N.Y., 1969, pp 284–288.
(41) (a) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958); (b) R. Ohme and E. Schmitz, *Angew. Chem., Int. Ed. Engl.*, **4**, 433 (1965).
(42) J. C. Stowell, *J. Org. Chem.*, **32**, 2360 (1967).
(43) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).
(44) I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *J. Am. Chem. Soc.*, **91**, 1220 (1969).
(45) P. S. Engel and C. Steel, *Acc. Chem. Res.*, **6**, 275 (1973).
(46) E. Farenhorst and E. C. Kooyman, *Recl. Trav. Chim. Pays-Bas*, **72**, 993 (1953).
(47) Carbon dioxide produced by photolysis of BPP was removed by an Ascarite trap in the inlet system of the mass spectrometer.
(48) "Mass Spectral Data", American Petroleum Institute Research Project 44, Serial No. (a) 62 and 548; (b) 5 and 131; (c) 13.
(49) (a) The factor of −0.64 in eq 18 can be neglected because it appears in every measurement of H_{44}/H_{45} and affects only the intercept and not the slope of the plot of [*i*-PrH]/[*i*-PrD] (or H_{44}/H_{45}) vs. [QH]/[RDS]. (b) The factor of −0.3 in eq 19 can likewise be neglected.
(50) With the Du Pont instrument, H_{43}/H_{44} for the *p*-chlorotoluene solution was 1.40 and H_{43}/H_{44} for the *p*-xylene solution was 1.57. With the CEC spectrometer, these values were 1.36 and 1.47, respectively. Both of the values measured on the Du Pont analyzer are larger than those measured on the CEC instrument, but the ratios are about equal (1.40/1.57 = 0.892 and 1.36/1.47 = 0.925).
(51) Although 2,3-dimethylbutane is rather low boiling (bp 58 °C), it does not have significant *m/e* 44 and 45 peaks[48c] and, therefore, does not interfere with the mass spectral analysis even if it is transferred into the mass spectrometer.

Substituent Effects on a Sigmatropic Reaction. Rearrangement of Some 3-Substituted 1,1-Diphenylindenes

William A. Pettit and Joseph W. Wilson*

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506. *Received November 5, 1975*

Abstract: The products of the irradiation of a series of 3-substituted 1,1-diphenylindenes **1** (substituents: H, CH_3, $COCH_3$, CO_2CH_3, CN) in benzene are either 3-substituted 1,2-diphenylindenes **3** (for $COCH_3$, CO_2CH_3, and CN) or 1-substituted 2,3-diphenylindenes **4** (for H and CH_3). The product-determining step is the thermal sigmatropic migration of a hydrogen atom on the middle carbon of an isoindene intermediate, **2**, to either neighboring carbon. The dependence of the direction of the hydrogen migration on the nature of the substituent is correlated with the substituent-dependent symmetry of the highest occupied molecular orbital of a model for the transition state. In methanol-benzene the irradiation of acetyl- and carbomethoxy-substituted **1** produced isomer **4**, the isomer not formed in benzene. In benzene-methanol-*O-d* the irradiation of 3-acetyl-1,1-diphenylindene yielded **4** that contained 10% deuterium. An anionic intermediate has been postulated to account for the results in methanol. The thermal, photochemical, and base-catalyzed interconversions of **3** and **4** have been examined also.

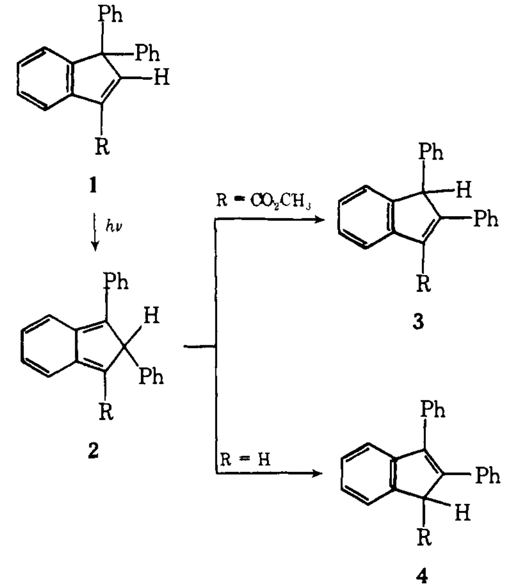
When a 3-substituted 1,1-diphenylindene (**1**) is irradiated in benzene solution, the primary product is either a 1,2-diphenyl 3-substituted indene (**3**)[1] or a 2,3-diphenyl 3-substituted indene (**4**)[2] (Scheme I). The reaction occurs in two steps. An isoindene **2**, shown to be an intermediate in a number of photochemical[1,3] and thermal[4–11] rearrangements of indenes,[12] is formed here in a photochemical step. The second step is a thermal rearrangement of **2** to either **3** or **4** depending on the direction of the hydrogen migration. McCullough[1] observed that **4a** was the major product from **1a**, whereas Huhtanen[2] found that **3c** was the only product from **1c**.

The general question of how substituents affect the course of a sigmatropic hydrogen migration was raised by these observations. The products of the series **1b–e** were identified and these results were correlated with the perturbing effects of the substituents on the symmetry of the highest occupied molecular orbital of a model for isoindene **2**.

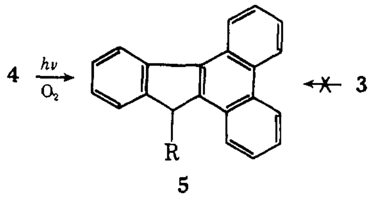
Results

Structure Assignment. The series **1b–e** was prepared by classical methods from 3,3-diphenyl-1-indanone. Both possible products (**3** and **4**) of the irradiation of **1** were prepared in each case. Where possible, structures were assigned to these isomeric pairs by method of synthesis, by photocyclization of isomer **4** to indenophenanthrene **5** (and by the absence of photocyclization for isomer **3**), and by an NMR correlation. The NMR

Scheme I



a (R = H), b (R = CH_3), c (R = CO_2CH_3), d (R = $COCH_3$), e (R = CN), f (R = CO_2H)



5

(2)

correlation proved to be a reliable and rapid empirical test for structure. Compounds of the 2,3-diphenylindene series **4** always showed two sharp peaks of nearly equal intensity in the aromatic region. The aromatic region in the spectra of compounds of the 1,2-diphenylindene series **3** followed no consistent pattern, but never showed the two sharp peaks of the 2,3 isomers.

