cipient formation of the olefin product (Figure 1c). A similar effect does not seem to occur in the sulfoxide case since the large, diffuse 3p orbital developing on sulfur (Figure 1d) experiences little repulsive interaction with the more remote oxygen at a dihedral angle of 90° [22] and is, therefore, of diminished influence on the attainment of the planar orbital arrangement necessary for linear H transfer. An alternative interpretation may be based on the relatively short O–N compared with the longer C–S distance. The longer S–X bond distance together with the more easily compressed X–S–Y compared with X–N–Y angles argues for a sulfoxide transition state that can more readily attain the planarity requirement for the pericyclic process than the amine oxide transition state.

It has been noted[14] that the large variation in rates correlated with certain structural changes in the sulfoxide substrate (e.g., steric acceleration) may be due to the oxygen and carbon centers being forced into closer proximity. This shortens the distance of separation of these centers in the transition state and results in the observation of quantum mechanical tunneling in H transfer. Possibly, this is also causing the variation of activation parameters (curvature of the Arrhenius plot) noticed before.[2] We are presently studying these aspects, and their mechanistic origin(s) more closely.

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Hydrogen Atom Transfer Reactions in the Photochemistry of Tetrasubstituted Cyclopropenes[1]

Sir:

The photochemical behavior of the cyclopropene ring has been shown to be remarkably dependent on the multiplicity of the excited state involved.[2–4] Singlet states react by σ-bond cleavage to give products which are explicable in terms of the chemistry of vinylcarbenes,[2] while triplet states, generated by sensitization techniques, give high yields of cyclopropene dimers.[3,5–9] We now wish to report that the triplet states of tetrasubstituted cyclopropenes which possess γ hydrogens undergo an intramolecular hydrogen-transfer reaction by a mechanism analogous to the well-known Norrish type II photoreaction of carbonyl compounds. In this communication we describe some of the salient features of this reaction.

Direct irradiation of 1,2-diphenyl-3-methyl-3-(3-phenylpropyl)cyclopropene (**1a**) in benzene with Pyrex-filtered light afforded a 1:1 mixture of 1,2,6-triphenyl-3-methyl-1,3-hexadiene (**2**) and 1,2-diphenyl-3-(3-phenylpropyl)-1,3-butadiene (**3**). The formation of **2** and **3** can be most economically accounted for by ring opening of the excited singlet state of **1** to

a, R_1 = H; R_2 = Ph
b, R_1 = R_2 = CH_3
c, R_1 = H; R_2 = CH_3
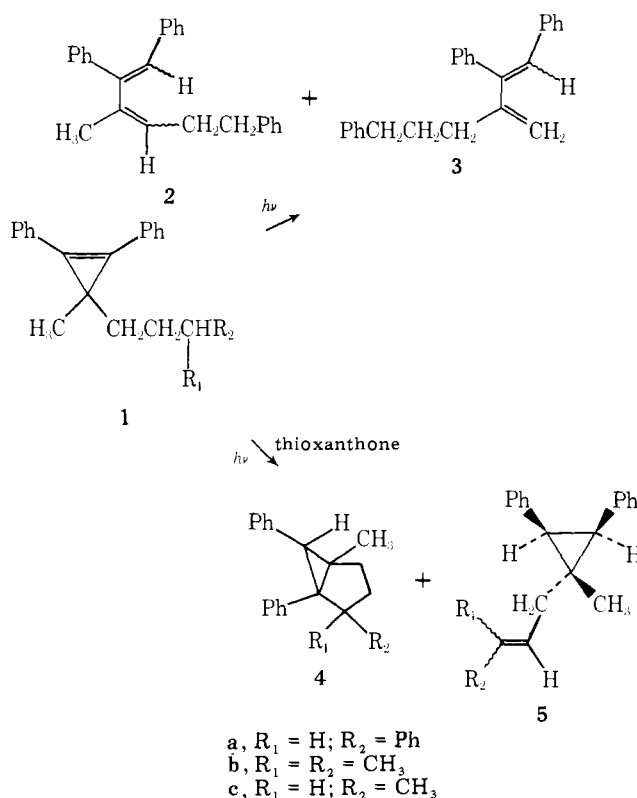
a vinylcarbene followed by intramolecular hydrogen abstraction. The sensitized irradiation of **1a** in benzene (thioxanthone), however, produced *endo-* and *exo-*5-methyl-1,2,6-triphenylbicyclo[3.1.0]hexane (**4a**, 30%) as well as *cis-*1,2-diphenyl-*cis-*3-methyl-3-(3-phenyl-2-propenyl)cyclopropane (**5a**, 70%) as a mixture of isomers.[11] Similar results were obtained with cyclopropenes **1b** and **1c**.

