activity can be correlated to a surprisingly high degree to axial distances. Third, structural data can provide meaningful insights into kinetic mechanisms by way of constrained model systems.

It is now necessary to summarize the detailed stereochemistry about the cobalt ions in the four closely related compounds. All of the molecules have crystallographically required $\overline{1}$ symmetry. In the dienes the equatorial Co-N bond distances are 1.977 (17) and 1.926 (16) A with the shorter distance corresponding to the imine Co-N and the longer to the amine Co-N; there is no significant difference between the two diene complexes. In the tetraene systems, the four equatorial nitrogens are all imines and show an average Co-N distance of 1.903 (20) Å with no systematic difference between the two oxidation states. Thus, in addition to equalization of the Co-N equatorial distances in the tetraene relative to the diene, there is some indication of an overall tightening. This may result from a relaxation of the framework due to four equivalent bonds.

The axial bond distances are 2.482(5) and 1.954(6) Å for the +2 and +3 dienes and 2.289 (13) and 1.972 (15) Å in the +2 and +3 tetraenes, respectively. The long bonds in the low spin +2 systems result from the unpaired electron in the antibonding d_{z^2} orbital. The dramatic difference in axial bond lengths between the cobalt(II) diene and cobalt(II) tetraene may have its origin in either steric or electronic effects. Although the nonplanar diene complexes might be thought to undergo more steric interactions (especially geminal methylwater) than the tetraenes, this argument is somewhat less compelling if we note that the planar low spin cobalt(II) porphyrin, Co(3-pic)₂(OEP), shows a similar long axial Co-N distance (2.386 Å).¹⁰ Scheidt has also reported a 2.436 Å Co-N distance in Pip₂CoTPP.¹¹ Moreover, comparison of torsion angles in cobalt diene systems with those in other metallodiene complexes provides no evidence of strain. The possibility of electronic effects resulting from interaction with the highly symmetric tetraene ring can only be tested with detailed molecular orbital calculations.

Intensity data for both the Co(II) and Co(III) complexes of ([14]tetraeneN₄) were collected on a Syntex P2₁ diffractometer using Mo K α radiation to a 2 θ of 45°. The Co^{II} complex crystallizes in $P2_1/a$ with cell parameters a = 11.58(1) Å, b = 14.542(9) Å, c = 6.939(5) Å, and $\beta = 94.64 (7)^{\circ}$; the Co^{III} complex crystallizes in $P2_1/c$ with cell parameters a = 17.829(3)Å, b = 9.656(1)Å, c= 18.220 (3) Å, and β = 133.11 (1)°. The Co(II) structure was solved by Patterson-Fourier techniques and refined by full-matrix least-squares procedures with isotropic thermal parameters for the macrocyclic atoms and anisotropic parameters for the remaining atoms. The perchlorate counterion showed considerable rotational disorder. The Co(III) solution was achieved by a combination of probability and Fourier techniques and refined by full-matrix least-squares procedures with all thermal motion treated anisotropically. In both structures the possibility of five-coordinate disorder models were considered and convincingly rejected. Final discrepancy factors were 0.076 for 507 data and

(10) R. G. Little and J. A. Ibers, J. Amer. Chem. Soc., 96, 4440 (1974): $Co(3-pic)_2(OEt) = 2,3,7,8,12,13,17,18$ -octaethylporphinatobis(3-methylpyridine)cobalt(II).

(11) W. R. Scheidt, J. Amer. Chem. Soc., 96, 84 (1974): Pip₂Co-TPP = bis(piperidine)- $\alpha_{\beta}\beta_{\gamma}\gamma_{\delta}\delta_{\gamma}$ tetraphenylporphinatocobalt(II). 0.067 for 1595 data for the Co^{II} and Co^{III} compounds, respectively.