In the acetyl case the assignment of structure could not be based on the method of synthesis. Both isomers were prepared photochemically; one at shorter times, the other during longer irradiation. The product of longer irradiation was also prepared by the reaction of acetyl chloride with the lithium salt of 1,2-diphenylindene. Structure **4d** was assigned to this product because it could be converted to **5d** on irradiation in air-saturated benzene. (The air probably acts to oxidize the initially formed dihydrophenanthrene to the phenanthrene.) Under these conditions **3d** was unchanged. (In the absence of air **3d** was converted to **4d** on irradiation as described below, but this conversion was inhibited by air.)

Photocyclization of **4e** to **5e** could not be used to assign structures in the cyano-substituted case because light caused the conversion of **4e** to **3e** (in the absence of oxygen), which was unaffected by further irradiation. However, **4e** was prepared under mild conditions from the carboxylic acid **4f**, the structure of which was established by its conversion to ester **4c**. Compound **4e** was easily isomerized to the more stable isomer **3e** by weak base, heat, or light.

Photoisomerization of Diphenylindenes 1 in Benzene. Table I shows the results of irradiating the series of 3-substituted 1,1-diphenylindenes. The major product from **1a** and **1b** was the 2,3-diphenyl isomer **4**. For the others (**1c**, **1d**, and **1e**) the 1,2-diphenyl isomer **3** was the major product at short irradiation times in benzene. For the cyano compound it was necessary to establish that **3e** was the first-formed product because the other isomer **4e** was rapidly converted to **3e** by irradiation in oxygen-free benzene. Evidence was provided by the observation that **4e** was not converted to **3e** when irradiated in air-saturated benzene (see Experimental Section), whereas **1e** was converted to **3e** under these conditions. In the acetyl case **3d** was converted to **4d** by irradiation, but slowly enough to show that the sequence is **1** to **3** to **4**.

Base-Catalyzed Isomerizations of 3 and 4. Base-catalyzed equilibration established that for all substituents except methyl and cyano, the 2,3-diphenyl isomer **4** is the more stable of the two. Essentially complete conversion of **3c** to **4c**, of **3d** to **4d**, and of **4e** to **3e** was accomplished with potassium acetate in methanol at room temperature. Isomer **3b** was converted to an equilibrium mixture of roughly equal amounts of **3b** and **4b** after standing in pyridine for 36 h at room temperature. Isomer **4b** was converted to the same mixture under these conditions. McCullough[1] found that **3a** was converted to **4a** on treatment with dimethylamine in pyridine for 12 h at 25 °C.[14b]

Thermal Isomerizations of 3 and 4. The base-stable isomer tends in general to be the thermally stable isomer. Compounds **3d** and **4e** were completely converted to **4d** and **3e**, respectively, by heating them above their melting points. When **3c** was heated under nitrogen at 143 °C for 1 h, it was converted to a mixture of **3c** and **4c** in the ratio of 1:3. Since Miller and Boyer[8] found that **1a** was converted only to **4a** on heating for 10 h at 280 °C, it is likely that **4a** is the thermally stable isomer. Koelsch and Johnson[15] found that **3b** was partially isomerized to **4b** when it was distilled. They also found that 1-methyl-1,3-diphenylindene (which must yield the same isoindene as does **1b**) was converted to **3b** and **4b** in the ratio of 1:2.2 after it had been heated to 470 °C.

Photoisomerization of 1 in Benzene–Methanol. The results of irradiating compounds **1b–e** in benzene-methanol-*O-d* (7:2 v/v) are included in Table I. The products were analyzed for deuterium by mass spectrometry with an estimated error of ±3%. Significant amounts of deuterium were incorporated in the product only in the case of **1d**. Control experiments showed that deuterium incorporation did not occur after **4d** was formed from **1d**: recovery of **4d** which had been dissolved in benzene–CH_3OD for 2 h yielded **4d** with a deuterium content of about 4% and when **4d** was irradiated in this solvent for 15 min, the deuterium content of **4d** was negligible. To show that the unexpected formation of **4d** was *not* the result of a rapid conversion of **3d** to **4d** in benzene–methanol, **3d** was irradiated for a short time in that solvent. Although a small amount of an unidentified new product (perhaps by reduction of the carbonyl group) was formed, no **4d** or **5d** was formed. Isomer **3d** is stable in the dark in methanol–benzene for at least 15 h.

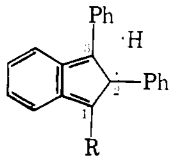
Table I. Products from the Irradiation of **1**

R	Time^a	Solvent	% **3**^{b}	% **4**	% other	% D^c
H^d (**1a**)	120	Hexane^e	25^f	75^n		
CH_3 (**1b**)	60	Benzene	11	79	10^g	
	15	Benzene–CH_3OD^{h}	13	77	10^g	2
CO_2CH_3 (**1c**)	30	Benzene^i	100	*n*		
	15	Benzene–CH_3OD^{h}	72	28		0
	15	CH_3OH	60	40		
$COCH_3$ (**1d**)	15	Benzene	85	15^n		
	120	Benzene		100		
	15	Benzene–CH_3OD^{h}		90+		10
	15	Benzene–CH_3OD^{h}		90+		12
CN (**1e**)	15	Benzene	100^n			
	90	Benzene	84		10^j	
	75	Benzene–CH_3OH^{k}	84		10^l	
	15	Benzene–CH_3OD^{h}	62		28^m	2.7

^{a} Minutes. ^{b} By NMR analysis except for **1a**. ^{c} By mass spectrometry. ^{d} McCullough, ref 1. ^{e} Similar results in ethanol. ^{f} Analysis by gas chromatography. ^{g} Indenophenanthrene. ^{h} v/v 70/20. ^{i} Same results in cyclohexane. ^{j} Possibly dimer. ^{k} v/v 300/130. ^{l} A three-component mixture. ^{m} See Experimental Section (part e). ^{n} Most stable isomer.

