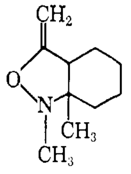

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In summary, our findings demonstrate an important extension to 1,3-dipolar additions of nitrones which impart added and predictable functionality through the use of cumulated double bonds. The special reactivity displayed by the products generated in this study are being further explored.

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Photoreactivity of p-Methoxyphenyl Ketones. Evidence for Hydrogen Abstraction from Equilibrium Concentrations of Upper n,π^* Triplets

Sir:

The difference in photoreactivity between aryl ketones with n,π^* lowest triplets and those with π,π^* lowest triplets has posed one of the oldest continuing problems in modern photochemistry.[1] Three years ago, Yang, McClure, and coworkers reported that several ring-substituted acetophenones undergo photoreduction with reasonable quantum efficiencies even though all spectroscopic evidence indicates that their lowest triplets are mostly π,π^* in nature.[2] Later, Yang[3] and we[4] both showed that methyl and methoxy substituents decrease the apparent reactivity of ketone triplet states in hydrogen abstraction reactions. Elegant spectroscopic investigations in several laboratories have established (1) that the "n,π^*" and "π,π^*" triplets of such phenyl alkyl ketones lie within a few kilocalories of each other, and (2) that the two states mix vibronically.[5] Consequently, Yang suggested[3] that the hydrogen abstraction reactions of the substituted phenyl ketones occur from the lowest triplet, which is mostly π,π^* in character but has enough n,π^* character to be *slightly* reactive. We originally felt[6] that mixing of states might be a chief determinant of triplet state reactivity and agreed that Yang's appealing suggestion was possible. However, there has been no evidence presented which eliminates the possible involvement of the upper n,π^* triplets. Since these are known to be reactive in hydrogen abstraction, and since the two states are so close together that they may well equilibrate thermally before decaying, this alternate possibility could not be dismissed.[4] We now present evidence that strongly suggests that the majority of hydrogen abstraction by p-methoxyphenyl alkyl ketones occurs from the upper ^{3}n,π^* state.

Equations 1–3 describe the quantum yield for type II photoelimination when only the lower triplet reacts, only the upper triplet reacts, or both react, respectively. In all cases, P_p represents the probability that the

$$\Phi = k_r^{\pi}\tau^{\pi}P_p = P_pk_r^{\pi}/(k_r^{\pi} + k_d^{\pi}) \quad (1)$$

$$\Phi = X_nk_r^{n}\tau_{eq}P_p = P_pX_nk_r^{n}/(X_nk_r^{n} + X_{\pi}k_d^{\pi}) \quad (2)$$

$$\Phi = (X_nk_r^{n} + X_{\pi}k_r^{\pi})\tau_{eq}'P_p = P_p(X_nk_r^{n} + X_{\pi}k_r^{\pi})/[X_nk_r^{n} + X_{\pi}(k_r^{\pi} + k_d^{\pi})] \quad (3)$$

1,4-biradical intermediate goes on to products;[7] the k_r's represent rate constants for hydrogen abstraction by the two states; k_d^{π} represents the rate of radiationless decay of the π,π^* triplet (k_d^{n} is thought to be negligibly small compared to k_r^{n});[7] X_n and X_{π} represent the fractions of n,π^* and π,π^* states populated at thermal equilibrium; and the excited state lifetimes are defined by the denominators of the right-hand equations. A Stern–Volmer quenching plot is linear in every case, *as long as there is not so much quencher present as to upset the equilibration of states.*

Determination of Φ and τ values allows one to estimate *apparent* k_r values but does not allow one to distinguish among the three kinetic possibilities. Variations in apparent k_r values as a function of the energy gap between the two triplets would be too subtle to interpret at present, because both X_n and k_r^{π} (proportional to the amount of state mixing) would decrease as ΔE increases. Moreover, accurate spectroscopic determination of ΔE values is by no means straightforward. Consequently, we have applied a more classic test and determined how the selectivity of the excited ketone depends on its reactivity.

Table I contains photokinetic data for five phenyl alkyl ketones containing different kinds of γ C–H bonds; Table II presents data for the analogous p-anisyl ketones. These data were all acquired by our usual method[7] of Stern–Volmer quenching with 2,5-dimethyl-2,4-hexadiene in degassed benzene solutions at 25°.

Table I. Photoelimination of Select Phenyl Ketones $PhCOCH_2CH_2R$[a]

R	Φ_{II}[b]	$k_q\tau$, M^{-1}[c]	k_r^{n}, 10^7 sec^{-1}[d]	Rel k_r
P1 CH_3	0.36	660	0.8	(1)
P2 CH_2CH_3	0.33	40	12.5	16 (1)
P3 $CH(CH_3)_2$	0.25	11	45.0	60
P4 $CH_2CH_2CO_2CH_3$	0.64	125	4.0	0.32
P5 CH_2CH_2CN	0.46	500	1.0	0.08

[a] 0.10 M ketone solutions irradiated at 3130 Å to 5% conversion. [b] Quantum yield of acetophenone formation in benzene. [c] Slope of Stern–Volmer quenching plot; all averages of duplicate runs. [d] $k_r^{n} = 1/\tau$, k_q assumed to equal 5×10^9: W. D. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969); G. Porter and M. R. Topp, *Proc. Roy. Soc., Ser. A*, **315**, 163 (1970).

