71.22, 40.86, 27.28, 25.26, 20.04 ppm] and the α-attack isomer: 123.2 mg; R_f 0.28; ^{1}H NMR (60 MHz) δ 7.2 (s, 5 H), 4.35 (dd, 2 H), 4.0–3.3 (m, 2 H); ^{13}C NMR (22.5 MHz) 138.00, 128.47 (2 C), 127.74 (3 C), 118.41, 81.20, 74.15, 71.48, 49.61, 31.59, 28.00, 17.95 ppm; ^{13}C NMR (for the bis ether, 22.5 MHz) 138.00 (2 C), 128.27 (4 C), 127.55 (6 C), 118.02, 80.55 (2 C), 71.41 (2 C), 47.78, 28.20 (2 C), 18.15 ppm. Also isolated from the column was 15 mg of a mixture of the two isomers, bringing the total yield up to 68%.

Acknowledgment. We thank Dr. Tom Keough, Dr. A. J. DeStefano, Mr. Bob Neal, and Mr. John Pryne for mass spectral analysis.

Registry No. **1a**, 25484-62-2; **1b**, 84124-38-9; **1c**, 84131-45-3; **1d**, 62894-14-8; **2a** (isomer 1), 84234-88-8; **2a** (isomer 2), 84234-89-9; **2b** (isomer 1), 84172-91-8; **2b** (isomer 2), 84172-92-9; **2c** (isomer 1), 84131-46-4; **2c** (isomer 2), 84172-93-0; **3a** (isomer 1), 84172-94-1; **3a** (isomer 2), 84172-95-2; **3b** (isomer 1), 84131-47-5; **3b** (isomer 2), 84172-96-3; **3c** (isomer 1), 84131-48-6; **3c** (isomer 2), 84172-97-4; **3d** (isomer 1), 84131-49-7; **3d** (isomer 2), 84172-98-5; **3d** ketone (isomer 1), 84131-50-0; **3d** ketone (isomer 2), 84172-99-6; **3e** (isomer 1), 84173-00-2; **3e** (isomer 2), 84173-01-3; **4** (isomer 1), 84173-02-4; **4** (isomer 2), 84173-03-5; **5**, 84124-51-6; **5** free acid, 84131-51-1; **6** (isomer 1), 84173-04-6; **6** (isomer 2), 84234-78-6; **6** free acid, 84234-80-0; **7** (isomer 1), 84131-53-3; **7** (isomer 2), 84173-06-8; **8** (isomer 1), 84173-07-9; **8** (isomer 2), 84173-08-0; **9** (isomer 1), 84173-09-1; **9** (isomer 2), 84173-10-4; **10**, 84124-49-2; **11**, 84131-54-4; **12**, 84173-11-5; **13**, 84124-52-7; **14a**, 84173-12-6; **14b**, 84173-13-7; **15a**, 84173-14-8; **15b**, 84173-15-9; **16a**, 84131-52-2; **16b**, 84276-40-4; **18a**, 84173-16-0; **18b**, 84172-71-4; **19a**, 84173-17-1; **19b**, 84173-18-2; **20a**, 84173-19-3; **20b**, 84173-20-6; **21**, 84131-55-5; **22**, 84131-56-6; **23**, 84131-57-7; **24**, 84131-58-8; **25**, 84131-59-9; **26**, 84131-60-2; **27**, 84131-61-3; **28**, 84131-62-4; **29**, 84131-63-5; **30**, 84131-64-6; **31**, 84131-65-7; **32**, 84131-66-8; **33**, 84131-67-9; (*S*)-octynol, 32556-71-1; (*R*)-octynol, 32556-70-0; (*S*)-octynol *tert*-butyl ether, 51051-11-7; (*R*)-octynol *tert*-butyl ether, 82311-64-6; *tert*-butyl 6-iodohexanoate, 67899-04-1; *tert*-butyl 9α-(methoxymethoxy)-7-oxa-15-oxoprost-13-ynoate, 84124-46-9; 3-*n*-butylcyclopentanone, 84131-68-0; 2-(benzyloxy)-5-butyl-1-cyclopentanol, 84131-69-1; 1,3-bis(benzyloxy)-2-butylcyclopentane, 84131-70-4; 3-(benzyloxy)-2-butyl-1-cyclopentanol, 84131-71-5; 2-(benzyloxy)-5-(1,3-dithian-2-yl)-1-cyclopentanol, 84143-07-7; 3-(benzyloxy)-2-(1,3-dithian-2-yl)-1-cyclopentanol, 84143-08-8; 3-(benzyloxy)-2-hydroxycyclopentaneacetonitrile, 84131-72-6; 3-(benzyloxy)-5-hydroxycyclopentaneacetonitrile, 84131-73-7; 2,5-bis(benzyloxy)cyclopentaneacetonitrile, 84131-74-8.

