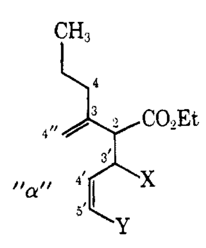
amounts of γ-alkylation (**4a**:**5a**, 44:56). As the desired 1,5-diene **5a** was readily separable from **4a** by chromatographic means, we were encouraged to continue our study. In contrast to the simple allyl system, however, the reaction of **1a** and **1b** with 3,3-disubstituted allyl bromides, 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.

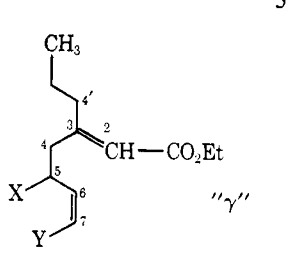
In contrast to the direct displacement process whereby the "α" product **4b** is produced, *the "γ" product* (**5c**) *derived from alkylation of the copper enolate* **1b** *with* **6** *appears to arise by a displacement involving nearly exclusively allylic transposition* (SN2′).[11,12] This was ascertained 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 direct-placement 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]



	X	Y
4a	H	H
b	H	D
c	D	H



	X	Y
5a	H	H
b	H	D
c	D	H

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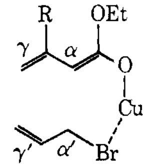
[10] For a related preparation of 3,3-dideuteroallyl alcohol, see K. D. McMichael, *J. Amer. Chem. Soc.*, **89**, 2943 (1967).

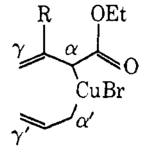
[11] K. Oshima, H. Yamamoto, and H. Nozaki, (*J. Amer. Chem. Soc.*, **95**, 7926 (1973)) have recently reported that the reaction of cuprous derivatives of allyl isopropyl sulfides with allylic halides gives exclusive γ-alkylation with complete transposition in the electrophile.

[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 complexation, 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.



A



B

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Received March 18, 1974

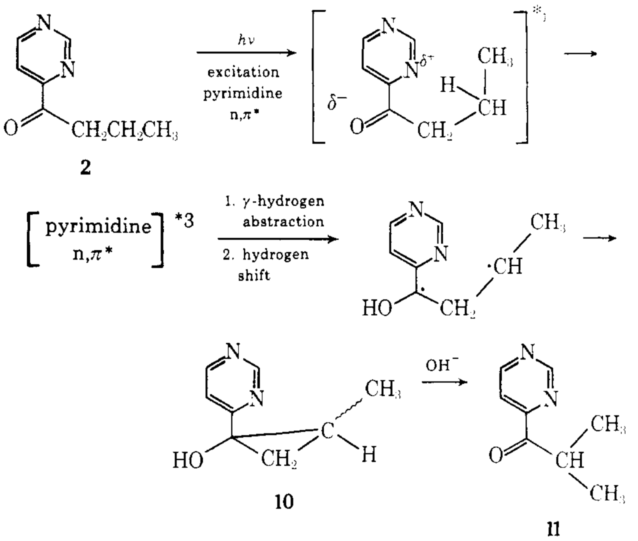
Nearby Nonequivalent n,π* Excited Triplet States. Anomalous Type II Photoelimination in Butyrylpyrimidines, Photochemical Cyclopropanol Formation

Sir:

Among the aromatic ketone systems that have been utilized, thus far, to study the general influence of ring substituents on triplet ketone reactivity,[1-5] virtually all have been derivatives of either benzene[5,6] or pyridine[7] and all have possessed a lowest lying excited configuration consisting of an n,π^* triplet state and a π,π^* triplet state. To date no work has been reported on the excited state properties of ketones possessing lowest lying nonequivalent n,π^* excited triplet states, and knowledge regarding the interactions of such states and their relationship to ring substitution and triplet ketone reactivity has remained unknown. Spectroscopic studies on aza aromatics indicate that the lowest lying triplet states of pyrimidine, pyrazine, pyridazine, and triazine are n,π^* and are lower in energy than the corresponding π,π^* states of benzene[8] and pyridine.[9] This suggests[10] that ketones derived from these aza aromatics are likely to possess lowest n,π^* states associated with both carbonyl and ring nitrogen excitation. This further suggests that a number of these ketones should be practical for studying the interactions of nonequivalent n,π^* triplet states and for determining the relationship of the interactions to ring substitution and triplet ketone reactivity. In this paper we wish to report some of our preliminary findings on the photobehavior of pyrimidyl ketones which indicate that the existence of nearby nonequivalent n,π^* states in aromatic ketones can lead to unusual photochemical behavior. Our findings are based on photochemical studies conducted on the 2-, 4-, and 5-butyrylpyrimidine systems, **1**, **2**, and **3**.