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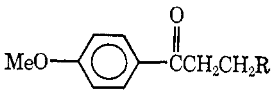
Table II. Photoelimination of Select *p*-Anisyl Ketones[a]



$MeO{-}C_6H_4{-}C(=O)CH_2CH_2R$

R	Φ^b	$k_q\tau$, M^{-1}	k_r, 10^6 sec^{-1}	k_d^π, 10^8 sec^{-1}	Rel k_r
A1 CH_3	0.04	3550	0.056	1.4	(1)
A2 CH_2CH_3	0.26	2300	0.56	1.6	10 (1)
A3 $CH(CH_3)_2$	0.67	1100	3.0	1.5	51
A4 $CH_2CH_2CO_2Me$	0.14	2500	0.28	1.7	0.50
A5 CH_2CH_2CN	0.015	2700	0.03	1.8	0.06

[a] Same conditions as in Table I. [b] *Maximum* quantum yield of ketone reaction: see P. J. Wagner and H. N. Schott, *J. Amer. Chem. Soc.*, **91**, 5383 (1969).

Comparison of ketones P1, P2, and P3 with A1, A2, and A3 indicates that the selectivity of the two carbonyl triplets toward primary, secondary, and tertiary C–H bonds is almost identical—if anything, the anisoyl triplet is slightly *less* selective—despite the fact that the reactivity of the triplet anisoyl group is only 0.5% that of the triplet benzoyl group. Note that the near constant k_d value provides an internal check of the accuracy of the data. These results must be contrasted to the behavior of α-diketones, whose triplets abstract hydrogens intramolecularly at much the same rates displayed by the anisyl ketones but with a significantly greater selectivity among C–H bonds of different strength.[8,9]

Comparison of ketones A2, A4, and A5 with P2, P4, and P5 is even more revealing. All have secondary C–H bonds at the γ position. Electron-withdrawing groups at the δ position deactivate the electrophilic[7,10] n,π^* triplet of the benzoyl group. They have an identical effect on the triplet state reactivity of the anisoyl group.

We feel that it would be extremely unlikely for the π,π^* triplet, which must have a relatively electron-rich oxygen atom (even if a few per cent n,π^* character is present), to be subject to the same inductive effects as the electrophilic n,π^* state. Consequently, most of the hydrogen abstraction probably occurs from a level approximately 3 kcal above the lowest vibrational level of the π,π^* state,[11] an upper level that is mostly n,π^* in character. Whether the $^3n,\pi^*$ state is discrete or entirely mixed with upper vibrational levels of the $^3\pi,\pi^*$ state[5c] is unimportant. The rate at which the lowest triplet returns to the reactive upper level is not known, but would be at least 10^9 sec^{-1} if only vibrational excitation is required The reasonably short-lived triplet of benzophenone apparently has time to equilibrate with the excited singlet *5 kcal* higher in energy.[12]

The question of how much n,π^*-like reactivity vibronic mixing can induce in the lowest vibrational level of the π,π^* triplet becomes academic if $X_n k_r^n > k_r^\pi$. We are investigating other aryl ketones in order to ascertain the generality of our conclusion.[13]

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(8) N. J. Turro and T. J. Lee, *J. Amer. Chem. Soc.*, **91**, 5651 (1969).

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(10) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3361 (1965).

(11) In contrast, phosphorescence excitation spectra of *p*-methoxyacetophenone in polar glasses at 77°K have been interpreted to indicate a 5–6 kcal energy separation.[2,5a] We feel that the actual separation at room temperature in a hydrocarbon solvent is lower.

(12) J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, **92**, 410 (1970).

(13) This work is being supported relatively generously by the National Science Foundation.

(14) Alfred P. Sloan Fellow, 1968–1970; to whom correspondence should be addressed.

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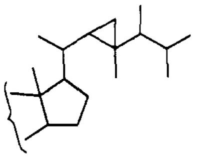
The Structure and Absolute Configuration of the Marine Sterol Gorgosterol

Sir:

Recently we reported[1] chemical evidence which demonstrated the occurrence of a biogenetically unprecedented side chain in the unusual marine sterol, gorgosterol. This evidence led us to conclude that gorgosterol possesses the cholesterol ring skeleton together with the side chain depicted in either partial structure I or II. In order to distinguish between these two structures and to establish the stereochemistry (32 possible stereoisomers), an X-ray diffraction analysis of 3β-bromogorgostene (III, R = Br) was undertaken. We wish to report now that gorgosterol is (22*R*,23*R*,24*R*)-22,23-methylene-23,24-dimethylcholest-5-en-3β-ol,[2] as shown in the three-dimensional structure III (R = OH).



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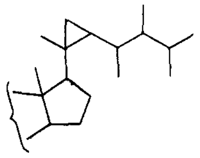
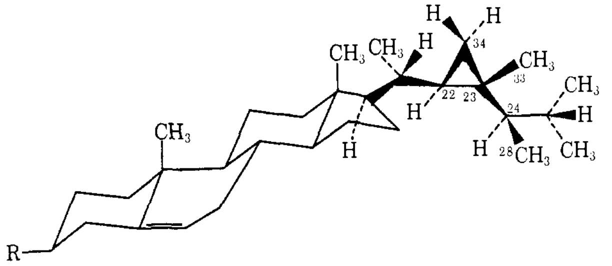


II



III

Treatment of an ethereal solution of gorgosterol with aluminum bromide[3] gave 3β-bromogorgostene (III, R = Br; mp 159–160°; $[\alpha]_D$ −34.7°; M^+ 488–490 = $C_{30}H_{49}Br$) which crystallized from acetone to give orthorhombic plates. Diffraction data collected on a single crystal (roughly spherical, 0.1-mm diameter) identified the space group as $P2_12_12_1$ with unit cell dimensions of $a = 10.719 \pm 0.06$, $b = 33.149 \pm 0.05$, $c = 7.786 \pm 0.04$ Å (measured by Syntex $P\bar{1}$ autodiffractometer); $V = 2766.6$ Å^3. The density (mea-

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