The irradiation of 1,2-diphenyl-3-methyl-3-*o*-toluylcyclopropene (**6**) provides another example of a system in which the products of the direct and triplet-sensitized photolysis are completely different. Thus, direct irradiation of **6** in benzene with Pyrex-filtered light afforded indene **7** in quantitative yield.

7, R = H
10, R = CH₃

6, R = H
9, R = CH₃

8, R = H
11, R = CH₃
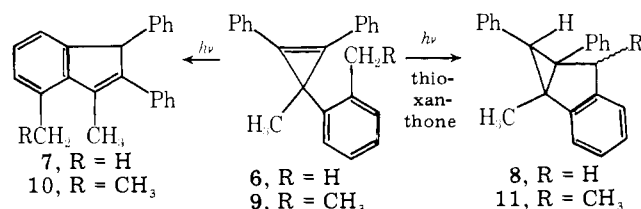
The sensitized photolysis (thioxanthone) of **6** produced benzobicyclo[3.1.0]hexane **8**. Similar behavior was observed with the closely related ethyl-substituted cyclopropene **9** (R = CH₃).

We propose a mechanism analogous to that accepted for the type II reaction of ketones to account for the formation of **4** and **5** upon sensitized irradiation of **1**. Thus, the excited triplet state of the cyclopropene abstracts a hydrogen from the γ-carbon atom via a six-membered transition state to produce a 1,5 biradical which either couples to give **4** or disproportionates to afford **5**. A similar sequence is suggested to rationalize the formation of benzobicyclo[3.1.0]hexane **8** and **11**.

1

⟶ 4 + 5
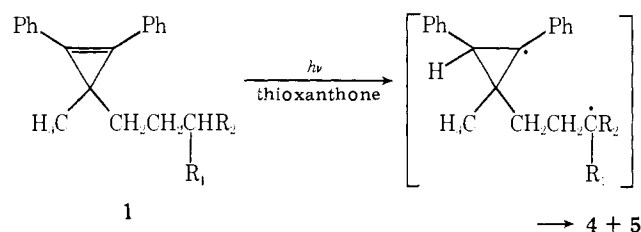
There are a number of reports in the literature which indicate that hydrogen-transfer reactions occur in the photochemistry of alkenes.[12-15] In fact, a closely related hydrogen atom transfer reaction of a cyclopropenyl ketone was previously proposed by Van Tamelen and Whitesides[16] and provides excellent chemical analogy for the first step of the above sequence.
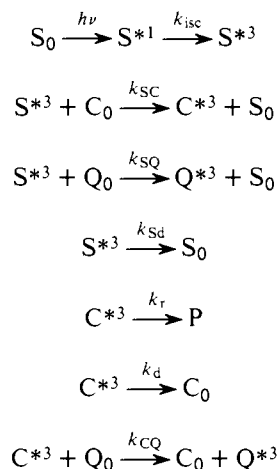
We found that *trans*-stilbene (E_T = 50 kcal/mol)[17] can act as a quencher for the triplet-sensitized hydrogen-transfer reaction of cyclopropenes **1a**–**1c**, **6**, and **9**. In these experiments, *trans*-stilbene intercepts both the sensitizer triplet and the cyclopropene triplet. It was assumed that both triplets (thioxanthone (E_T = 65.5 kcal/mol)[17] and cyclopropene (E_T = 60 kcal/mol)[3]) were quenched at the same diffusion-controlled rate. The kinetic expression for the triplet photosensitized reaction, involving sensitizer S_0, cyclopropene C_0, and quencher Q_0 to give bicyclo[3.1.0]hexane P, was derived from Scheme I. The extent of conversion of triplet cyclopropene to bicyclo[3.1.0]hexane in benzene was studied as a function of the concentration of *trans*-stilbene as quencher. Plots of Φ_0/Φ_q at varying quencher concentration but with constant [Q]/[C] ratios ([Q]/[C] = 1/50) give lines whose intercepts afford k_{SQ}/k_{SC} ratios and whose slopes divided by the intercepts give $k_{CQ}\tau^3c$ values.[18]

$$\Phi_0/\Phi_q = \left[1 + \frac{k_{SQ}[Q]}{k_{SC}[C]}\right] + \left[1 + \frac{k_{SQ}[Q]}{k_{SC}[C]}\right]k_{CQ}\tau^3c[Q]$$