Photochemical Synthesis of Some Propellanes through [2 + 2] Cycloaddition of Indeno[2,1-*a*]indene with Several Olefins

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Some interesting propellanes were synthesized by the photochemical cycloaddition of indeno[2,1-*a*]indene, a *trans*-stilbene analogue, with several olefins. Irradiation of indeno[2,1-*a*]indene with electron-rich olefins yielded only two indeno[2,1-*a*]indene dimers without giving cross adducts. While irradiation of the compound in the presence of moderately electron-poor olefins gave propellanes through [2 + 2] cycloaddition reaction, an ene-reaction product was obtained as a major product in the photoreaction of the compound with dimethyl fumarate, an electron-deficient olefin. The fluorescence quenching and kinetic studies indicated the reaction to proceed through a singlet exciplex intermediate.

Photochemical [2 + 2] cycloaddition reactions of *trans*-stilbene with various olefins which are different in electron affinity have been reported and are known to occur via singlet exciplex intermediates.[1] However, relatively little is known about the photochemical cycloaddition reaction of the stilbene chromophore incorporated into a small ring system.

Both direct irradiation and triplet-sensitized excitation of diphenylvinylene carbonate in the presence of dienes results in the formation of mixtures of [2 + 2] cycloadducts[2] in contrast to the failure of excited singlet *cis*-stilbene and triplet *cis*- and *trans*-stilbene to react with olefins. The differences in photochemical reactivity between stilbene and diphenylvinylene carbonate are attributed to the fact that the incorporation of the stilbene chromophore into a small ring increases the lifetime of both the planar singlet and triplet excited state since twisting around the $C{=}C$ bond is forbidden.

It was reported that indeno[2,1-*a*]indene, a *trans*-stilbene analogue, has similar spectral[3] and photochemical[4] properties with *trans*-stilbene other than the cis $\rightleftharpoons$ trans photoisomerization. Kaupp and Stark synthesized several interesting propellanes by trapping electronically excited stilbene and diphenylacetylene with bicyclic alkenes.[5] We report here a synthesis of some interesting propellanes through the [2 + 2] (C_4) photocycloaddition of indeno[2,1-*a*]indene with several acyclic olefins.

Results and Discussion

Characterization of Products. Irradiation of 2,3-dimethyl-2-butene, 1,4-cyclohexadiene, or 1,2-dihydropyran solutions of indeno[2,1-*a*]indene (30 mg/10 mL of indeno[2,1-*a*]indene) gave only two isomeric C_4 cyclodimers of indeno[2,1-*a*]indene without yielding cross-addition products (Scheme I). Reaction mixtures were analyzed by TLC and ^{1}H NMR spectrometry, but there was no product other than two dimers and starting materials in

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(1) (a) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152. (b) Lewis, F. D.; DeVoe, J. R. *J. Org. Chem.* **1980**, *45*, 948. (c) Green, B. S.; Rejtö, M.; Johnson, D. E.; Hoyle, C. E.; Simpson, J. T.; Correa, P. E.; Ho, T.-I.; McCoy, F.; Lewis, F. D. *J. Am. Chem. Soc.* **1979**, *101*, 3325.

(2) (a) Lewis, F. D.; Hirsch, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 5914. (b) Lewis, F. D.; Hirsch, R. H. *Tetrahedron Lett.* **1975**, 2651.

(3) (a) Saltiel, J.; Khalil, G. E.; Schanze, K. *Chem. Phys. Lett.* **1980**, *70*, 233. (b) Saltiel, J.; Marinari, A.; Chang, D. W.-I.; Mitchener, J. C.; Megarity, E. D. *J. Am. Chem. Soc.* **1979**, *101*, 2982.

(4) Shim, S. C.; Chae, J. S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1310.

(5) Kaupp, G.; Stark, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 758.