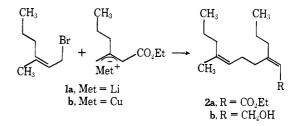
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Regioselectivity in the Alkylation of Lithium and Copper Ester Dienolates. An Allylic Transposition Associated with γ -Alkylation of Copper Dienolates

Sir:

Although dienolate anions, derived from α,β -unsaturated carbonyl compounds, undergo certain condensation reactions (Reformatsky,¹ Darzens,² and Aldol^{3,4}) selectively at the γ position, alkylation and protonation take place at the α position with high selectivity.^{5,6} Nevertheless, we were attracted to a γ alkylation approach to the synthesis of the novel codling moth alcohol, **2b**,⁷ because of its inherent simplicity.



In a model study, we found that the lithium dienolate 1a, formed by treatment of ethyl (*E*)-3-methyl-2-hexenoate (3)^{7b} with lithium diisopropylamide in THF, underwent alkylation with allyl bromide nearly exclusively at the α position, producing the isomeric esters 4a and 5a in a 95:5 ratio.⁸ The copper dienolate (1b)⁹ (from 3 by reaction with trityllithium and then cuprous iodide), however, gave substantially greater

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(4) For an alternative method of γ -condensation, using a γ -phosphonoenoate, see E. J. Corey and B. W. Erickson, J. Org. Chem., **39**, 821 (1974).

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(7) (a) L. M. McDonough, D. A. George, B. A. Butt, J. M. Ruth, and R. Hill, *Science*, 177, 177 (1972); (b) S. B. Bowlus and J. A. Katzenellenbogen, *Tetrahedron Lett.*, 1277 (1973); (c) M. P. Cooke, *ibid.*, 1281 (1973); (d) S. B. Bowlus and J. A. Katzenellenbogen, *J. Org. Chem.*, **38**, 2733 (1973); (e) M. P. Cooke, *Tetrahedron Lett.*, 1983 (1973).

(8) (a) Glpc analysis or nmr were used to quantitate the ratio of isomers. (b) Each reported product displays spectroscopic properties consistent with its assigned structure. (c) Isolated yields of alkylated products are generally in the range of 65-70%. (d) The geometrical configuration of the γ -alkylated product has not been established.

(9) The alkylation of copper enolate species has been described in several recent publications: R. M. Coates and L. O. Sandefur, J. Org. Chem. 39, 275 (1974); R. K. Boeckman, Jr., *ibid.*, 38, 4450 (1973); I. Kuwajima and Y. Doi, *Tetrahedron Lett.*, 1163 (1972).

amounts of γ -alkylation (4a: 5a, 44: 56). As the desired 1.5-diene 5a was readily separable from 4a by chromatographic means, we were encouraged to continue our study. In contrast to the simple allyl system, however, the reaction of 1a and 1b with 3,3-disubstituted allyl bromides, such as are required for the construction of isoprenoid-type systems, gave nearly exclusively α alkylation in both cases.

To investigate the possibility that γ -alkylation involves an allylic transposition of the alkylating agent, we studied the reaction of the dienolates 1a and 1b with (Z)-3deuteroallyl bromide (6).¹⁰ In both cases, the isomeric alkylation products were separated by glpc, and their 100 MHz pmr spectra were compared with those of the respective proteo derivatives 4a and 5a. The " α " products from alkylation of both the lithium and copper dienolates were shown to correspond to the direct displacement product 4b. The position and integrated intensities of the resonances in the allylic region (δ 1.9-2.7; methylenes C-3' and -4) were identical with those in 4a. Deuterium substitution at C-5', however, does sharpen the resonances of the C-3' hydrogens by removing some of the allylic coupling. The vinylic pattern at δ 4.8–5.2 (H's on C-5' and -4''), corresponding to 4 H in 4a, was reduced in area to 3 H in 4b. Furthermore, the coupling pattern in this region, as well as at δ 4.5–4.9 (C(4')H), was considerably simplified.