The pyrimidyl ketones, **1** and **2**, were prepared in 40–45% yield by treatment of the corresponding 2- and 4-substituted nitriles[11-13] with *n*-propylmagnesium bromide. Pyrimidyl ketone **3** was prepared in 85% yield by chromic acid oxidation of 1-(5-pyrimidyl)-1-butanol.[14] Each of the butyryl ketones, **1**, **2**, and **3**, was irradiated in benzene, and their respective reactions were followed by vapor phase chromatography.[15] The 2-butyrylpyrimidine (**1**) underwent photoconversion in 6 hr to methyl (2-pyrimidyl) ketone (**4**), 1-(2-pyrimidyl)-1-cyclobutanol (**5**), 1-(2-pyrimidyl)-1-butanol (**6**), and 1-(2-pyrimidyl)-1-ethanol (**7**).[17] The 5-substituted butyrylpyrimidine (**3**) was irradiated for 3 hr and underwent photocleavage to 5-acetylpyrimidine (**8**) with little to no apparent occurrence of cyclobutanol formation or photoreduction. In marked contrast to the photobehavior of the 2- and 5-butyryl ketones, **1** and **3**, irradiation of 4-butyrylpyrimidine (**2**) in benzene led to a 40:60 mixture of 4-acetylpyrimidine (**9**) and 1-(4-pyrimidyl)-2-methyl-1-cyclopropanol (**10**). When the irradiation was carried out in *tert*-butyl alcohol the pyrimidyl cyclopropanol (**10**) was found to be the exclusive product, whereas irradiation in hexane afforded virtually only type II products.

The cyclopropanol (**10**) is a white crystalline solid mp 119°. Its structure was elucidated on the basis of spectral data: infrared $\lambda_{\max}$ (CCl_4) 2.80 μ; nmr (220 MHz) ($CDCl_3$) cyclopropyl δ 1.07 (2 overlapping doublets, 2 H (methylene)), 1.35 (doublet, J = 6.0 Hz, 3 H (methyl)), 1.59 (multiplet, 1 H (methine)), 3.57 (broad singlet, 1 H (hydroxyl)), aromatic δ 7.43 (doublet, J = 4.5 Hz, 1 H), 8.60 (doublet, J = 4.5 Hz, 1 H), 9.00 (singlet, 1 H); mass spectrum (*m/e*) 150 M^+, 149, 135, 107, 94, and 80 (base peak). The structure of the pyrimidyl cyclopropanol (**10**) is also based on chemical evidence. Upon treatment with 0.1 *N* NaOH, alcohol **10** rearranges[18] smoothly to 4-isobutyrylpyrimidine (**11**).



The formation of cyclopropanol (**10**) can best be accounted for in terms of a mechanism involving the n,π^* triplet state associated with excitation of a ring nitrogen atom. Evidence for the triplet state assignment is derived from the fact that the reaction can be suppressed with known triplet quenchers. γ-Hydrogen abstraction by the excited nitrogen atom located on the 3 position of the pyrmidine ring, followed by a hydrogen shift, would lead to a 1,3-biradical which could collapse to the observed cyclopropanol (**10**). γ-Hydrogen abstraction in nitrogen aromatics is not without precedence,[19] although this does represent the first case of

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(15) In a typical preparative run 10^{-2} *M* ketone was irradiated under nitrogen in an air-cooled Rayonet reactor at 3000 Å. For quantitative measurements degassed samples were mounted on a rotating merry-go-round apparatus with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L-450W). A filter solution consisting of 0.002 *M* potassium chromate and 1% potassium carbonate was used to isolate the 3130 Å mercury line.[7] Benzophenone–benzhydrol actinometry[16] was used for quantum yield determinations, and photoconversions were carried to 15% or less.

(16) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Amer. Chem. Soc.*, **83**, 2789 (1961).

(17) All spectral and analytical data for the compounds reported in this paper are consistent with their structural assignments and will be presented in a full paper.

(18) C. De Puy, *Accounts Chem. Res.*, **1**, 33 (1968).

(19) F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *J. Amer. Chem. Soc.*, **92**, 2745 (1970).

such a reaction in a nitrogen aromatic ketone. This also represents the first reported case of "photochemical cyclopropanol formation" in aryl alkyl ketones involving direct hydrogen abstraction.[20]