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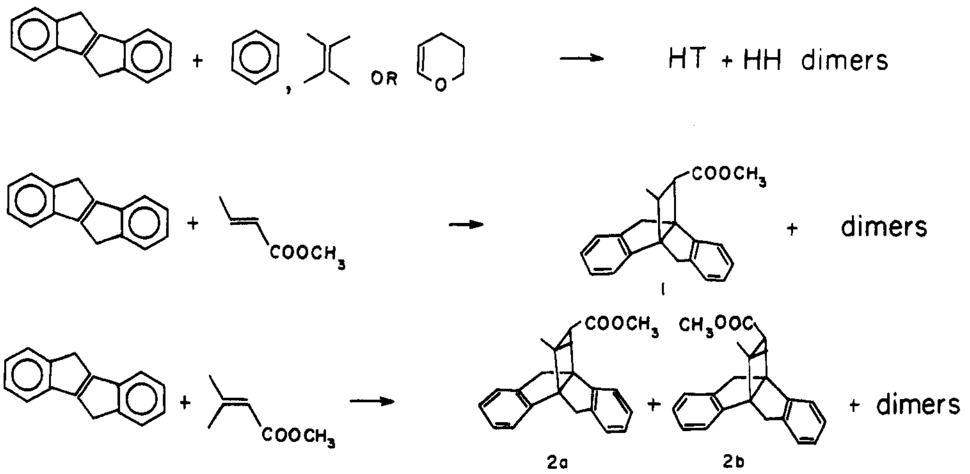
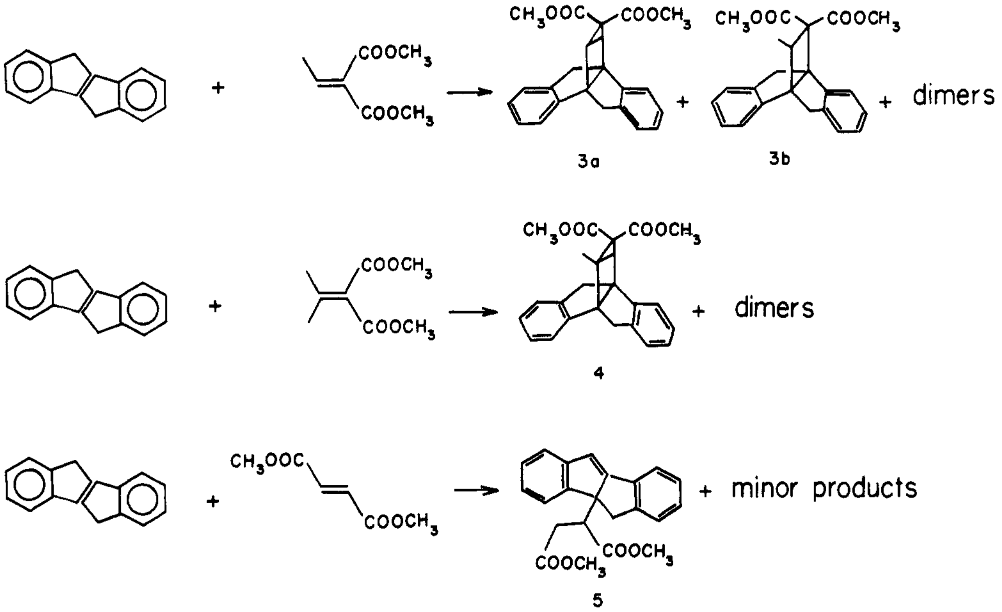
Scheme I



Scheme II



contrast to *trans*-stilbene which forms a photocycloadduct with 2,3-dimethyl-2-butene very efficiently ($\Phi_\infty = 1$).

Preparative photolysis of a benzene solution of indeno[2,1-*a*]indene and methyl crotonate led to the formation of C_4 cycloadduct **1** and C_4 cyclodimers. The major product **1** was separated by column chromatography and characterized by various physical methods.

The elemental analysis data are consistent with the molecular formula $C_{21}H_{20}O_2$. The chemical ionization (CI) mass spectrum of **1** shows a molecular ion peak at *m/e* 315 (M + 1) which is the sum of the molecular weight of indeno[2,1-*a*]indene and that of methyl crotonate. The base peak appears at *m/e* 101, which is the molecular weight of methyl crotonate, and a strong peak at *m/e* 205 (99.2%) is the molecular weight of indeno[2,1-*a*]indene. These indicate that compound **1** easily undergoes splitting into starting materials on chemical ionization, suggesting **1** to be a C_4 cycloadduct.