Discussion

Isomers **3** and **4** are formed from **2** in benzene by a concerted suprafacial hydrogen migration which is symmetry allowed in this system when it occurs between two neighboring carbon atoms with coefficients of the same sign in the highest occupied molecular orbital (HOMO). Simple Hückel molecular orbital calculations on a model[9] for the transition state, **7**, were used to predict the effect of substituents on the nature of the product. Substituent effects were incorporated into the calculations by modifying the resonance and Coulomb integrals in the usual manner.[16] Table II lists the literature values of *h* (modification of the Coulomb integral *α*) and *k* (modification of the resonance integral *β*) used in these calculations. The calculated coefficients of the HOMO at the three carbons of the indene ring are listed in Table III. Only the signs are important except for R = H, where it should be noted that C_2 is close to zero. In the unsubstituted indenyl radical, C_2 is nodal in the HOMO (i.e., the coefficient at that atomic orbital is zero). The addition



7

Table II. Modifications of Coulomb (h) and Resonance (k) Integrals

Element	Group	h	k	Ref
	CH_3	2.0	0.7	17
O	C=O	2.0	1.414	18
N	C≡N	0.3		19
C	C≡N	0.05	1.5	19
	OCH_3	3.0	0.9	20

Table III. Coefficients of HOMO

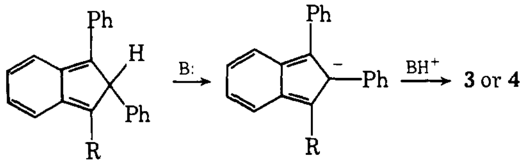
R	C_1	C_2	C_3
H	-0.34351^a	+0.09924	$+0.36901^b$
CH_3	$+0.40606^{a,b}$	+0.31977	−0.20575
CN	+0.44437	−0.64712	$-0.47260^{a,b}$
CO_2CH_3	+0.30590	−0.23256	$-0.43849^{a,b}$
$COCH_3$	+0.30481	−0.23305	$-0.43783^{a,b}$

[a] Migration to this position observed. [b] Migration to this position predicted.

of two phenyl groups to the system shifts the node only slightly away from C_2. The addition of an R group (except for CH_3) shifts the node substantially toward the R substituted carbon. For R = CH_3 the shift is toward the phenyl substituted carbon, carbon 3.

Table III shows that the experimental results are in accord with the predictions based on the HMO method (except for R = H, for which the C_2 coefficient is close to zero). The limitations of this method are well known. Among the many simplifying assumptions employed is our assumption that the phenyl substituents are coplanar with the indene ring in the transition state. Also, the positions of the nodes are sensitive to the choice of modifying parameters, h and k. For example, if $h = -0.2$ (instead of zero) for R = H, the coefficient at C_2 becomes −0.015. With this value for C_2, the observed direction of migration matches the predicted direction. Though the calculations are oversimplified, the reasonable agreement between prediction and observation and the absence of alternative explanations (explanations based on product stability, steric effects, or proton acidity can be ruled out on the basis of the data of Table I) attest to the validity of this model.

Irradiation of **1d** in methanol-benzene unexpectedly yielded **4d** instead of the **3d** formed in benzene. This result is interpreted in terms of the carbanion mechanism shown below. Isoindene **2d** should be fairly acidic for the following reasons.



2 **6**

The pK_a of indene itself is about 20.[21a] Phenyl and acetyl substituents should lower it significantly. Because the *iso*indene is less stable than the corresponding indene and because the same anion is formed from both, methanol should be a sufficiently strong base to generate **6d** from **2d.** Though formation of the more stable isomer **4d** from **6d** represents an exception to the Hughes-Ingold rule, exceptions to the rule are well known.[21b] Presumably the acetyl substituted carbon in **6** is the site of highest electron density.

As shown in Table I, the irradiation of **1d** in benzene-methanol-*O-d* yielded **4d,** containing 10–12% of one atom of deuterium. This result is consistent with the carbanion mechanism if it is assumed to be a measure of the intramolecularity[21c] of the isomerization (and possibly also of a solvent isotope effect). Bergson and Weidler[22,23] observed complete intramolecularity in the base-catalyzed isomerization of 1-methylindene in pyridine-D_2O; i.e., no deuterium was incorporated during this proton transfer. Also consistent with this mechanism is the fact that **1c** yielded a product ratio that is different in methanol (**3c**:**4c** = 60:40) than it is in benzene (100:0). Because **2c** should be less acidic than **2d,** the absence of deuterium incorporation in benzene-methanol-*O-d* is not surprising. The acidity of **2e** should be similar to that of **2c,** so the observed absence of deuterium incorporation in **4e** when it is formed from **1e** in benzene-methanol-*O-d* is parallel to the case of **1c**. No change in the nature of the product was expected in this case (**1e**), because only in this case is isomer **4** more stable than isomer **3**. That **1b** showed no solvent effect and no deuterium incorporation within experimental error reflects the diminished acidity of **2b**.

Although attention was directed mainly to the rearrangement of **2,** two other sigmatropic shifts in this system were observed: the photochemical 1,3 hydrogen migrations in **3d** and **4e** and the thermal isomerizations of **3a–d** and **4e** to the more stable isomers. The photochemical isomerizations are probably symmetry-allowed 1,3-hydrogen shifts, though the present evidence does not explain why the reaction is restricted to **3d** and **4e** or why only the more stable isomers accumulate. The thermal isomerizations must be a series of 1,5 shifts that involve **2** as an intermediate. More systematic investigations of this reaction of indenes have been reported by Miller and coworkers[8] and by Almy and Cram.[9] It should be noted that these thermal interconversions require temperatures that are significantly higher than the temperatures at which the photochemical reactions were conducted.

