not be separated by chromatography. Replacing the *tert*-butyl ether (**2**) by the free alcohol (4 equiv) afforded **4a** + **4b** directly (70%). Reduction of the latter with $LiAlH_4$ in THF at 70° for 16 hr produced a mixture of olefins (80%), which was readily separated by tlc on 2-mm silica gel plates with ethyl acetate–chloroform 1:4 into the diastereomeric olefinic alcohols **5a** and **5b** (40% each). The faster moving isomer (**5a**) had mp 45–46°[12] (ether–hexane), $[\alpha]$D +28.1°, and the slower one (**5b**) mp 89–90° (ether–hexane), $[\alpha]$D −28.4°. A faster moving fraction (5%) [ir 5.10 μ; nmr τ 4.58 (m) and 4.83 (m)] was assigned the 13,14-allenic structure. Alkylation of the olefinic diols **5a** and **5b** with *tert*-butyl ω-iodohexanoate (4 equiv) using dimsyl anion in DMSO at 25° afforded with remarkable specificity the ring-alkylated products **6a**, $[\alpha]$D +12.4°, and **6b**, $[\alpha]$D −6.6°, respectively, both in 30% yield, in addition to 50% of unchanged starting material. Structures **6a** and **6b** were verified by oxidation with DDQ in dioxane to the α,β-unsaturated ketones ($\lambda_{\max}^{\text{alc}}$ 233 nm (ϵ 10,500)). Treatment of the *tert*-butyl esters with 7% KOH in methanol for 20 hr at 25° furnished the corresponding carboxylic acids (95%) **7a**, $[\alpha]$D +17.2°, and **7b**, $[\alpha]$D −11.3°. Debenzylation was effected after conversion into the 1,15-dianion with sodium hydride in THF, followed by reduction with excess lithium in ammonia. Column chromatography on silica gel furnished in 50% yield, respectively, crystalline (+)-7-oxa-$PGF_{1\alpha}$ (**9a**), mp 65–67°; $[\alpha]$D +6.8°, and (+)-15-epi-7-oxa-$PGF_{1\alpha}$ (**9b**), mp 70–72°; $[\alpha]$D +6.2°. Repeating this sequence of reactions with (*R*)-(+)-3-*tert*-butyloxy-1-octynyldimethylalane instead of its *S* antipode furnished, *via* (−)-**5a** (mp 45–46°; $[\alpha]$D −29.2°) and (+)-**5b** (mp 89–90°; $[\alpha]$D +28.6°), (−)-7-oxa-$PGF_{1\alpha}$ ((−)-**9a**, mp 65–67°, $[\alpha]$D −6.2°) and (−)-15-epi-7-oxa-$PGF_{1\alpha}$ ((−)-**9b**, mp 70–72°; $[\alpha]$D −5.3°). Cocrystallizing equal amounts of the respective antipodes gave (±)-7-oxa-$PGF_{1\alpha}$, mp 90.5–90.7° and (±)-15-epi-7-oxa-$PGF_{1\alpha}$, mp 72–74°.[13]

To determine the absolute configuration of this series of compounds the dextrorotatory enantiomer **8a** of known absolute configuration[5] was oxidized with selenium dioxide and the resulting (15*S*) and (15*R*) hydroxy derivatives reduced with $LiAlH_4$ to a mixture of **5a** and its 15-epimer ($[\alpha]$D +16°). After tlc separation **5a** had mp 41–43°, $[\alpha]$D +34°, and (+)-**5b** had mp 84–86°, $[\alpha]$D +26°. Since both **5a** and the antipode of **5b** derived from **8a** are dextrorotatory, **5a** and **5b** obtained by the present procedure must be assigned the absolute configurations shown.