The carbonyl stretching at 1725 cm^{-1} and bending of the methyl group at 1379 cm^{-1} were apparent in the IR spectrum of **1**, and $\lambda_{\max}$ at 314.5 nm of indeno[2,1-*a*]indene had disappeared in the UV absorption spectrum. These observations further substantiated the proposal that compound **1** is a [2 + 2] cycloaddition product.

The ^1H NMR spectrum of compound **1** in chloroform-*d* shows a quartet of methyl protons at δ 0.95 (q, 3 H), a multiplet at δ 2.5–2.7 (m, 2 H), four doublets of methylene protons at δ 3.03 (d, 1 H, J = 17 Hz), 3.10 (d, 1 H, J = 17 Hz), 3.22 (d, 1 H, J = 17 Hz), and 3.44 (d, 1 H, J = 17 Hz), a singlet of methoxy protons at δ 3.57 (s, 3 H), and a multiplet at δ 7.16 (m, 8 H) ppm. The data are in good agreement with C_4 cycloadduct **1**. The stereochemistry of **1** was determined by comparing the chemical shift of the methyl protons with that of compound **4**.

Irradiation of a benzene solution of indeno[2,1-*a*]indene in the presence of excess methyl β,β-dimethylacrylate yields the two isomeric cycloadducts **2a** and **2b** in 1.5:1 ratio. The elemental analysis data of **2a** and **2b** are consistent with the molecular formula $C_{22}H_{22}O_2$.

Stereochemical assignments are based on the NMR data. H^e, the proton of methylene bridge of **2b**, is deshielded by the carbonyl group. Therefore, the resonance of this proton appears at a lower field than that of **2a**, and the methoxy proton H^c of **2b** is more deshielded by the phenyl ring current than that of **2a** because of the steric hindrance of the methylene group.

Preparative photolysis of indeno[2,1-*a*]indene with dimethyl ethylidenemalonate yielded two isomeric cycloadducts (**3a** and **3b**, Scheme II) in a 3:1 ratio. The elemental analysis data of **3a** and **3b** are consistent with the molecular formula $C_{23}H_{22}O_4$. Stereochemical assignments are based on the chemical shift of methyl group protons.

In **3a**, the methyl group has a lower chemical shift than that of **3b** because of the shielding by the phenyl ring current.

Irradiation of indeno[2,1-*a*]indene with dimethyl isopropylidenemalonate results in the formation of a single cycloadduct **4**. The elemental analysis of **4** shows the molecular formula to be $C_{24}H_{24}O_4$. In the ^1H NMR spectrum of **4**, the methyl protons (H^a) resonate at 0.83 ppm and H^b appears at 1.52 ppm because H^a is shielded by phenyl ring current while H^b is deshielded by the phenyl ring current on the other side. These values of chemical shifts can be used as references for the determination of the stereochemistry of other indeno[2,1-*a*]indene–olefin [2 + 2]-type cycloadducts.

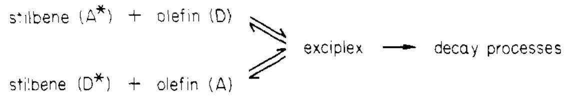
Photoreaction of indeno[2,1-*a*]indene with dimethyl fumarate yielded compound **5** and minor amounts of other products. The elemental analysis data of **5** are consistent with the molecular formula $C_{22}H_{20}O_4$. The electron impact (EI) mass spectrum of **5** shows a molecular ion peak at *m/e* 308 which is the sum of the molecular weight of indeno[2,1-*a*]indene and that of dimethyl fumarate. The base peak appears at *m/e* 202 (indeno[2,1-*a*]indene – H_2), and a peak appears at *m/e* 146 (dimethyl fumarate + H_2). This pattern is different from that of the mass spectra of the C_4 cycloadducts we obtained in the previous section. These results suggest that **5** is not a C_4 cycloadduct. This is further substantiated by the UV and IR spectra. In the UV absorption spectrum, λ_{max} at 313 and 237 nm appear, and a C=C stretching band appears at 1600 cm^{-1} in the IR spectrum of **5**, indicating that the central C=C double bond remains intact on the photolysis.

The ^1H NMR spectrum of **5** shows two singlet peaks at δ 3.48 (s, 3 H) and 3.48 (s, 3 H), a vinyl proton peak at δ 6.65 (s, 1 H), and a multiplet at δ 7.17 (m, 8 H). These data are in good agreement with the structure **5**.

