

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*)-3-deuteroallyl 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 (S_N2').^{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 direct-displacement product **5b**, together with *ca.* 10–20% of the transposed isomer **5c**.

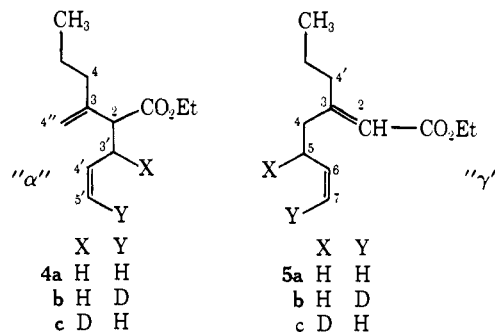
As the structure of the lithium and copper dienolates cannot be precisely formulated at present, a mechanistic rationale for the counterion influence on alkylation regioselectivity must remain a matter of speculation.¹³

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

(11) K. Oshima, H. Yamamoto, and H. Nozaki, (*J. Amer. Chem. Soc.*, **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-

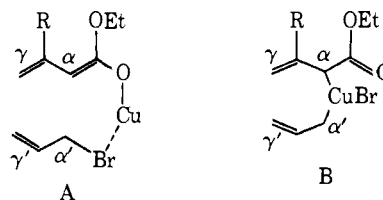


However, we have made some additional observations which support the association of allylic transposition with γ -allylation in these copper dienolate systems.

Reaction of **1b** with methyl iodide or benzyl bromide, both reagents which cannot undergo S_N2' 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 substituent 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 γ - γ' bond formation, thus favoring α - α' coupling. With the lithium dienolate, alkylation would occur without such pronounced interaction between the reacting partners, thus allowing both α - α' and γ - α' 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