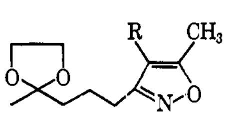
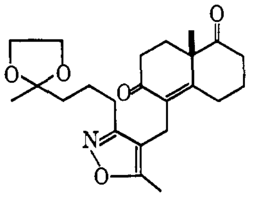


V, R = CO_2Et
VI, R = CH_2OH
VII, R = CH_2Cl



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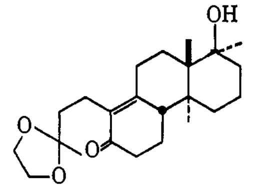

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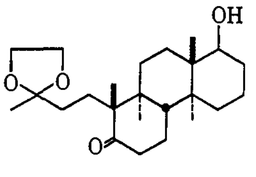

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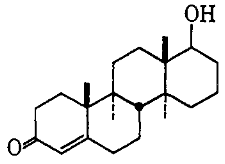
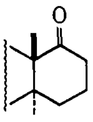


XII

to the D-homo-17a-methyl-$\Delta^{4,17(17a)}$-androstadien-3-one (XV), mp 145–146°.[7] Treatment of the crude mono-



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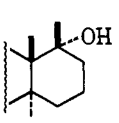

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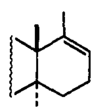
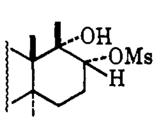
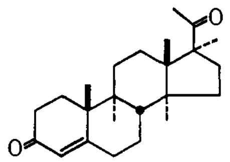


XV



XVI



XVII

mesylate XVI of the glycol derived from the osmium tetroxide hydroxylation of XV with potassium *t*-butoxide in dry *t*-butyl alcohol for 16 hr at 60° gave *dl*-progesterone (XVII), mp 182–184° (lit.[13] mp 183–185°), spectral properties identical with those of the natural material.

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for their support of this work.

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Received August 11, 1967

On the Mechanism of the Paterno–Büchi Reaction

Sir:

Recently there has been considerable interest on the nature of reactive states in photocycloaddition reactions.[1] A common photocycloaddition reaction of carbonyl compounds is their addition to olefins to form oxetanes, *i.e.*, the Paterno–Büchi reaction.[2] Contributions from many laboratories suggested that the reaction of simple phenyl carbonyl compounds proceeds *via* their n,π* triplet state. One interesting feature of this reaction is that polynuclear aromatic aldehydes with low-lying π,π* triplet states react with olefins to yield oxetanes in much higher quantum yields than the quantum yields of photoreduction of these aldehydes. In this communication we wish to demonstrate that the Paterno–Büchi reaction of benzaldehyde proceeds *via* its n,π* triplet state while the reaction of 9-anthraldehyde proceeds *via* a triplet state and another short-lived excited state.

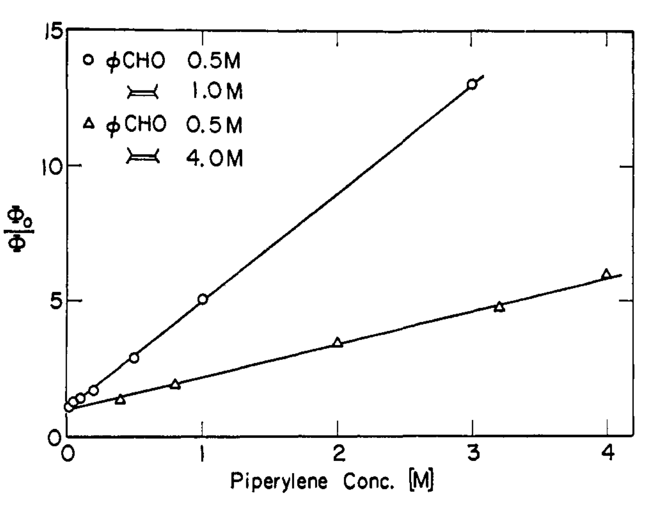

Figure 1.

When the photochemical addition of benzaldehyde (0.5 *M*) to 2,3-dimethyl-2-butene was carried out in the presence of piperylene, the reaction was quenched to various extents depending on the quencher concentration. The apparatus used has been reported earlier.[3] The formation of oxetane was followed by vpc analysis on a SF-96 (20%) on Firebrick column (0.25 in. × 5 ft) at 128° and the consumption of carbonyl compounds was analyzed by infrared spectrometry at their respective carbonyl maxima with a Beckman IR-7 infrared spectrophotometer. The reactions follow zero-order kinetics up to 25% completion. In most kinetic runs, the reaction was followed to no more than 15% completion. Linear Stern–Volmer plots were obtained for benzaldehyde at two different olefin concentrations (4 and 1 *M*) (Figure 1), indicating the reaction proceeds *via* a single reactive state which is assigned the n,π* triplet state. In a separate experiment it was demonstrated that piperylene is just as effective a quencher as di-*t*-butyl nitroxide for the photochemical addition of benzaldehyde to 2,3-dimethyl-2-butene.

The absolute quantum yield of benzaldehyde consumption or oxetane formation was found to be de-

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(3) D. R. Coulson and N. C. Yang, *J. Am. Chem. Soc.*, **88**, 4511 (1966).

