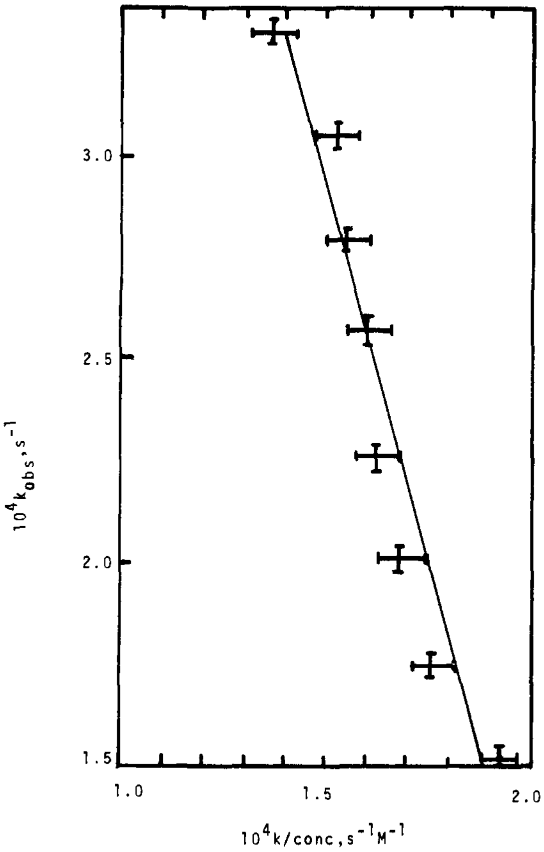

Figure 2. Scatchard plot of the acrylonitrile data of Figure 1 (A).

nitrile evidently is in an intermediate range, since neither the first-order nor the second-order extremes of behavior predicted by mechanism b is observed.

One could hope to achieve the first-order extreme with a trapping agent more reactive than acrylonitrile. Previous direct competition studies[1,3] have shown that at 60 °C, maleic anhydride is 52 times more reactive toward the singlet than is acrylonitrile. If this preference persists or increases at the temperature of the present experiments (−55 °C), a change in kinetic behavior with maleic anhydride might be expected. Indeed, Figure 1 shows that the pseudo-first-order rate constant is virtually insensitive to the concentration of maleic anhydride in the experimental range. This constancy is characteristic of mechanism b when the rate-determining step is unimolecular formation of the reactive intermediate (**2** → **1**-S).

It is a distinguishing feature of mechanism b that a common reactive intermediate is formed, regardless of the trapping agent. Accordingly, the intercepts, $1/k_1$, of the double-reciprocal plots for all trapping agents should be the same. As Figure 1 shows, this requirement is met. The values of k_1 from the acrylonitrile and maleic anhydride plots are 8.43 and 9.06×10^{-4} s^{-1}, which agree within 7%.

Mechanism b treats the singlet biradical **1**-S kinetically as a local minimum in a potential-energy surface, not as a transition state. In this model, a finite barrier opposes the ring-closure step **1**-S → **2**. Independent experimental evidence for the existence of such a barrier in the singlet species derived by photolytic deazetation of the diazene **3** already has been deduced[4] from the temperature dependence of the distribution of photoproducts (**2** vs. **1**-T).

We now find further confirmation in the observation that photolysis of diazene **3** in the presence of 2 M acrylonitrile at −78 °C gives a mixture of 80% of hydrocarbon **2** and 20% of cycloadducts **4** and **5**, with **4** predominant. Moreover, the same experiment using 1.0 M maleic anhydride instead of acrylonitrile gives <5% of **2** and >95% of the analogous cycloadducts. The origin of the cycloadducts cannot be a simple thermal reaction of hydrocarbon **2** with the trapping olefin, since control experiments show that process to be immeasurably slow at −78 °C.

These results indicate the formation of a discrete, trappable intermediate[9] in the thermolysis of **2** and in the photolysis (and thermolysis[1-3]) of **3**. This species cannot be a bicyclo[3.1.0]hex-1-ene (**6**), since derivatives of this ring system behave in an entirely different manner.[8] Nor can the triplet **1**-T be the intermediate, since its chemistry is also different.[1-3] It is difficult to propose candidates other than **1**-S for the role of the singlet species, the identification of which now brings to a total of four (**1**-S,**1**-T,**2**, and **6**) the explicitly recognizable entities of the 2-isopropylidenecyclopentane-1,3-diyl family.

6

The present work rules out any explanation of the observed[1,10,11] regiospecificity of the singlet cycloadditions in terms of direct $[{}_2\pi_s + {}_2\pi_s + {}_2\sigma_s]$ reaction of the bicyclic hydrocarbon **2** with the olefin. A more general explanation[10,11] based on the frontier MO properties of biradical **1**-S clearly is preferred.