In summary, simple molecular orbital theory has been used to rationalize successfully the course of a concerted thermal hydrogen migration in **2** to form either **3** or **4** depending on the nature of substituent R. Though this type of argument has not to our knowledge been used before to describe thermal sigmatropic rearrangements, several authors have used simple molecular orbital arguments to rationalize the effects of substituents on light-induced methyl and hydrogen shifts in cycloheptatrienes. Noncyclic models were used in two of these reports to rationalize hydrogen[24] and methyl[25] migrations in cycloheptatrienes perturbed by methoxy[24] and methyl[25] substituents. Libit[26] used an argument based on excited state charge densities to rationalize the directive effects[27] of a variety of substituents on photochemical hydrogen migration in cycloheptatriene. The theory of substituent effects on sigmatropic shifts has been examined recently by several authors.[28] However, they were concerned mainly with the stereochemistry of the migrating group. A primary objective of the present study, the identification of a system in which the calculated effects of substituent perturbations in thermal isomerizations can be evaluated experimentally, has been realized.

Experimental Section

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Beckman IR-8 spectrophotometer, ultraviolet spectra on a Perkin-Elmer 202 UV-visible spectrophotometer, and NMR spectra on a Varian T-60 spectrometer. Chemical shifts (δ values) are given in parts per million relative to Me_4Si as an internal standard. Mass spectra were recorded on a Hitachi Perkin-Elmer double-focusing RMU-7 mass spectrometer at an ionizing voltage of 70 V. Data acquisition and reduction were done with a DEC PDP-8/I computer that employed ADR softwave and interface. Perfluorokerosene was used as a calibrant in the mass determinations. For column chromatography W. R. Grace silica gel (60–200 mesh) was used. Analyses were performed by PCR, Inc., Gainesville, Fla. Hückel molecular orbital calculations were carried out on an IBM 360 computer. The program employed a standard Jacobi diagonalization routine.

1,1-Diphenyl-3-(bromomethyl)indene.[2] A mixture of 18.0 g (0.0639 mol) of 1,1-diphenyl-3-methylindene,[29] 150 mL of CCl_4, 11.5 g (0.0645 mol) of *N*-bromosuccinimide, and a few crystals of benzoyl peroxide was refluxed for 6 h. The disappearance of starting material was monitored by NMR. After the flask had cooled the succinimide was removed by filtration and washed with CCl_4. The filtrate and washings were concentrated in vacuo. The pale orange solid was recrystallized from hexane. The product weighed 16.5 g (71%): mp 124–125 °C; NMR (CCl_4) δ 7.1 (m, 14 H, aromatic), 6.7 (t, 1 H, vinyl, $J = 1$ Hz), 4.2 ppm (d, 2 H, methylene, $J = 1$ Hz); IR (neat) 3060, 3010, and 1580 cm^{-1}.

1,1-Diphenyl-3-(hydroxymethyl)indene. A mixture of 10.1 g (0.0319 mol) of 1,1-diphenyl-3-bromoethylindene, 10.0 g (0.101 mol) of potassium acetate, and 50 mL of dry *N,N*-dimethylformamide (DMF) was heated to 100 °C for 1 h. After the flask had cooled, water was added to separate the ester as an oil, and the ester was extracted into 100 mL of ether. The ether extract was washed with 2 × 100 mL of water, dried over sodium sulfate, decanted, and evaporated to an oily residue on a steam cone. The dark brown oil weighed 9.4 g: NMR (CCl_4) δ 7.2 (m, 14 H, aromatic), 6.8 (t, 1 H, vinyl, $J = 1$ Hz), 5.2 (d, 2 H, methylene, $J = 1$ Hz), and 2.1 ppm (s, 3 H, methyl).

The crude ester was taken up in 150 mL of methanol and mixed with 50 mL of 5% potassium hydroxide in water. The mixture was refluxed for 3 h. The flask was cooled, and 150 mL of water was added. The resulting suspension was extracted with 100 mL of ether. The ether layer was washed with 2 × 100 mL of water, dried over sodium sulfate, decanted, and evaporated to dryness on a steam cone. The crude product was recrystallized from hexane and weighed 7.4 g (82%): mp 124–125 °C; NMR (CCl_4) δ 7.2 (m, 14 H, aromatic), 6.7 (T= [H, vinyl, $J = 1$ Hz), 4.7 (d, 2 H, methylene, $J = 1$ Hz), and 1.8 ppm (s, broad, 1 H, hydroxyl); IR (neat) 3350, 3090, and 1590 cm^{-1}.

1,1-Diphenyl-3-formylindene. A solution of 10.0 g (0.0338 mol) of 1,1-diphenyl-3-hydroxymethylindene in a flask in 60 mL of dry acetone was cooled in an ice bath and stirred while 8.9 mL of 2.5 M chromic acid solution (0.0223 mol) was added dropwise from a buret over 0.5 h at such a rate that the temperature of the mixture was maintained at about 5 °C. The stock acid solution was prepared from 17.5 g of chromic oxide and 15.0 mL of concentrated sulfuric acid diluted to 70 mL with water. The cold reaction mixture was stirred for an additional 45 min and 100 mL of water and a few milliliters of concentrated hydrochloric acid were added. The tan solid was collected by filtration, washed with water, and dried. It weighed 8.9 g (89%), mp 172–177 °C. One recrystallization from acetone gave prisms: mp 180–182 °C; NMR (CCl_4) δ 10.0 (s, 1 H, aldehydic), 8.0 (m, 1 H, aromatic). 7.5 (s, 1 H, vinyl), and 7.2 ppm (m, 13 H, aromatic); IR (neat) 3060, 3010, 1670, and 1560 cm^{-1}; UV (EtOH) λ_{max} 210, 235, 295 nm; mass spectrum mol wt (calcd for $C_{22}H_{16}O$, 296.1200) 296.1235.

1,1-Diphenyl-3-cyanoindene (1e). A mixture of 500 mg (1.69 mmol) of 1,1-diphenyl-3-formylindene, 140 mg (2.02 mmol) of hydroxylamine hydrochloride, 220 mg (4.94 mmol) of sodium formate, and 30 mL of 97–100% formic acid was refluxed for 1 h. After the flask had cooled 50 mL of water was added. The solution was decanted from the orange oil that resulted. The residue was dissolved in boiling 95% ethanol. Pale yellow crystals weighing 156 mg (31%), mp 153–154 °C, were obtained. One recrystallization from hexane gave colorless prisms: mp 160–161 °C; NMR (CCl_4) δ 7.1–7.4 ppm (m, aromatic and vinyl); IR (neat) 3010, 3061, and 2225 cm^{-1}; UV (EtOH) λ_{max} 220 and 275 nm; mass spectrum mol wt (calcd for $C_{22}H_{15}N$, 293.1204) 293.0970.