The ^1H NMR spectral data of the cycloadducts are summarized in Table I and the reactions are shown below.

Fluorescence Studies. Electronic excitation of organic molecules enhances both the electron donor and acceptor properties. As a consequence, excimers and exciplexes are obtained from donor–acceptor pairs on excitation even though they do not form stable ground-state complexes.[6]

In the *trans*-stilbene–olefin exciplexes, excited *trans*-stilbene is the electron acceptor (A*), and olefins are electron donors (D) when they are electron-rich compounds. However, excited *trans*-stilbene will be the electron donor (D*), and olefins will be electron acceptors (A) when they are electron-poor compounds.[1c] Thus, the fluorescence of *trans*-stilbene is quenched by various olefins which are different in electron affinity, and the Stern–Volmer constants ($k_q\tau$) for fluorescence quenching of *trans*-stilbene by olefins first decrease and then increase with increasing olefin electron affinity as shown in Table II. This trend is consistent with the formation of a charge-transfer-stabilized exciplex in which *trans*-stilbene acts as both a donor or an acceptor as shown below.



The fluorescence of indeno[2,1-*a*]indene is quenched by olefins, and the Stern–Volmer constants for fluorescence quenching increase only with increasing olefin electron affinity. This trend is attributed to the formation of only the D*-A-type exciplex between the electron-rich singlet excited state of indeno[2,1-*a*]indene and ground-state olefins and not to electron transfer from the olefins to indeno[2,1-*a*]indene. However, no fluorescence of an excimer or exciplexes was observed.

Scheme III

$$I \xrightarrow{h\nu} I^*$$

$$I^* \xrightarrow{k_f} I + h\nu_f$$

$$I^* \xrightarrow{k_d} I$$

$$I^* + I \underset{k_{-em}}{\overset{k_{em}}{\rightleftharpoons}} \text{excimer}$$

$$\text{excimer} \xrightarrow{k_{dim}} \text{dimers}$$

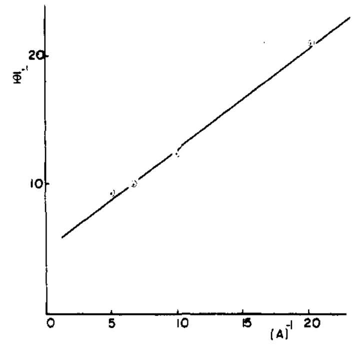


Figure 1. Plot of the reciprocal of the quantum yield for C_4 photocycloaddition vs. the reciprocal of the concentration of methyl crotonate.

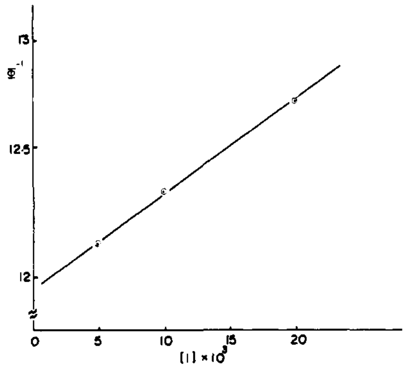


Figure 2. Plot of the reciprocal of the quantum yield for C_4 photocycloaddition vs. indeno[2,1-*a*]indene concentration.

The fluorescence quenching constants are generally larger for indeno[2,1-*a*]indene than those for *trans*-stilbene. This is at least partly due to the longer singlet lifetime of the former (τ_F = 1.99 ns)[4] compared to that for *trans*-stilbene (0.07 ns).[7]

Reaction Mechanism. The mechanistic scheme shown in Scheme III can be written for the photoreaction of indeno[2,1-*a*]indene with olefins if an exciplex intermediate is assumed, where I is indeno[2,1-*a*]indene and A is olefin. By the steady-state approximation, eq 1 can be derived

$$\Phi_a^{-1} = \frac{(k_{-ep} + k_a + k_{epd})}{k_{ep}k_a}\left[(k_f + k_a) + \frac{k_{em}(k_{dim} + k_{emd})}{k_{-em} + k_{dim} + k_{emd}}[I]\right][A]^{-1} + \left(1 + \frac{k_{epd}}{k_a}\right)$$

for the quantum yield of the C_4 cycloaddition reaction. A linear relationship between Φ_a^{-1} and $[A]^{-1}$ when [I] is kept constant and between [I] and Φ_a^{-1} when [A] is kept con-