Table I. Kinetic Data for the Triplet Sensitized Hydrogen Abstraction Reaction

Cyclopropene	Φ	$k_{CQ}\tau^3c$, M⁻¹	$1/\tau$, 10^6 s⁻¹
1a	0.57	1280	4.03
1b	0.36	2880	1.77
1c	0.03	5050	1.02
6	0.09	4850	1.03
9	0.68	4200	1.23

Scheme I

$$S_0 \xrightarrow{h\nu} S*^1 \xrightarrow{k_{isc}} S*^3$$

$$S*^3 + C_0 \xrightarrow{k_{SC}} C*^3 + S_0$$

$$S*^3 + Q_0 \xrightarrow{k_{SQ}} Q*^3 + S_0$$

$$S*^3 \xrightarrow{k_{Sd}} S_0$$

$$C*^3 \xrightarrow{k_r} P$$

$$C*^3 \xrightarrow{k_d} C_0$$

$$C*^3 + Q_0 \xrightarrow{k_{CQ}} C_0 + Q*^3$$

The modified Stern–Volmer plots obtained were linear with the slopes listed in Table 1 as $k_{CQ}\tau^3c$ values. The value of k_{CQ} in benzene is taken to be 5×10^9 L mol⁻¹ s⁻¹.[19] Quantum yields and $(k_r + k_d)$ values (i.e., $1/\tau$) are given in Table 1 for the five cyclopropenes studied. If the biradical intermediate reverts to cyclopropene, then the mechanism shown in Scheme I would have to be modified and the expression for Φ_0 would include a factor representing the fraction of biradicals that go on to product. This latter fraction is not known, though a minimum value for it is given by the reaction quantum yield. As a consequence, one cannot readily separate $1/\tau$ values for k_r and k_d.

Several results in Table 1 are of interest and merit comment. First, the triplet lifetimes of the cyclopropenes are ~100 times greater than those for the related phenyl alkyl ketones.[20] The longer lifetime of the cyclopropenes may very well reflect the weaker C–H bond being formed in the abstraction reaction. Secondly, the quantum efficiency decreases as the strength of the C–H bond increases, as expected for a hydrogen atom transfer process. This would tend to suggest that biradical reversion is not so important here as is the case with the phenyl alkyl ketone system.[20] We are investigating other tetrasubstituted cyclopropenes to ascertain the generality of our conclusions.

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A Total Synthesis of Racemic and Optically Active Ibogamine. Utilization and Mechanism of a New Silver Ion Assisted Palladium Catalyzed Cyclization

Sir:

The potential for partial synthesis of the clinically important antitumor alkaloid vinblastine[1] provides stimulus for the creation of more efficient synthetic approaches to the iboga alkaloid family.[2-4] We wish to report (a) a short, stereocontrolled synthesis of ibogamine, (b) the discovery of a new silver-palladium catalyzed olefin arylation, (c) the potential of this approach as a chiral synthesis of this alkaloid family, and (d) mechanistic insight into the nature of the olefin arylation.

Scheme I outlines the synthesis of racemic ibogamine (**1**). The boron trifluoride etherate catalyzed Diels–Alder reaction of 1-acetoxy-1,3-hexadiene (**2**) and acrolein (PhCH$_3$, −10 °C, 18 h, 90%) yielded only the desired regio- and stereoisomer of the cyclohexene **3**.[6] Formation of the Schiff base of **3** with tryptamine (PhCH$_3$, MgSO$_4$, −10 to −5 °C) followed by workup with NaBH$_4$ (MeOH, 0 °C) gave the desired aminoacetate **4** in 93% yield. Palladium catalyzed cyclization of **4** [Pd(PPh$_3$)]$_4$[7] (CH$_3$CN, 70 °C, 3–6%) produced the isoquinuclidine **5** (45%) after chromatography (preparative TLC, silica gel, 9:1:0.1 EtOAc–MeOH–NEt$_2$, R_f 0.6). The critical cyclization was effected by the reaction of **5** with bis(acetonitrile)palladium chloride,[8,9] silver tetrafluoroborate, and triethylamine (CH$_3$CN, 1 h at room temperature, 12 h at 70–75 °C) followed by a NaBH$_4$ workup (0 °C, MeOH, 1 h) to reduce the intermediate palladium species. Medium-pressure liquid chromatography[10] gave **1** in 40–45% yield (mp 126–128 °C, cf. ref 3a,d). ^{1}H NMR (270 MHz), mass spectra, and ^{13}C NMR (60 MHz)[11] of synthetic material were identical with those obtained from natural ibogamine.[12]

Of the possible mechanisms for the cyclization of the isoquinuclidine **5** to give **1**, two seemed most likely (Scheme II).[13] ^{1}H NMR (270 MHz) spectra of material obtained using NaBD$_4$–MeOD[14] reductive workup in the cyclization reaction showed the disappearance of the resonance at δ 1.63 (nondeuterated, ddd, J = 13.5, 7.5, 4.0 Hz) assigned to C(17) exo H and collapse of the signal at 2.06 (nondeuterated, dddd, J = 13.5, 11.5, 3.0, 3.0 Hz) to a doublet of multiplets (J = 11.5 Hz) assigned to C(17) endo H. Identification of the product as deuterioibogamine (**1b**) provided strong evidence for mechanism b.