Anal. Calcd for $C_{22}H_{15}N$: C, 90.10; H, 5.12; N, 4.78. Found: C, 89.78; H, 5.24; N, 4.52.

This compound was prepared more efficiently from **1f** as follows. A mixture of 3.0 g of 1,1-diphenylindene-3-carboxylic acid (**1f**) (which was also prepared directly from 1,1-diphenyl-3-hydroxymethylindene without isolation of 1,1-diphenyl-3-formylindene) and 20 mL of thionyl chloride was refluxed for 1.5 h with stirring. Excess thionyl chloride was removed in vacuo to yield a white solid, which was then dissolved in 50 mL of benzene. The solution was cooled in ice while ammonia was bubbled through the stirred solution for 1 h. The solid product was collected by filtration, washed with water, and recrystallized from 95% ethanol to yield 1,1-diphenylindene-3-carboxamide as white needles: 2.32 g (78%) mp 248–249 °C; NMR (acetone-d_6) δ 7.4–7.6 (strong singlet with several smaller peaks, aromatic), 7.7 (s, vinyl), 8.3 (m); IR (KBr) 3420, 3330, 3190, 1655, 1645, 1605, 1590 cm^{-1}.

A solution of all of this amide and 10 mL of phosphorus oxychloride in 300 mL of acetonitrile was refluxed for 2 h. The solution was filtered while hot to remove a small amount of suspended material. The solvent was removed on the rotary evaporator and ice and water were mixed with the residue. This solid was collected by filtration and recrystallized from 95% ethanol to yield 1.66 g (76%) of the nitrile, **1e**, mp 159–161 °C.

1,1-Diphenylindene-3-carboxylic Acid (1f). A solution of 1.00 g (3.38 mmol) of 1,1-diphenyl-3-formylindene in 100 mL of dry acetone was cooled to 0–5 °C and 1.0 mL of the stock chromic acid solution (2.5 M, 2.5 mmol) was added dropwise from a buret over 30 min. The mixture was stirred for 30 min at 0 °C and for 30 min at room temperature. The dark green solution was then partially evaporated in vacuo. Water was added to complete precipitation of the product. A few milliliters of concentrated hydrochloric acid was added to dissolve a green residue that contaminated the acid. The precipitate was collected by filtration and recrystallized from ether–hexane to yield colorless prisms weighing 882 mg (81%): mp 128–130 °C; NMR ($CDCl_3$) δ 8.1 (m, 1 H, aromatic), 7.8 (s, 1 H, vinyl), and 7.2 ppm (m, 13 H, aromatic); IR (neat) 3440, 1685, and 1590 cm^{-1}; mass spectrum mol wt (calcd for $C_{22}H_{16}O_2$, 312.1150) 312.1140.

Methyl 1,1-Diphenylindene-3-carboxylate (1c).[2] A mixture of 200 mg (0.642 mmol) of 1,1-diphenylindene-3-carboxylic acid, 20 mL of dry benzene, and 5.0 mL of thionyl chloride was refluxed for 1.5 h and then allowed to cool. The solvents were removed in vacuo. The resulting oily brown solid was dissolved in 50 mL of anhydrous methanol and the solution was refluxed for 1 h. When the flask had cooled, the methanol was evaporated in vacuo until a solid appeared in the flask. The solid was redissolved in the remaining methanol and cooled to yield white crystals weighing 139 mg (71%): mp 160–161 °C; UV (95% EtOH) λ_{max} 212, 227, and 288 nm; NMR (CCl_4) δ 8.0 (m, 1 H, aromatic), 7.5 (s, 1 H, vinyl), 7.2 (m, 13 H, aromatic), and 3.8 ppm (s, 3 H, methyl); IR (neat) 3090, 2960, 1720, and 1590 cm^{-1}; mass spectrum mol wt (calcd for $C_{22}H_{18}O_2$, 326.1306) 326.1411, 326.1190.

1,1-Diphenyl-3-ethylindene. To a solution of 0.1 mol of ethylmagnesium bromide in 150 mL of ether (prepared from 10.9 g (0.100 mol) of ethyl bromide and 2.50 g (0.107 mol) of magnesium) was added 20.0 g (0.071 mol) of 3,3-diphenyl-1-indanone[30] dissolved in 100 mL of dry benzene. The reaction mixture was refluxed for 2 h. The flask was cooled and ice, water, and enough concentrated hydrochloric acid to dissolve the inorganic salts were added. The two phases were separated and the aqueous layer was extracted with 50 mL of ether. The combined organic extracts were dried over sodium sulfate, decanted, and evaporated to a brownish-yellow oil. The oil was dissolved in 150 mL of glacial acetic acid containing 1 mL of sulfuric acid and was refluxed for 3 h. This solution was cooled, diluted with water, and extracted with 2 × 100 mL of ether. The organic layer was washed with sodium carbonate solution, dried over sodium sulfate, decanted, and evaporated to dryness on a steam cone. The residual solid gave light tan prisms, 12.1 g (57%), from 95% ethanol: mp 85–86 °C; IR (neat) 3000, 2940, and 1570 cm^{-1}; NMR (CCl_4) δ 7.1 (m, 14 H, aromatic), 6.3 (t, 1 H, vinyl, $J = 2$ Hz), 2.6 (m, 2 H, methylene), and 1.3 ppm (t, 3 H, methyl, $J = 8$ Hz).