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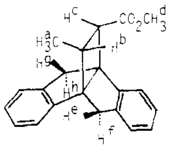
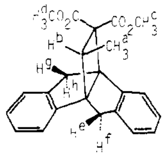
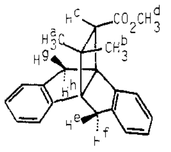
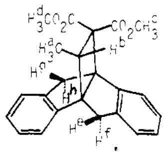
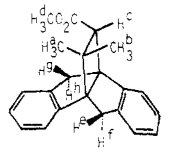
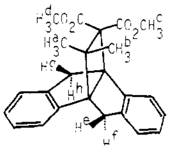
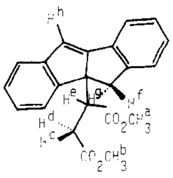
[6] Förster, T. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 333.

[7] Charlton, J. L.; Saltiel, J. *J. Phys. Chem.* **1977**, *81*, 1940.

Table I. ^1H NMR Spectral Data of Cycloadducts

compd	hydrogen	shift,[a] δ	compd	hydrogen	shift,[a] δ
 1	a b, c d e-h	0.95 (q) 2.5-2.7 (m) 3.57 (s) 3.03 (d, J = 17), 3.10 (d), 3.22 (d), 3.44 (d)	 3a	a c d e-h	1.27 (d, J = 7) 3.38 (s) 3.77 (s) 2.95-4.03 (d's, J = 17)
 2a	a b c d e-h	0.95 (s) 1.13 (s) 2.94 (s) 3.55 (s) 2.9 (d, J = 17), 3.07 (d), 3.33 (d), 3.47 (d)	 3b	a c d e-h	0.87 (d, J = 7) 3.41 (s) 3.53 (s) 2.95-4.65 (d's, J = 17)
 2b	a b c d e-h	0.8 (s) 1.35 (s) 3.02 (s) 3.72 (s) 3.25 (d, J = 17), 3.35 (d), 3.5 (d), 3.95 (d)	 4	a b c d e-h	0.84 (s) 1.57 (s) 3.23 (s) 3.73 (s) 3.03 (d, J = 17), 3.40 (d), 3.43 (d), 4.37 (d)
			 5	a, b c-g h	3.43 (s) 3.48 (s) 1.83-3.6 (m) 6.65 (s)

[a] Multiplicities and J values (in hertz) are given in parentheses.

Table II. Stern-Volmer Quenching Constants for Fluorescence Quenching

quencher	$E(A/A^+)$,[a] V	IP,[b] eV	$k_q\tau$, M^{-1} *trans*-stilbene	 indeno-[2,1-*a*]indene
2,5-dimethyl-2,4-hexadiene		7.48	4.5[c]	
1,4-cyclohexadiene				0.087
1,3-cyclohexadiene		8.3	1.5[c]	
2,3-dimethyl-2-butene		8.3	0.24	0.11
methyl β,β-dimethylacrylate			0.08[e]	5.8
methyl crotonate		10.1	0.19[e]	7.2
dimethyl ethylidenemalonate			0.41[e]	21
dimethyl isopropylidenemalonate	-2.13		1.0[e]	35
dimethyl fumarate	-1.54	10.7	7.6[f]	38
fumaronitrile	-1.36	11.2	7.0[f]	80

[a] Reduction potential in aprotic solvents. The values (vs. Ag/Ag^+ in DMF) are from: Petrovich, J. P.; Baizer, M. M.; Ort, M. R. *J. Electrochem. Soc.* **1969**, *116*, 743. [b] Ionization potential. [c] Data from: Lewis, F. D.; Hoyle, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 3779. [d] Data from: Champman, O. L.; Lura, L. D. *Ibid.* **1970**, *92*, 6325. [e] Data from: Lewis, F. D.; et al. *Ibid.* **1979**, *101*, 3325.

stant is expected if the proposed mechanism is valid.

A good linear relationship in the plots of Φ_a^{-1} vs. $[A]^{-1}$ and Φ_a^{-1} vs. [I] as shown in Figures 1 and 2 indicates that the mechanistic scheme is reasonable and that the C_4 photocycloaddition reaction between indeno[2,1-*a*]indene and olefins occurs via a singlet exciplex intermediate.

The quantum yields of photocycloaddition of indeno[2,1-*a*]indene with olefins were measured in benzene solution and are shown in Table III.