The anomalous photobehavior observed in the 4-butyrylpyrimidine (**2**) relative to the 2- and 5-butyrylpyrimidines (**1** and **3**) is not easily explained on the basis of present experimental information. However, 4-substituents are known[23] to affect the n,π* absorption characteristics of pyrimidine to a greater extent than 2- and 5-substituents, and we do in fact observe a bathochromic shift in the n,π* absorption band of 4-butyrylpyrimidine (**2**) relative to the 2- and 5-butyryl isomers, **1** and **3**. The unusual behavior may reflect, then, a closer proximity of the ring nitrogen and carbonyl n,π* states in 4-pyrimidyl ketones and greater triplet interactions. There are two plausible mechanisms that can account for the solvent effect observed in the formation of cyclopropanol (**10**). The first involves a vibronically mixed[3] triplet state which undergoes hydrogen abstraction by both the excited carbonyl and ring nitrogen to form a normal 1,4-biradical and a 1,3-biradical. In nonpolar solvents formation of the 1,4-biradical is favored and leads primarily to type II products. In polar solvents the 1,3-biradical is favored and leads to a predominance of cyclopropanol product. Alternatively, the solvent effect could be rationalized in terms of two lowest lying nonequivalent n,π* excited triplet states existing in thermal equilibrium.[2] If greater charge separation is associated with the nitrogen n,π* state than with the corresponding carbonyl n,π* state, the nitrogen n,π* triplets would predominate in polar solvents and reaction in such solvents would lead primarily to cyclopropanol. Our present data do not allow distinguishing between either mechanism, and the observed solvent effect is being investigated further.

The reactions of the butyrylpyrimidines, **1**, **2**, and **3**, were quenched using 1,3-pentadiene and triplet lifetimes were determined from linear Stern–Volmer plots. A summary of the triplet reactivities and reaction quantum yields is shown in Table I. Although the quantum efficiencies for reaction of the butyrylpyrimidines **1**, **2**, and **3** are found to be comparable to those reported[7] for related phenyl and pyridyl ketone systems, the triplet reactivities of ketones **1**, **2**, and **3** are enhanced. The magnitudes of the observed rate enhancements toward type II elimination, however, are in line with what might be expected for diaza ring substitution,[7] and the increased reactivities appear to result from the added inductive effect of two ring nitrogen atoms on the electrophilic n,π* triplet state.[2]

Table I. Quantum Yields and Photoreactivity of Butyrylpyrimidines in Type II Photoelimination[a]

Ketone	Φ_{II}	$\Phi_{-\text{ketone}}$	Slope ($k_q\tau$, M^{-1})	10^8 ($1/\tau$), sec^{-1}
(**3**) 5-Pyrimidyl	0.34	0.42	90	0.55
(**1**) 2-Pyrimidyl	0.09	0.23	47.5	1.03
(**2**) 4-Pyrimidyl	0.13, 0.18[b]	0.36	30[c]	1.67[c]

[a] In benzene solvent (originally 0.05 *M* in ketone). [b] Cyclopropanol formation. [c] In 50% benzene–*tert*-butyl alcohol.

Work designed to further elucidate the role of aza substitution on the photoreactivity of pyrimidyl alkyl ketones is in progress. We are also engaged in the synthesis of a number of the related aza aromatic ketone systems and will begin studying their photochemistry shortly.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Corporation for support of this work. We also thank Dr. P. J. Wagner for helpful comments.

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Received April 29, 1974

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[20] Other reports of photochemical cyclopropanol formation in aryl alkyl ketones appear to involve electron-transfer processes.[21,22]

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[22] A. Padwa and R. Gruber, *J. Amer. Chem. Soc.*, **92**, 107 (1970).

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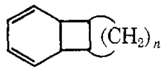
Selective Trapping of Dienes by Benzylideneacetoneiron Tricarbonyl. Synthesis and Thermal Rearrangement of Tricyclo[4.4.0.0^{2,5}]deca-7,9-diene and Tricyclo[4.3.0.0^{7,9}]nona-2,4-diene

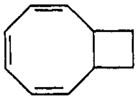
Sir:

Binding transition metals to a polyolefin capable of tautomerism can have a substantial effect upon both the position of tautomeric equilibrium and the rates of interconversion of the tautomers. Cotton[1] has recently reported the isolation of stable iron tricarbonyl complexes of Ib–Id by reaction of the olefinic ligands with diiron nonacarbonyl. The isolation of the complex of Ib is of particular interest in that in the free ligand system the triene tautomer, II, is substantially favored at equilibrium over the tricyclic diene tautomer, Ib.

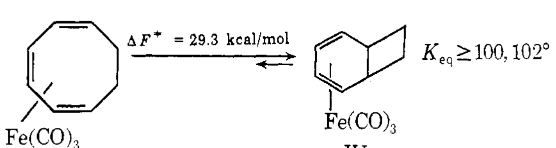
We have recently reported the ring closure of cyclooctatrieneiron tricarbonyl (III) to bicyclo[4.2.0] octadieneiron tricarbonyl (IV) ($\Delta F^{\ddagger}$ = 29.3 kcal/mol, 102°) and a lower limit to the equilibrium ratio of IV/III of 100 at 102°.[2] This represents a substantial shift in the equilibrium toward the bicyclic diene tautomer relative to the free ligand system in which the equilibrium ratio of 1,3,5-cyclooctatriene to bicyclo[4.2.0]octadiene is 85:15 at 100°.[3] The origin of this shift was ascribed to distortion of the preferred tub conformation of cyclo-



Ia, $n = 1$; b, $n = 2$
c, $n = 3$; d, $n = 4$



II



III

IV

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