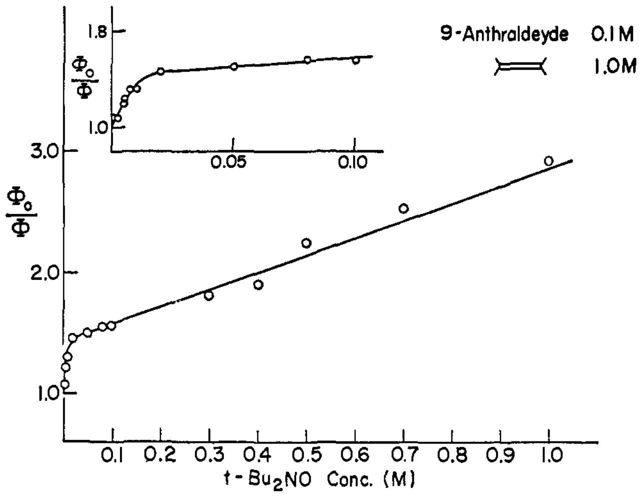

Figure 2.

pendent on the olefin concentration (Table I). However, the quantum yield is lower in neat olefin than in 4 *M* olefin, indicating that the deactivation of excited singlet state by olefin may have occurred.[2e] When the photochemical addition of benzophenone (0.5 *M*) to 2,3-dimethyl-2-butene (1 *M*) was carried out in benzene, benzophenone was found to be considerably less reactive than benzaldehyde (Table I). A linear Stern–Volmer plot was also obtained in the case of benzophenone reaction with a slope of 3 M^{-1}.

Table I

Carbonyl compd	2,3-Dimethyl-2-butene, *M*	ϕ(>C=O)	ϕ(oxetane)
Benzaldehyde	1	0.55 ± 0.02	0.465 ± 0.005
Benzaldehyde	4	0.61 ± 0.02	0.527 ± 0.005
Benzaldehyde	Neat		0.397 ± 0.005
Benzophenone	1	0.09 ± 0.02	
9-Anthraldehyde	1	0.024 ± 0.005	
9-Anthraldehyde	4	0.048 ± 0.005	

When the photochemical addition of 9-anthraldehyde to 2,3-dimethyl-2-butene in benzene was carried out in the presence of various concentrations of di-*t*-butyl nitroxide, quite different results were obtained. The Stern–Volmer plot was nonlinear. The absolute quantum yield of aldehyde consumption decreased sharply at low quencher concentration, followed by a much slower decrease at higher quencher concentration (Figure 2). This result indicated that there are two different reactive species in the photochemical addition of anthraldehyde to 2,3-dimethyl-2-butene. One of them, which accounts for a minor portion of the reaction (23%), is easily quenchable by di-*t*-butyl nitroxide, while the other one, which accounts for the major portion of the reaction (77%), is quenched with difficulty.

The Paterno–Büchi reaction may be expressed by the following steps.

$$\mathrm{ArCOR} \xrightarrow{h\nu} [\mathrm{S}]^* \tag{1}$$

$$[\mathrm{S}]^* + \text{olefin} \xrightarrow{k_s} \text{products} \tag{2}$$

$$[\mathrm{S}]^* \xrightarrow{k_{\text{intersystem crossing}}} [\mathrm{T}]^* \tag{3}$$

$$[\mathrm{T}]^* + \text{olefin} \xrightarrow{k_t} \text{products} \tag{4}$$

$$[\mathrm{T}]^* + \text{quencher} \xrightarrow{k_q} \mathrm{ArCOR} \tag{5}$$

$$[\mathrm{T}]^* \xrightarrow{k_{-t}} \mathrm{ArCOR} \tag{6}$$

where these steps represent excitation, singlet-state reaction, intersystem crossing, triplet-state reaction, quenching, and radiationless decay of the triplet state, respectively.

The rates of these reactions may be estimated from the slope of Stern–Volmer plots. Assuming the quenching rate is diffusion controlled and is 5 × 10^9 l./mole sec, the k_t for benzaldehyde is approximately 1 × 10^9 l./mole sec and k_{-t} is approximately 3 × 10^8 sec^{-1}.

The rates for the radiationless transitions between various electronic states are dependent on the energy gaps between these states. The intersystem crossing efficiency of anthracene is less than that of benzene as measured by fluorescence,[4] and the intersystem crossing efficiency of 2-acetonaphthone is less than that of acetophenone.[5] The energy gap between the n,π^* singlet and the low-lying triplet state of anthraldehyde is considerably larger than that of benzaldehyde, and the rate of radiationless transition between these two states ($k_{\text{intersystem crossing}}$) may become sufficiently slow to be competitive with the rate of singlet-state reaction (k_s). It is conceivable that both states of anthraldehyde are reactive in the Paterno–Büchi reaction. *We wish to emphasize, however, that our experimental data are also consistent with the fact that the short-lived excited state may be an upper triplet state.*

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[6] NASA Trainee, 1965–1967.

[7] National Science Foundation Undergraduate Research Participant, 1966.

[8] The authors wish to thank the National Science Foundation for its support and Professor L. A. Singer for many stimulating discussions.

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Photoreduction of Acetophenone and Substituted Acetophenones

Sir:

The correlation of photochemical reactions of organic compounds with the nature of their excited states has been a subject of current interest.[1] In a series of elegant investigations, Hammond and his co-workers demonstrated that the triplet state is the reactive state in the photoreduction of aryl ketones and that the photoreactivity of aryl ketones depends on the nature of their low-lying triplet state.[1a,b] The importance of n,π^* *vs.* π,π^* low-lying triplet states is illustrated by the fact that acetophenone, with a low-lying $^3[\mathrm{n},\pi^*]$ state, is photoreduced with ease, while 2-acetonaph-

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