Although the fluorescence quenching by olefins is most efficient with electron-poor olefins, the photocycloaddition of indeno[2,1-*a*]indene with methyl crotonate is the most efficient of the tested olefins as shown in Table III. These results can be explained by the frontier orbital theory (FMO) which indicates that cycloaddition is most efficient when the interacting frontier orbitals are nearly isoenergetic.[1b]

Conclusion

The photochemistry of indeno[2,1-*a*]indene, a *trans*-stilbene analogue, was studied in order to elucidate the mechanism of the C_4 photocycloaddition reaction and to find a new synthetic method for propellane derivatives. Photoreaction of indeno[2,1-*a*]indene with the electron-rich olefins 2,3-dimethyl-2-butene, 1,4-cyclohexadiene, and 1,2-dihydropyran did not yield any cross-addition products but yielded two C_4 cyclodimers of indeno[2,1-*a*]indene while the irradiation of benzene solutions of indeno[2,1-*a*]indene and the moderately electron-deficient olefins methyl crotonate, methyl β,β-dimethylacrylate, dimethyl

Table III. Quantum Yields of Photoaddition of Indeno[2,1-*a*]indene with Olefins[a]

olefin	10^2(quantum yield of C_4 cycloaddition)	chemical yield, %	
		adducts	dimers
methyl β,β-dimethylacrylate	2.7		36
methyl crotonate	8.1	49	23
dimethyl ethylidenemalonate	6.1		5
dimethyl isopropylidenemalonate	2.3	51	20
dimethyl fumarate	?	23	0

[a] Concentrated of indeno[2,1-*a*]indene = 1.0×10^{-2} M; concentrated of olefins = 1.0×10^{-1} M; chemical yields were measured when the reactions were completed.

isopropylidenemalonate, and dimethyl ethylidenemalonate gave C_4 photocycloadducts along with the same C_4 cyclodimers. Among the tested olefins, methyl crotonate is the most efficient in the C_4 photocycloaddition reaction, and the stereochemistry of photocycloadducts is mainly influenced by the secondary π-orbital overlap in an exciplex intermediate. In the photoreaction of indeno[2,1-*a*]indene with dimethyl fumarate, an ene-reaction product is obtained as a major product. Photolysis of indeno[2,1-*a*]indene with fumaronitrile yields no product.

From the linear relationship between Φ_a^{-1} and $[A]^{-1}$, the quantum yields of photocycloaddition, and the stereochemistry of photocycloadducts, it appears reasonable to conclude that the C_4 photocycloaddition reaction of indeno[2,1-*a*]indene with olefins occurs through a singlet exciplex intermediate and that their rate is controlled by the stability of this exciplex intermediate.

Experimental Section

Materials. Indeno[2,1-*a*]indene was synthesized from benzyl chloride and recrystallized from ethyl acetate and then from acetone.[8] 2,3-Dimethyl-2-butene, 1,4-cyclohexadiene, and 2,3-dihydropyran were distilled immediately prior to use. Methyl crotonate,[9] methyl β,β-dimethylacrylate, dimethyl ethylidenemalonate,[10] and dimethyl isopropylidenemalonate were prepared and purified by vacuum fractional distillation. Dimethyl fumarate was prepared by esterification of fumaric acid and sublimed prior to use. Benzene was purified prior to use according to the standard method.

Spectra and Physical Data. UV spectra were recorded on a Cary-17 spectrophotometer. IR spectra were taken on a Perkin-Elmer 267 spectrophotometer by using KBr pellets. NMR spectra were measured on a Varian T60A Spectrometer against Me_4Si as an internal standard in chloroform-*d*. Mass spectra were determined with a Hewlett-Packard 5985A GC/MS system. Fluorescence spectra were recorded with an Aminco Bowman spectrofluorophotometer with an Aminco X-Y recorder. GLC analyses were performed by using a 6 ft × $^1/_8$ in. column of 3% OV-17 on Chromosorb W on a Varian Series 2800 gas chromatograph with an FID detector.

Quantum Yield Measurements. Benzene solutions of indeno[2,1-*a*]indene and olefins were placed into Pyrex ampules and degassed by three freeze–pump–thaw cycles ($<10^{-4}$ mmHg) with cooling in liquid nitrogen, and the ampules were then sealed. Thus-prepared samples were irradiated in a merry-go-round unit with a 450-W Hanovia medium-pressure mercury arc lamp (Type 679A36). A Corning glass filter of (No. 7-54) and a solution filter of 2.5×10^{-3} M potassium chromate in 1% sodium carbonate aqueous solution were used to isolate monochromatic light of 313 nm. The light intensity was measured by tris(oxalato)ferrate(III) actinometry.[11] The amounts of photochemical C_4 cycloadducts with olefins were measured by GLC with anthracene as an internal standard.