1,1-Diphenyl-3-(1-bromoethyl)indene. A mixture of 13.0 g (0.044 mol) of 1,1-diphenyl-3-ethylindene, 8.0 g (0.045 mol) of *N*-bromosuccinimide, a few crystals of benzoyl peroxide, and 150 mL of carbon tetrachloride was refluxed for 4 h. The succinimide was filtered and washed with 20 mL of carbon tetrachloride. Removal of solvent in vacuo yielded an orange oil that was dissolved in boiling pentane. The crystalline bromide weighed 13.1 g (79%): mp 103 °C; NMR (CCl_4) δ 7.2 (m, 14 H, aromatic), 6.7 (d, 1 H, vinyl, $J = 1$ Hz), 5.1 (quartet of doublets, 1 H, methine, $J = 1$ and 7 Hz), and 2.1 ppm (d, 3 H, methyl, $J = 7$ Hz).

1,1-Diphenyl-3-(1-acetoxyethyl)indene. A solution of 2.0 g (0.053 mol) of 1,1-diphenyl-3-(1-bromoethyl)indene and 2.0 g (0.21 mol) of potassium acetate in 50 mL of dry DMF was heated on a steam cone for 1 h with frequent shaking. When the flask cooled, 100 mL of water and 50 mL of ether were added, the layers were separated, and the ether layer was washed with 3 × 100 mL of water, dried over sodium sulfate, decanted, and evaporated in vacuo to yield a brown oil. The crude acetate (contaminated with DMF) weighed 1.7 g (90%): NMR (CCl_4) δ 7.2 (m, 14 H, aromatic), 6.6 (d, 1 H, vinyl, $J = 1$ Hz), 5.9 (quartet of doublets, 1 H, methine, $J = 1$ and 7 Hz), 2.0 (s, 3 H, acetate methyl), and 1.6 ppm (d, 3 H, methyl, $J = 7$ Hz); IR (neat) 3060, 2990, and 1750 cm^{-1}.

1,1-Diphenyl-3-(1-hydroxyethyl)indene. A mixture of 9.8 g (0.277 mol) of the impure acetate (several batches combined; NMR indicated only 40% pure acetate) in 200 mL of 2 N potassium hydroxide solution in 3:1 methanol-water was refluxed on a steam cone for 3 h. When the flask had cooled, its contents were added to 200 mL of water and this mixture was extracted with 2 × 50 mL of ether. The combined ether extracts were washed with 2 × 100 mL of water, dried over sodium sulfate, decanted, and evaporated in vacuo. The residue was dried overnight in a desiccator. The brownish mixture of oil and crystals was digested in pentane. Faint orange crystals (3.1 g, 36%) resulted: mp 112-113 °C; NMR (CCl_4) δ 7.2 (m, 14 H, aromatic), 6.5 (d, 1 H, vinyl, $J = 1$ Hz), 4.8 (quartet of doublets, 1 H, methine, $J = 1$ and 6 Hz), 2.0 (s, broad, 1 H, hydroxyl), and 1.4 ppm (d, 3 H, methyl, $J = 6$ Hz); IR (neat) 3400, 3080, 3000, and 1600 cm^{-1}.

1,1-Diphenyl-3-acetylindene (1d). A solution of 11.2 g (0.028 mol) of crude 1,1-diphenyl-3-(1-hydroxyethyl)indene in 50 mL of dry acetone was cooled to 0 °C, and a solution of 5.7 g (0.057 mol) of chromic oxide in 25 mL of concentrated sulfuric acid and 150 mL of water was added slowly so that the temperature of the reaction mixture was maintained below 7 °C. The cold mixture was stirred for an additional 2.5 h, water was added, and the precipitate that formed was extracted into 100 mL of ether. The ether extract was washed with 100 mL of water, dried over sodium sulfate, and evaporated to dryness in vacuo. The crude product was recrystallized from acetone as colorless plates (4.1 g, 24%): mp 197-198 °C; UV (EtOH) λ_{max} 210, 230, and 295 nm; NMR (CCl_4) δ 8.2 (m, 1 H, aromatic), 7.2 (m, 14 H, aromatic and vinyl), and 2.5 ppm (s, 3 H, methyl); IR (KBr) 3090, 1665, and 1600 cm^{-1}; mass spectrum mol wt (calcd for $C_{23}H_{18}O$, 310.1357) 310.1479, 310.1257.

Anal. Calcd for $C_{23}H_{18}O$: C, 89.03; H, 5.80. Found: C, 88.91; H, 5.91.

1,2-Diphenylindene (3a).[2] A modification of the procedure of Shriner and Knox[31] was used. A mixture of 100 g of zinc dust, 100 mL of 10% hydrochloric acid, and 8.0 g of mercuric chloride was shaken for 10 min and the aqueous phase was decanted. A solution of 50 g of chromic chloride hexahydrate[32] in 200 mL of 5% hydrochloric acid was added to the amalgam. Then 30 g (0.106 mol) of 2,3-diphenyl-1-indenone,[33] 1500 mL of 95% ethanol, and 120 mL of concentrated hydrochloric acid were added, and the mixture was refluxed for 2 h. Ice and water were added to dilute the mixture to approximately 3 L. The crude product was dissolved in 500 mL of warm benzene; the solution was dried and its volume was reduced to about 100 mL. Heptane (100 mL) was added and the crystals were collected by filtration. Recrystallization from heptane afforded 10.9 g (38%) of the indene: mp 178-180 °C (lit.[31] 175-177 °C); NMR (CCl_4) δ 7.1 (m, 15 H, aromatic and vinyl) and 4.8 ppm (s, 1 H, allylic).

2,3-Diphenylindene-1-carboxylic Acid (4f).[2] A flask containing a solution of 4.00 g (0.149 mol) of 1,2-diphenylindene in 100 mL of dry benzene was degassed three times at room temperature and aspirator pressure and then filled with dry nitrogen. Nitrogen was passed through the system throughout the reaction. Ten milliliters of 21.8% butyllithium in hexane was added through the stopcock with a syringe. The solution was refluxed for 15 min. A thick yellow precipitate formed during this time. The reaction mixture was cooled in ice and carbon dioxide was bubbled slowly through the mixture for 45 min. To dissolve a light orange gelatinous material that formed during this time, 100 mL of 6 N hydrochloric acid was added slowly to the cold reaction mixture. The benzene layer was separated, dried, and evaporated in vacuo. The acid, 2.20 g (47%), was obtained by recrystallizing the residue from ether-hexane: mp 195-200 °C (decarboxylated); NMR ($CDCl_3$) δ 7.8 (m, 14 H, aromatic) and 5.0 ppm (s, 1 H, allylic); IR (KBr) 3400, 3060, 1690, and 1600 cm^{-1}; mass spectrum mol wt (calcd for $C_{22}H_{16}O_2$, 312.1150) 320.1148.

