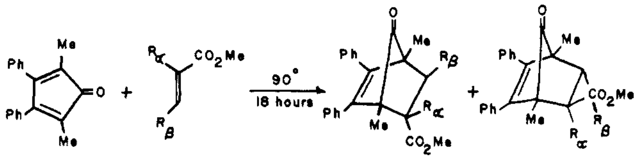
The Influence of Steric Interactions on Endo Stereoselectivity

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

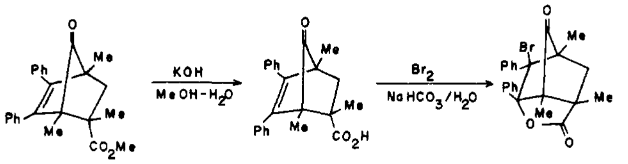
Table I. Adduct Ratios

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°.