7-Oxa-$PGF_{1\alpha}$, its 15-epimer, and their antipodes were tested for their *in vitro* activities in three widely differing systems with the result that only **9a**, in which *all* chiral centers possess the absolute configuration of the prostaglandins, exhibits typical prostaglandin activity, while the others are either inactive or act as antagonists. Thus, **9a** possessed 5% of the activity of $PGF_{1\alpha}$ in the gerbil colon assay showing a dose response curve (50 ng–10 μg) paralleling that of $PGF_{1\alpha}$. On the other hand, **9b** was inhibitory at the 1 μg/ml level toward $PGF_{1\alpha}$ (250 ng to 2 μg/ml), and (−)-**9a** and (−)-**9b** were without any effect on the gerbil colon at the 1 μg/ml level.[14] Similarly, **9a** at 100 μg/ml stimulated the formation of cyclic AMP in the mouse ovary[6] (activity 0.1 × $PGF_{1\alpha}$), while the remaining three isomers were inactive at the same dose levels.[15] Thirdly, only **9a** proved to be a substrate for the highly specific prostaglandin 15-dehydrogenase from swine lung (K_m 0.4 m*M*; $PGF_{1\alpha}$, 0.02 m*M*)[16,17] while the remaining three isomers were competitive inhibitors of the enzyme (K_i ranging from 0.4 to 0.5 m*M*).[18]

Acknowledgment. Support for this work by the National Institute for Arthritis and Metabolic Diseases, the National Institutes of Health, is gratefully acknowledged.

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(12) All new substances, amorphous or crystalline, were characterized by nmr, ir, and mass spectra as well as elemental analyses.

(13) Purification of the mixture of (±)-7-oxa-$PGF_{1\alpha}$ and its 15-epimer, obtained by the procedure of ref 1, *via* the methyl esters gave (±)-7-oxa-$PGF_{1\alpha}$, mp 88.5–88.7° by direct crystallization.

(14) We are indebted to Dr. Jane E. Shaw and Dr. Peter Ramwell of Stanford University for these results.

(15) We wish to thank Dr. F. A. Kuehl, Merck Institute for Therapeutic Research, for these results.

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Received July 24, 1971

Mechanism for the Quenching of Alkanone Singlets by Conjugated Dienes[1]

Sir:

The interactions of electronically excited states with 1,3-dienes have aroused considerable interest and represent an important area of current study, as indicated by numerous reports which have appeared on synthetic,[2] mechanistic,[3] and theoretical[4] studies concerning the chemical basis of these interactions. Recently the risk of using 1,3-dienes as *specific* quenchers of triplet states of ketones has been shown, since at high concentrations (>0.1 *M*) of *trans*-1,3-pentadiene substantial quenching of alkanone singlet states occurs.[5] We report here our work which explores the mechanism of the interaction of dienes with singlet alkanones by introducing variations in both the ketone and diene structures. By examining the quenching of ketone fluorescence we obtain a sensitive and quantitative measure of the rates of interaction.

The data in Table I summarize the effects of systematically hindering the carbonyl function of the

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Table I. Quenching of the Fluorescence of Norcamphor Derivatives by Dienes Compared to Quenching by *cis*-Diethoxyethylene (*c*-DEE) and *trans*-Dicyanoethylene (*t*-DCE)

	$k_q \times 10^{-8}$, M^{-1} sec$^{-1\,a}$			
Alkanone	*trans*-1,3-Pentadiene	2,5-Dimethyl-2,4-hexadiene	*c*-DEE[b]	*t*-DCE[b]
1	0.32	3.7	13	52
2	0.33		13	56
3	0.18		8.5	23
4	0.14	1.3	5.7	12
5	<0.07	0.19	1.3	17
6	0.28		14	10

[a] Obtained from $k_q\tau_f{}^0$ (slopes of static fluorescence quenching plots) using $\tau_f{}^0$ values measured by the single photon counting technique. [b] Reference 6.