Preparative Photolyses. Preparative photolyses were generally carried out in benzene (500 mL) by using 5 mmol of indeno[2,1-*a*]indene and 50 mmol of olefins. Samples were degassed by bubbling oxygen-free nitrogen through the solutions and irradiated in a Rayonet photochemical reactor (The Southern New England Ultraviolet Co.) for 50–200 h. The progress of the reaction was monitored by TLC, and reaction mixtures were analyzed by GLC and NMR.

Photoaddition to Methyl Crotonate. The indeno[2,1-*a*]indene and methyl crotonate were irradiated with 313-nm UV light, the reaction mixture was chromatographed on a silica gel column with 0.5% ethyl acetate in carbon tetrachloride as an eluent, and the product was recrystallized from ethanol. Adduct **1** was obtained as white crystals, mp 88.2 °C. Anal. Calcd for $C_{21}H_{20}O_2$: C, 82.89; H, 6.58; O, 10.52. Found: C, 82.60; H, 6.48; O, 10.92.

Addition to Methyl β,β-Dimethylacrylate. The indeno[2,1-*a*]indene and methyl β,β-dimethylacrylate reaction mixture was chromatographed on a silica gel column with 0.5% ethyl acetate in carbon tetrachloride as an eluent. Oily cycloadduct **2a** was eluted after the cyclodimers and was followed by oily cycloadduct **2b**. Anal. Calcd for $C_{22}H_{22}O_2$: C, 83.02; H, 6.92; O, 10.06. Found for **2a**: C, 83.12; H, 6.90; O, 9.98. Found for **2b**: C, 82.91; H, 6.82; O, 10.27.

Addition of Dimethyl Ethylidenemalonate. The indeno[2,1-*a*]indene–dimethyl ethylidenemalonate reaction mixture was chromatographed on a silica gel column with 1% ethyl acetate in carbon tetrachloride as an eluent. The oily product **3a** was eluted after cyclodimers and was followed by **3b** which was obtained as white needles from ethanol; mp 154.7 °C. Anal. Calcd for $C_{23}H_{22}O_4$: C, 76.21; H, 6.08; O, 17.67. Found for **3a**: C, 76.31; H, 6.03; O, 17.66. Found for **3b**: C, 76.34; H, 6.00; O, 17.66.

Addition of Dimethyl Isopropylidenemalonate. The indeno[2,1-*a*]indene–dimethyl isopropylidenemalonate reaction mixture was chromatographed on a silica gel column with 1% ethyl acetate in carbon tetrachloride. The cyclodimers were eluted first, followed by the product 4. The curde product was recrystallized from ethanol. Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.60; H, 6.38; O, 17.02. Found: C, 76.56; H, 6.35; O, 17.09.

Addition of Dimethyl Fumarate. A solution of indeno[2,1-*a*]indene (1 g) and dimethyl fumarate (10 g) in 500 mL of benzene was irradiated for 200 h. The solvent was evaporated, and unreacted dimethyl fumarate was removed by sublimation. The residue was chromatographed on a silica gel column with 5% ethyl acetate in carbon tetrachloride. The recrystallization from ethanol gave the major product **5** as white needles, mp 136.9 °C. Anal. Calcd for $C_{22}H_{20}O_4$: C, 75.86; H, 5.75; O, 18.39. Found: C, 75.89; H, 5.48; O, 18.63.

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Registry No. 1, 84109-38-6; **2a**, 84109-39-7; **2b**, 84170-87-6; **3a**, 84109-40-0; **3b**, 84170-88-7; 4, 84109-41-1; 5, 84109-42-2; indeno[2,1-*a*]indene, 248-58-8; methyl crotonate, 18707-60-3; methyl β,β-dimethylacrylate, 924-50-5; 2,3-dimethyl-2-butene, 563-79-1; 1,4-cyclohexadiene, 628-41-1; 1,2-dihydropyran, 110-87-2; dimethyl ethylidenemalonate, 17041-60-0; dimethyl isopropylidenmalonate, 22035-53-6; dimethyl fumarate, 624-49-7.

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