Scheme I. Synthesis of Ibogamine
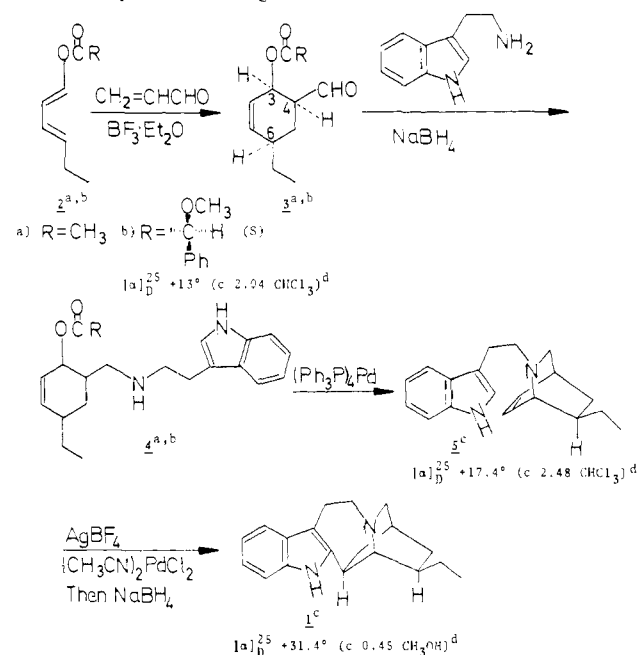
a In a series, compound is racemic. *b* In b series, only major enantiomer, 3*R*,4*S*,6*R*, is depicted. *c* In series derived from 3a, this compound is racemic. In series derived from 3b, this represents major enantiomer (5, 7*S*; 1, 16*S*,20*R*) obtained. *d* These represent the directly observed rotations, uncorrected for the optical purity of the mandelate unit.

Scheme II. Two Possible Mechanisms of Cyclization *a*
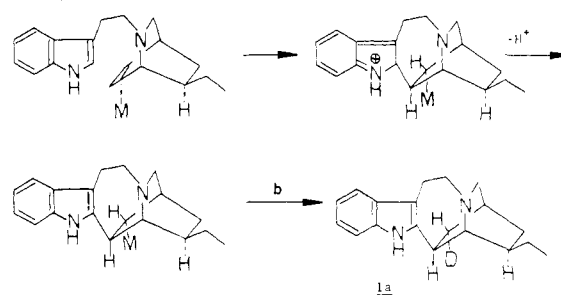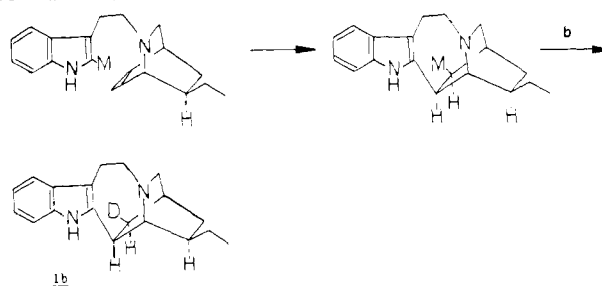
a M is either a silver–palladium mixed salt complex or a partially ionized palladium salt. *b* NaBD$_4$, CH$_3$OD.

Since the chirality of the product is established in the initial cycloaddition, this approach lends itself to a chiral synthesis. Indeed, (*E*,*E*)-1-(*S*-2′-phenyl-2′-methoxyacetoxy)-1,3-hexadiene)**2b**)[15] and acrolein (10% boron trifluoride etherate, PhCH$_3$, −10 °C, 48 h, 92%)[16] gave 80% (3*R*,4*S*,6*R*)-**3b** and 20% 3*S*,4*R*,6*S* isomer. The use of the *O*-methylmandeloyl group as the chiral inducing agent also has the advantage of allowing direct determination of the optical purity by NMR spectroscopy[16,17] (see Scheme I). Reductive amination of **3b** with tryptamine and NaBH$_4$, followed by Pd(PPh$_3$)$_4$ catalyzed cyclization and palladium–silver catalyzed olefin arylation