In contrast to the direct displacement process whereby the " α " product 4b is produced, the " γ " product (5c) derived from alkylation of the copper enolate 1b with 6 appears to arise by a displacement involving nearly exclusively allylic transposition (SN2').^{11,12} This was ascertained by pmr analysis. The allylic hydrogen resonance region in 5a consists of a complex pattern at δ 2.0–2.3 (4 H corresponding to methylenes at C-5 and -4') and at δ 2.5–2.8 (2 H, methylene C-4). In the " γ " product from 1b and 6, the integrated intensity of the upfield pattern is reduced to 3 H, consistent with deuterium substitution at C-5 as in 5c. The coupling pattern of the C-4 methylene is also simplified. The resonances in the vinylic region further support structure 5c, as part of the vinylic coupling of C(6)H and the allylic coupling of C(7)H has been removed, but the integrated intensities of these resonances are unchanged from 5a.

The " γ " product derived from the alkylation of the lithium dienolate 1a with 6, a very minor constituent (5%; vide infra), appears to be a mixture of the directplacement product 5b, together with ca. 10-20% of the transposed isomer 5c.

As the structure of the lithium and copper dienolates cannot be precisely formulated at present, a mechanistic rationale for the counterion influence on alkylation regioselectivity must remain a matter of speculation.13

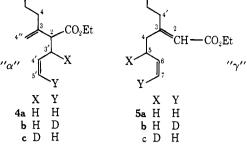
95, 7926 (1973)) have recently reported that the reaction of cuprous derivatives of allyl isopropyl sulfides with allylic halides gives exclusive γ -alkylation with complete transposition in the electrophile.

(12) Control experiments have established that 5a does not arise via Cope rearrangement from 4a under the reaction conditions employed in these studies.

(13) In spite of the absence of detailed structural information on the copper vs. lithium reagents, it is tempting to advance a rationale for the effect of copper on the alkylation regioselectivity and the allylic transposition associated with γ -allylation. One might imagine, in the case of alkylation of the copper enolate, that a species is formed in which the two reacting partners have their relative positions fixed (either by complexa-



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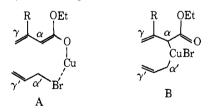
 CH_3

However, we have made some additional observations which support the association of allylic transposition with γ -allylation in these copper dienolate systems.

Reaction of 1b with methyl iodide or benzyl bromide, both reagents which cannot undergo SN2' attack, produces exclusively the α -alkylated products. Reaction of 1b with 3-chloro-1-butene and (E)-1-chloro-2-butene gives a mixture of alkylated products consisting mainly of the " α -direct" and " γ -transposed" isomers, although, in these cases, the methyl substitutent has considerable influence on the α/γ ratio. Further studies on the influence of reactant structure and the nature of the medium and metal ion on the regioselectivity of alkylation of unsaturated ester enolates are underway.

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tion, as formulated in the O-enolate A, or as a result of oxidative addition, as in the C-enolate B). The geometric restrictions inherent in these species would dictate that completion of the carbon-carbon bond formation must occur either by conjoining of the α - and α' -carbons (α alkylation with direct displacement) or the γ - and γ' -carbons (γ -alkylation with transposition). Such a model permits one to rationalize the reluctance to the 3,3-disubstituted allyl bromides toward undergoing γ -alkylation with the copper enolates, as the steric hindrance of these substituents in A or B would directly interfere with $\gamma - \gamma'$ bond formation, thus favoring $\alpha - \alpha'$ coupling. With the lithium dienolate, alkylation would occur without such pronounced interaction between the reacting partners, thus allowing both $\alpha - \alpha'$ and $\gamma - \alpha'$ coupling.



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Nearby Nonequivalent n, π^* Excited Triplet States. Anomalous Type II Photoelimination in Butyrylpyrimidines, Photochemical **Cyclopropanol Formation**

Sir:

Among the aromatic ketone systems that have been utilized, thus far, to study the general influence of ring

⁽¹⁰⁾ For a related preparation of 3,3-dideuteroallyl alcohol, see K. D. McMichael, J. Amer. Chem. Soc., 89, 2943 (1967).
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