The slope and intercept of Figure 1 give the ratio $k_{-1}/k_2 = 3.7$ M. We are not aware of other examples in which competition between intramolecular ring closure and intermolecular capture of a hydrocarbon singlet biradical has been demonstrated kinetically.

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[9] (a) The value of $k_1 = 8.75 \times 10^{-4}$ s^{-1} at 218.1 K corresponds to $\Delta G^‡ = 15.6$ kcal/mol for the ring opening **2** → **1**-S. $\Delta S^‡$ would be expected to be near zero for this reaction,[9b] so that $\Delta H^‡ \simeq 15.6$ kcal/mol. This is significantly *higher* than the value $E_a - RT = 13.3$ kcal/mol observed for the pyrolysis of **1** in the absence of a trapping agent. Nevertheless, the apparent discrepancy does not exclude **1**-S as a common intermediate for the two processes. It can be shown that the observed activation energy, E_a, for the pyrolysis of **2** in the absence of trapping agent is given by $E_a \simeq E_1 - E_{-1}$ where E_1 and E_{-1} are the activation energies for the formation and recyclization of **1**-S. The "discrepancy" of ~2.3 kcal/mol (15.6–13.3) then would be a measure of E_{-1}. (b) Gajewski, J. J.; Chow, S. D. *J. Am. Chem. Soc.* **1977**, *99*, 5696. Roth, W. R.; Wegener, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 758.

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Oxygen-Atom Transfer from Iodosobenzene to Ketenes, α-Keto Carboxylic Acids, and Ketones

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Recently, Groves et al.[1] showed that iodosobenzene, $C_6H_5I{=}O$, could serve as a source of an oxygen atom for a porphyrin, which in turn effected olefin epoxidation and alkane hydroxylation. Furthermore anaerobic oxygenation of cytochrome P450 has been achieved by using $C_6H_5I{=}O$ as the oxygen-atom donor.[2,3]

[†] On a leave of absence from Kurukshetra University, Kurukshetra, India.

[1] J. T. Groves, T. E. Nemo, and R. S. Myers, *J. Am. Chem. Soc.*, **101**, 1032 (1979).

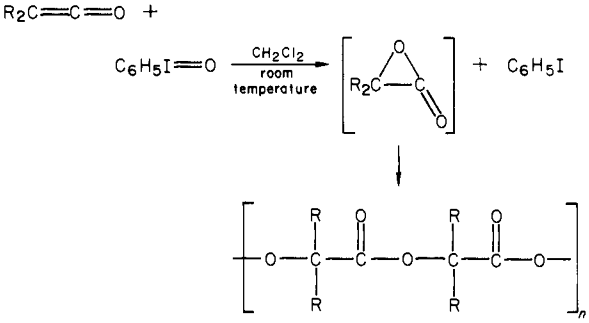
Table I. Oxidation of Ketenes with Iodosobenzene[a]

entry	ketene	olefin	$C_6H_5I{=}O$, equiv	polyester,[b] %	iodobenzene,[c] %
1	$(CH_3CH_2)C{=}C{=}O$		1	67	60
			2	53	53
2	$n(C_4H_9)_2C{=}C{=}O$		1	81	60
			2	70	38
3	$(C_6H_5)(CH_3)C{=}C{=}O$		1	88	70
			2	90	70
4	$(C_6H_5)_2C{=}C{=}O$		1	63	
			2	63	
5	$(CF_3)_2C{=}C{=}O$		1	32	
					48
6		TCNE	1	74[e]	

[a] Reactions are carried out in CH_2Cl_2 for 4–12 h at room temperature. The reactions are homogeneous with 1 equiv. [b] Yields of polyesters were determined by chromatographic separation on silica gel. [c] Glc analysis showed no volatile products other than iodobenzene. [d] The reactions were followed iodometrically. No reaction occurs at −78 °C and at −23 °C the reaction of diphenylketene is 12% complete after 4 h. The structures of the polyesters were proven by infrared comparison with known samples. Methanolysis of the polyester from **4** yielded α-methoxydiphenylacetic acid. [e] Epoxide.

A focus of our research has been the identification of systems, of general type DO, which may transfer an oxygen atom to an acceptor molecule, A, to yield the oxygenated acceptor, AO, and the deoxygenated donor molecule, D (eq 1).

Pyridinium *N*-oxides[4a–c] and 1-pyrroline 1-oxide[5] are stable molecules which behave in this manner. The carbonyl oxide intermediate acts as an oxygen-atom transfer agent,[6] and oxo-transition metals[7] may also be considered in the above formalism as "oxene bound" donors. Iodosobenzene, $C_6H_5I{=}O$, appeared to be a potential member of this class of reagents, and we now report that such behavior prevailed in three systems. The first is in the epoxidation of ketenes (Table I) to yield, initially, α-lactones which polymerized to polyesters (eq 2).