Methyl 2,3-Diphenylindene-1-carboxylate (4c).[2] A solution of 3.2 g (0.01 mol) of 2,3-diphenylindene-1-carboxylic acid and a few drops of concentrated sulfuric acid in 50 mL of methanol was refluxed for 5 h. Water was added and the mixture was extracted with ether. The residue after the ether had been dried and evaporated was recrystallized from hexane to yield 2.6 g (80%) of the ester: mp 154-155 °C; IR (KBr) 1725 cm^{-1}; UV max (95% ethanol) 237 nm (log ϵ 4.20); NMR ($CDCl_3$) δ 3.52 (s, 3 H, methoxy), 4.84 (s, 1 H, benzyl), 7.09, 7.17, 7.32 (m, 14 H, aromatic).

Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.62; H, 5.56. Found: C, 84.39; H, 5.47.

2,3-Diphenylindene-1-carboxamide. A solution of 3.00 g (0.0998 mol) of 2,3-diphenylindene-1-carboxylic acid in 20 mL of thionyl chloride was refluxed for 1.5 h. The excess thionyl chloride was removed in vacuo and replaced with sodium-dried benzene which was also removed in vacuo. The brown residue was dissolved in 50 mL of dry benzene. The solution was cooled in an ice bath and saturated with anhydrous ammonia by bubbling the gas through the solution slowly for 20 min. The precipitate that formed was filtered and washed with water. No additional precipitate formed in the filtrate when ammonia was added. The solid was recrystallized from 95% ethanol as white prisms that weighed 2.02 g (65%): mp 215-218 °C; mass spectrum (70 eV) *m/e* (parent) 311; IR (KBr) 3400, 3200, 1655, and 1400 cm^{-1}; NMR ($CDCl_3$) δ 7.7 (m, 1 H, aromatic), 7.3 (m, 13 H, aromatic), 5.2 (s, broad, 2 H, amide), and 4.9 ppm (s, 1 H, allylic).

1,2-Diphenyl-3-cyanoindene (3e). A mixture of 200 mg (0.643 mmol) of 2,3-diphenylindene-1-carboxamide, 2.0 mL of phosphorus oxychloride, and 50 mL of chloroform was refluxed for 2 h and then allowed to cool. The chloroform and excess phosphorus oxychloride were removed in vacuo and the oily residue was stirred with ice. The cream-colored solid was dried, taken up in the boiling hexane, and filtered. Colorless needles formed in the filtrate, 122 mg (65%): mp 139-140 °C; NMR (CCl_4) δ 7.2 (m, 14 H, aromatic) and 5.1 ppm (s, 1 H, allylic). The physical properties of this material were identical with those of the irradiation product of 1,1-diphenyl-3-cyanoindene.

2,3-Diphenyl-1-cyanoindene (4e). A solution of 200 mg (0.643 mmol) of 2,3-diphenylindene-1-carboxamide and phosphorus oxychloride in 50 mL of acetonitrile was stirred and heated to 45 °C for 2 h. The volatile material was removed in vacuo. The pasty residue was mixed with ice and water, filtered, and dissolved in 50 mL of hot hexane. This solution (while still hot) was filtered through sodium sulfate and allowed to cool slowly. Colorless needles, 116 mg (61%), of the 2,3-diphenyl-1-cyanoindene were formed: mp 118-122 °C (remelted 139-140 °C); NMR (CCl_4) δ 7.5 (m, 1 H, aromatic), 7.2 (m, 13 H, aromatic), and 4.8 ppm (s, 1 H, allylic); IR ($CHCl_3$) 3025, 2240, and 1600 cm^{-1}; mass spectrum mol wt (calcd for $C_{22}H_{15}N$, 293.1204) 293.1233. Concentration of the filtrate to a volume of 10-15 mL afforded the other isomer, 1,2-diphenyl-3-cyanoindene, also as colorless needles, 37 mg (19.5%), mp 138-140 °C.

2,3-Diphenyl-1-acetylindene (4d). A flask containing 1.23 g (4.3 mmol) of 1,2-diphenylindene in 40 mL of dry benzene was degassed twice at aspirator pressure and room temperature and then filled with dry nitrogen. Nitrogen was bubbled through another flask containing 5.00 g of acetyl chloride in 20 mL of dry benzene. Then 2.60 mL of 2.35 M methyllithium (6.11 mmol) was added by syringe through the stopcock to the indene solution. The solution was refluxed for 30 min. When the yellow precipitate of the lithium indenide had formed, the thick slurry was transferred in three portions by syringe to the flask containing the acetyl chloride solution. Each addition took 5-10 min and the contents of both flasks were kept under nitrogen during the transfer. After addition was complete, the mixture was allowed to stand for 4 h. Fifty milliliters of water was cautiously added. The benzene layer was separated, dried over sodium sulfate, decanted, and evaporated in vacuo. The crude solid was recrystallized from methanol, 578 mg (43%): mp 169-172 °C; NMR (CCl_4) δ 7.2 (m, 14 H, aromatic), 4.8 (s, 1 H, allylic), and 1.6 ppm (s, 3 H, methyl); IR (neat) 1700 and 1600 cm^{-1}; mass spectrum mol wt (calcd for $C_{23}H_{18}O$, 310.1357) 310.1333.

This compound was identical with the one obtained on irradiation of 1,1-diphenyl-3-acetylindene for "long" periods of time.