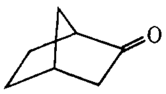
Table II. Quenching of Norcamphor Fluorescence in Benzene[a]

Diene	$k_q\tau_f{}^0$, $M^{-1\,b}$	k_q, M^{-1} sec^{-1} × 10^{-8}
cis,cis-1,3-Cyclooctadiene	0.093	0.16
2-Methyl-1,3-butadiene	0.17	0.29
trans-1,3-Pentadiene	0.19	0.32
trans-2-Methyl-2,4-hexadiene	0.74	1.3
1,3-Cyclohexadiene	1.3	2.4
2,5-Dimethyl-2,4-hexadiene	2.1	3.6

[a] Quenching of the fluorescence lifetime of norcamphor using the single photon counting technique. [b] The $k_q\tau_f{}^0$ values are the slopes obtained by plotting the relationship $\tau_f{}^0/\tau_f = 1 + k_q\tau_f{}^0\cdot$[diene]; $\tau_f{}^0$ for norcamphor is 5.7×10^{-9} sec.

ketone, and the data in Table II summarize the wide variation in rate constants observed as the structure of the diene is altered. It is informative to also consider the responses of an electron-rich olefin, *cis*-1,2-diethoxyethylene (*c*-DEE), and an electron-deficient olefin, *trans*-1,2-dicyanoethylene (*t*-DCE), toward the same variation in ketone structure,[6] and these data are also included in Table I.

A simple but useful model of the n,π* singlet state of ketones illustrates its amphoteric nature; *i.e.*, promotion of a nonbonding electron to the π* orbital results in an increase in electron density in the π system perpendicular to the carbonyl plane and a proportional decrease in electron density in the plane of the carbonyl. Thus, one expects electrophilic species to interact preferentially with the π system above and below the carbonyl plane and nucleophilic species to interact preferentially with the half-vacant n orbital at the sides of the carbonyl. The ketones studied fall into three categories: (1) those which are relatively unhindered from the top and sides, **1** and **2**; (2) those which offer some hindrance at both the top and sides, **3** and **4**; and (3) two ketones which selectively hinder the sides, **5**, and top, **6**.



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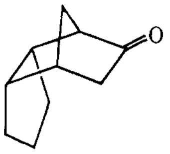

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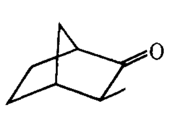

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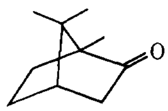

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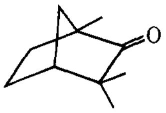

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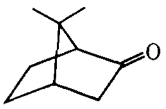

6

Indeed the previously reported results using *c*-DEE and *t*-DCE are in accord with this model.[6] Interestingly, the results with 1,3-pentadiene demonstrate a selectivity toward the key compounds **5** and **6** which parallels that of the electron-rich olefin. The rate of quenching decreases by a factor of 2 when one substituent blocks the side of the carbonyl plane (compare **1** and **2** to **3** and **4**). At least another twofold decrease is observed when the sides are fully substituted, **5**. However, the introduction of considerable steric hindrance from the top (**6**) has virtually no effect. The rates of quenching by 2,5-dimethyl-2,4-hexadiene of ketones **1**, **4**, and **5** exhibit a similar trend. We conclude from this stereoelectronic preference that the diene behaves as a nucleophilic species in its preferential interaction with the electrophilic half-vacant n orbital of the ketone.

The general effect of substituents near the carbonyl is further exemplified by our results comparing norcamphor (**1**), acetone, and propionaldehyde. The rate constants for quenching of the ketone fluorescence by 1,3-cyclohexadiene are 2.4×10^8, 1.1×10^9, and 5.1×10^9 M^{-1} sec^{-1}, respectively. Notice that the rate constant for quenching of the aldehyde is essentially equal to that for diffusion in the solvent, benzene!