(2)

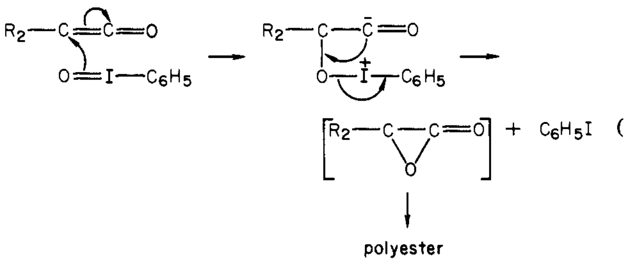
Table I lists yields of polyesters and iodobenzene. No other products were obtained. α-Lactones have previously been synthesized in the ozonation of ketones[8–10] and via the addition of triplet dioxygen to ketenes.[11] In a somewhat related reaction the formation of α-iodoacetic anhydride from the reaction of ketene, iodine, and $C_6H_5I{=}O$ has been reported.[12]

Table II. Decarboxylation of α-Keto Acids with Iodosobenzene[a]

entry	α-keto acid	acid	yield,[b] %
1	α-ketoglutaric	succinic	95
2	α-ketopimelic	adipic	76–80
3	benzoylformic	benzoic	75
4	phenylpyruvic	phenylacetic	80
5	*o*-nitrophenylpyruvic	*o*-nitrophenylacetic	30

[a] The reactions were carried out in anhydrous dioxane by using 1.01 equiv of $C_6H_5I{=}O$ at room temperature for 6–15 h. [b] The yield is in terms of the isolated acid. The other products of the reaction are CO_2 which was determined by absorption on ascarite and iodobenzene which was isolated. Amounts of these products are essentially equivalent to the yield of acid.

We propose a nucleophilic attack of the oxygen end of the iodine–oxygen bond to the ketene double bond followed by loss of iodobenzene with α-lactone formation (eq 3).



(3)

In support of this pathway is the observation that tetracyanoethylene, upon treatment with 1 equiv of $C_6H_5I{=}O$, yields tetracyanoethylene oxide in 74% yield. The essential mechanistic feature of the above processes is that oxygen-atom transfer is accomplished by nucleophilic attack of $C_6H_5I{=}O$ upon the double bond followed by loss of C_6H_5I. Nucleophilic attack upon ketenes is well documented,[13] and the overall reaction follows the formalism expressed in eq 1.

The linear polymer of *p*-iodosostyrene was synthesized by iodination of polystyrene, followed by oxidation with peracetic acid 40%,[14,15] and treatment with base.[16] Iodimetric titration of the iodoso polymer revealed 30% iodoso sites. Treatment of diphenylketene with the polymer beads yielded 23% of the soluble (CH_2Cl_2) polyester derived from polymerization of the α-lactone.

The concept of $C_6H_5I{=}O$ as an oxygen-atom transfer reagent was extended to the reaction of α-keto acids. As shown in Table

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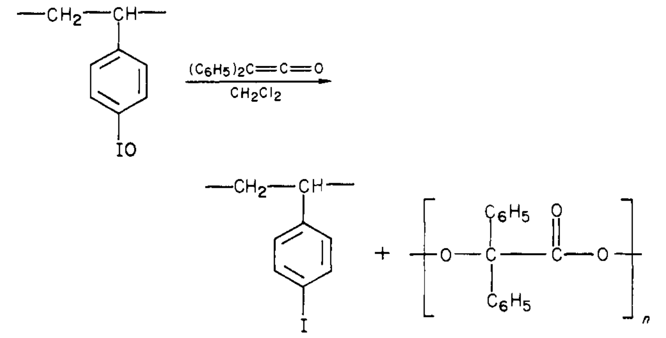
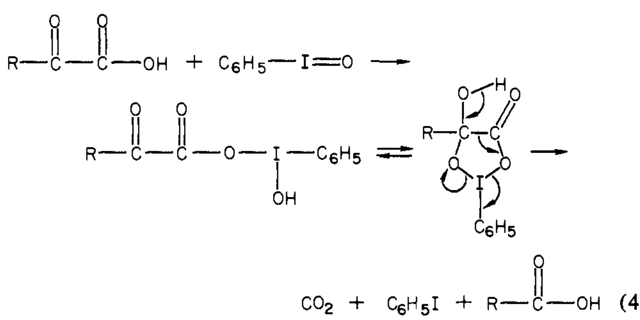


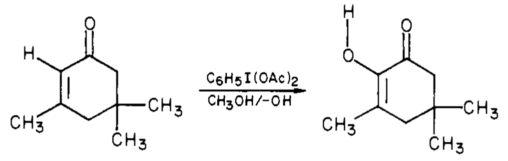
II, high-yield oxidative decarboxylation occurs, affording the lower homologous carboxylic acid, CO_2, and C_6H_5I. The mildness of these reaction conditions relative to H_2O_2 in base[17] which also effects oxidative decarboxylation is evident.