Examination of the variation in diene structure (Table II) reveals a large effect on the quenching rate. Three salient features arise from this quenching order. First, increasing substitution of the diene exerts a substantial increase in rate in a manner which opposes the trend in steric hindrance, but which parallels the order of decreasing ionization potential of these dienes.[7] The value for 1,3-cyclooctadiene is low as might be expected on the basis of poorer overlap of its π system.[8] Second, the order of quenching is similar to that observed in the singlet quenching of aromatic hydrocarbons[9] and aliphatic azo compounds.[10] In each of these systems, including the ketones, classical energy transfer is rendered unlikely on the basis of the high endothermicity of the process. Finally, this study urges the use of less reactive dienes such as isoprene or piperylene for triplet quenching studies when the possibility of singlet quenching exists.

Vinyl oxetanes have been found when ketones and aldehydes are irradiated in the presence of high concentrations of dienes.[11-13] In each case the quantum yield (extrapolated to neat diene) is far less than unity in spite of the fact that over 95% of the fluorescence is quenched for the examples involving cyclohexadiene

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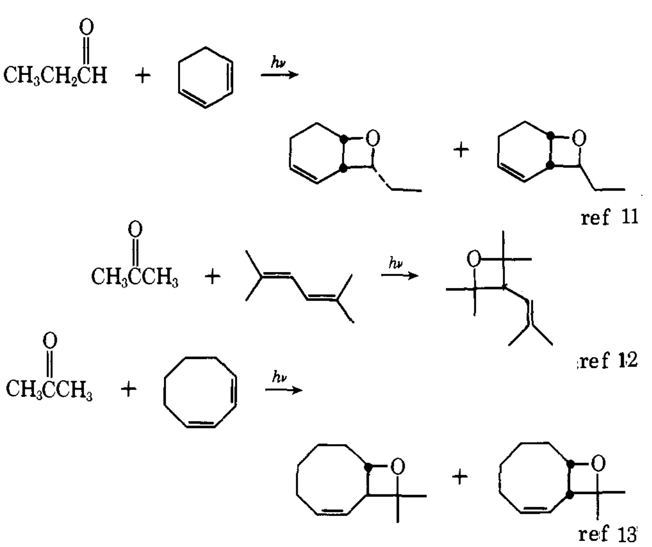

and 2,5-dimethyl-2,4-hexadiene. A mechanism consistent with all of these observations involves the formation of a charge-transfer stabilized exciplex which can collapse to vinyl oxetanes or undergo radiationless decay to the ground-state molecules, a process which is seemingly favorable for exciplexes. Examination of data from the literature on the variation of quantum yield for oxetane formation as a function of diene concentration, in combination with our values for the singlet lifetimes, yields rate constants for exciplex formation assuming this mechanism. The value of $4 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ so obtained from the data of Kubota and coworkers[11] is in good agreement with our value of $5 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$ for the propionaldehyde–cyclohexadiene system. A similar analysis using the data of Barltrop and Carless[12] for the acetone–dimethylhexadiene study gives rise to a rate constant of $7 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ which is in poorer agreement with our value from fluorescence quenching of $1.2 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$. It is possible that an experimental anomaly arising from consumption of the diene during the experiment (disproportionately affecting the results obtained at low diene concentrations) can account for this discrepancy.[14] The example involving acetone and cyclohexadiene, however, cannot be accommodated by a mechanism involving the singlet state of the ketone. The rate constant obtained from analysis of the data of Shima and coworkers[13] is $3 \times 10^9\ M^{-1}\ \mathrm{sec}^{-1}$. Our fluorescence experiments show that the singlet state of acetone is quenched by 1,3-cyclohexadiene with a rate constant of only $7 \times 10^7\ M^{-1}\ \mathrm{sec}^{-1}$. Thus, we feel that oxetane formation in the latter case occurs predominantly from the triplet state of acetone. The fact that a chemical reaction can compete with triplet energy transfer to cyclooctadiene probably again reflects the decrease in diene character for the eight-membered ring.