A reasonable mechanistic pathway for this reaction would involve intervention of the cyclic intermediate A formed either from a precursor mixed anhydride or from direct nucleophilic attack of $C_6H_5I{=}O$ upon the ketonic carbonyl group. We favor initial mixed-anhydride formation because $C_6H_5I{=}O$ is an effective catalyst for anhydride formation[18] (eq 4).


(4)

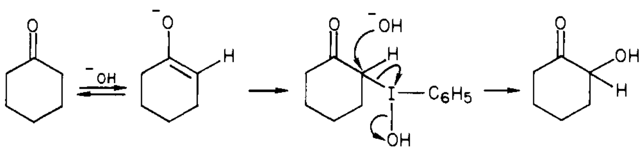
The cleavage reaction of mandelic acid to benzaldehyde and CO_2 with $C_6H_5I(OAc)_2$ is known[19] and a cyclic intermediate has been proposed in this case.[20]

Our next objective was to learn whether $C_6H_5I{=}O$ might serve as the synthetic equivalent of the hydroperoxide anion in the epoxidation of α,β-unsaturated ketones.[21] Reaction of isophorone (**1**) with $C_6H_5I(OAc)_2/{}^-OH$[22] yielded the enolic 3,5,5-trimethyl-1,2-cyclohexanedione (**2**).[23]



1 **2**

This reaction does not involve the epoxy ketone as an intermediate since this compound is stable under the reaction conditions. α-Hydroxylation with $C_6H_5I(OAc)_2$ is not restricted to α,β-unsaturated ketones since cyclohexanone yields α-hydroxycyclohexanone (80%)[24] under the above conditions.[25] Although the overall stoichiometry conforms to eq 1, the source of the oxygen atom is possibly from the attachment of -OH upon the α-iodoso ester.



One may conclude that $C_6H_5I{=}O$ may function as an effective reagent for the transfer of an oxygen atom. Other known examples of this type of reaction are the conversion of a metal-carbenoid complex into a carbonyl product, $(EtO)(C_6H_5)W(CO)_5 \rightarrow C_6H_5COOEt$ (36%),[26] and the conversion of benzyl chloride into benzaldehyde.[18]

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Synthetic Studies on Arene-Olefin Cycloadditions: Total Synthesis of (±)-α-Cedrene

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The meta- or 1,3-photoaddition of olefins to arenes[1] (eq 1) is unique among cycloaddition reactions. It proceeds from readily

(1)

available materials under mild conditions with the development of three new rings and up to six stereocenters[2] and provides a cycloadduct which could serve as a precursor to a variety of synthetically important ring systems.[3] Since its discovery in 1966 by Wilzbach and Kaplan[4a] and Bryce-Smith, Gilbert, and Orger,[4b] the intermolecular version of this reaction has understandably attracted considerable interest[1] while the intramolecular variant, uncovered by Morrison[5] in his elegant studies on bichromophoric molecules,[1b,c] has received little attention.[6] In connection with

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[†] Fellow of the Alfred P. Sloan Foundation.

[1] For reviews pertinent to this and related arene photochemistry, see: (a) Wagner-Jauregg, T. *Synthesis* **1980**, 165. (b) Morrison, H. *Acc. Chem. Res.* **1979**, *12*, 383. (c) Morrison, H. *Org. Photochem.* **1979**, *4*, 143. (d) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309. (e) *Ibid.* **1977**, *33*, 2459. (f) Noyes, W. A.; Al-Ani, K. E. *Chem. Rev.* **1974**, *74*, 29. (g) Bryce-Smith, D. *Pure Appl. Chem.* **1973**, *34*, 213. (h) *Ibid.* **1968**, *16*, 47. (i) Gilbert, A. *Photochemistry* **1970-1979**, *1-10*.

[2] These criteria, which define in part the inherent value of a method(ology), i.e., its capability to efficiently translate simple systems into the more complex, allow one to more fully appreciate the potential of this cycloaddition and its relationship to other more thoroughly explored and exploited cycloadditions such as the Diels-Alder reaction.

[3] The translation of the tricyclo[3.3.0.0^{2,8}]oct-3-ene cycloadduct into three-, five-, and seven-membered carbocycles, bicyclo[3.3.0]octanes, and bicyclo[3.2.1]octanes is possible (cf. ref 1).

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