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(14) We wish to thank Professor N. C. Yang for pointing out this possible explanation to us, for a preprint of his unpublished work on quenching of alkanone singlets by dienes, and for stimulating discussions concerning the mechanism of the quenching action; N. C. Yang, M. H. Hui, and S. A. Bellard, *J. Amer. Chem. Soc.*, **93**, 4056 (1971).

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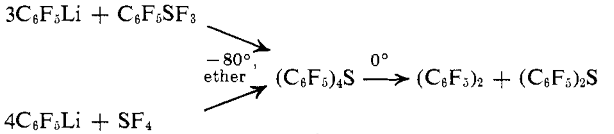
Received May 13, 1971

Tetraarylsulfuranes

Sir:

Tetrakis(pentafluorophenyl)sulfurane (**1**), the first observed pentacoordinated sulfur derivative with four carbon–sulfur bonds, has been prepared in solution at −80° from the reaction of (pentafluorophenyl)lithium with (pentafluorophenyl)trifluorosulfurane or sulfur tetrafluoride. At 0° it decomposes to decafluorobiphenyl and bis(pentafluorophenyl) sulfide.



$$3C_6F_5Li + C_6F_5SF_3 \text{ or } 4C_6F_5Li + SF_4 \xrightarrow[\text{ether}]{-80°} (C_6F_5)_4S \xrightarrow{0°} (C_6F_5)_2 + (C_6F_5)_2S$$

1

Recently, considerable interest has developed in pentacoordinated sulfur compounds (sulfuranes),[1,2] particularly as intermediates in the reaction of organolithiums with arylsulfonium salts.[1] However, only sulfuranes with a minimum of two electronegative noncarbon ligands, such as phenyltrifluorosulfurane[3] or dialkoxydiarylsulfurane,[2b] have been isolated. Earlier we found that phenyltrifluorosulfurane or sulfur tetrafluoride reacted vigorously with phenyllithium to give diphenyl sulfide and biphenyl.[3] The recent studies by Trost[1] strongly support the postulate that tetraphenylsulfurane was formed, but direct detection is needed to show that the sulfurane exists as an intermediate and not just as a transition state. The marked effect of strong electron-withdrawing ligands in stabilizing four and six valence states of sulfur[4] suggested that the pentafluorophenyl group should be more effective than phenyl in stabilizing the sulfurane[5] and in addition provide a unique probe through ^{19}F nmr to detect intermediates stable only in solution at low temperature.

(Pentafluorophenyl)lithium reacts rapidly and exothermically with SF_4 or $C_6F_5SF_3$[6] at −80°. The solution gradually turns pale yellow and a white solid slowly precipitates. At concentrations higher than 5% considerable solid precipitates but redissolves to a great extent on warming to about −40°. The ^{19}F nmr resonance corresponding to the S–F fluorines disappears and only a single new set of pentafluorophenyl resonances is observed at −159.1, −151.9, and −140.1 ppm[7] in the ratio of 2:1:2 corresponding to the expected pattern for ortho, para, and meta. The ortho and meta peaks show no fine structure but are normal band width for pentafluorophenyl fluorines; the para resonance is a triplet, $J = 20$ Hz.[8] No

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(5) The σ_I value for C_6F_5 is 0.25 *vs.* 0.08 for C_6H_5: W. A. Sheppard, *J. Amer. Chem. Soc.*, **92**, 5419 (1970).

(6) (Pentafluorophenyl)trifluorosulfurane ((pentafluorophenyl)sulfur trifluoride) was prepared by reaction of silver difluoride with bis(pentafluorophenyl) disulfide by the procedure reported for preparation of arylsulfur trifluorides.[3]

(7) Measured from 5% internal C_6F_6 and corrected to standard scale by subtracting 163.0 ppm.

(8) A first-order coupling for the para fluorine is often observed for the pentafluorophenyl system but the meta and ortho fluorines usually have complex patterns.