2,3-Diphenyl-1-indanone. Ten grams (0.035 mol) of 2,3-diphenyl-1-indenone,[33] 200 mL of 95% ethanol, and 0.50 g of 10% palladium on carbon were shaken under hydrogen at about 40 psi for 3 h. The mixture was heated with ethanol and the solution was filtered. The saturated ketone, 4.11 g (41%), crystallized from it as white needles: mp 151-154 °C; NMR ($CDCl_3$) δ 7.0 (m, broad, 14 H, aromatic) and 4.7 (AB quartet, 2 H, benzylic, $J = 8$ Hz); IR (KBr) 3010 and 1680 cm^{-1}. The melting point of this material is different from the melting point (100-101 °C) of the 2,3-diphenyl-1-indanone prepared by Koelsch[34] from 3,3,3-triphenylpropanoic acid by a Freidel-Crafts method. We assume that Koelsch prepared the trans isomers and that the cis isomer is the one described above. The stereochemistry of this ketone, however, has little effect on the elimination reaction leading to the next product **3b**.

1,2-Diphenyl-3-methylindene (3b). This compound was prepared by the procedure of Koelsch and Johnson:[15] 42% yield; mp 89-91 °C (lit. 91 °C); NMR (CCl_4) δ 7.0 (m, 14 H, aromatic) 4.7 (quartet, 1 H, allylic, $J = 2$ Hz), and 2.2 ppm (d, 3 H, methyl, $J = 2$ Hz). In an

NMR decoupling experiment irradiation of the quartet caused the doublet at 2.2 ppm to collapse to a singlet.

General Procedure for Irradiation. A 450-W Hanovia mercury arc in a quartz water-cooled immersion well was used in all cases. The solution to be irradiated was placed in a vessel outside this well. Unless otherwise noted, nitrogen (deoxygenated by the method of Meites and Meites[35] and dried through a column of Dierite) was bubbled through the stirred solution for at least 30 min before irradiation and while the lamp was on. Unless otherwise noted a Corex tube, inserted over the lamp inside the well, was used as a filter. In the descriptions below the weight of the sample being irradiated, the volume of the solvent used and the duration of the irradiation are listed in that order. These are followed by any special conditions used and the analysis of the residue remaining after the solvent was removed by rotary evaporation at room temperature and aspirator pressure. Solvents: reagent grade benzene dried over sodium; methanol-*O-d* (99%) purchased from Diaprep, Inc., and from Aldrich Chemical Co. The relative amount of each product was determined from the relative area of a resonance appropriate for each isomer. The methyl resonances were used in the methyl, acetyl, and carbomethoxy cases; the allylic resonances were used in the cyano case.

Irradiation of 1,1-Diphenyl-3-methylindene (1b). (a) **1** (200 mg, 0.710 mmol); 150 mL of benzene; 1.0-h irradiation; no Corex filter. The NMR spectrum (CCl$_4$) of the residue revealed doublets at 1.2, 1.6, and 2.2 ppm with areas in the ratio of 79:10:11, respectively. No other absorptions in this region were observed. The residue was dissolved in approximately 1 mL of carbon tetrachloride and placed on a 22.0 × 2.5 cm silica gel column slurry-packed in hexane. The column was eluted with 3 L of hexane, 900 mL of 2% benzene in hexane, 400 mL of 5% benzene in hexane, 700 mL of 10% benzene in hexane, and 300 mL of 50% benzene in hexane. Fractions of 100 mL each were collected and monitored by NMR. The last two hexane fractions contained 10 mg of the 2,3-diphenyl isomer and the indenophenanthrene derivative. The first 800 mL of the 2% benzene washings contained 173 mg of the 2,3-diphenyl compound and its cyclized derivative. The 5% benzene fractions gave 9 mg of a pale yellow oil (not identified). The third and fourth fractions of the 10% benzene washings produced 18 mg (0.64 mmol) of 1,2-diphenyl-3-methylindene. This material had the same NMR spectrum as an authentic sample and when the colorless oil was mixed with methanol a solid was obtained, mp 90–91 °C (lit.[15] 91 °C). The residues from the hexane and 2% benzene washings were combined and recrystallized from ethanol to give 94 mg (47%) of white needles of 2,3-diphenyl-1-methylindene: mp 107.5–108.5 °C (lit.[15] 105–106 °C); NMR (CCl$_4$) δ 7.2 (m, 14 H, aromatic), 3.9 (quartet, 1 H, allylic, J = 7 Hz), and 1.2 ppm (d, 3 H, methyl, J = 7 Hz).

(b) **1** (50 mg); 70 mL of benzene and 20 mL of CH$_3$OD; 15-min irradiation; no Corex filter. The spectrum of the residue revealed the doublet absorptions corresponding to the 1,2-diphenyl isomer, the 2,3-diphenyl isomer, and the indenophenanthrene in the ratio 7:40:5, respectively. Mass spectral analysis of P and P + 1 for the 282 parent in the residue showed 2.1% (±1%) of one atom of deuterium.

Irradiation of 1,1-Diphenyl-3-cyanoindene (1e). (a) **1** (100 mg, 0.341 mmol); 150 mL of benzene; 15-min irradiation. The NMR spectrum of the oily residue showed only absorptions of 1,2-diphenyl-3-cyanoindene contaminated with benzene. The residue produced colorless needles from hexane, 55 mg (55%): mp 139–140 °C; NMR (CCl$_4$) δ 7.2 (m, 14 H, aromatic) and 5.1 ppm (s, 1 H, allylic); IR (neat) 3090, 3020, 2230, and 1600 cm^{-1}; mass spectrum mol wt (calcd for C$_{22}$H$_{15}$N, 293.1204) 293.1233.

(b) **1** (50 mg); 150 mL of benzene; 15-min irradiation; air was bubbled through the solution for 5 min prior to and for 5 min during the 15-min irradiation. The NMR spectrum of the residue showed only **3**.

(c) **1** (100 mg, 0.341 mmol); 100 mL of benzene; 1.5 h. The NMR spectrum of the residue contained a broad multiplet at 7.2 ppm and singlets at 5.1 and 5.3 ppm. The product was mixed with approximately 1 g of silica gel in 20 mL of ether. The ether was removed in vacuo and the resulting solid placed over a 2.5 × 18 cm silica gel column slurry packed in hexane. The column was eluted with 300 mL of 5% ether in hexane. The residue from this eluate gave 84 mg (84%) of 1,2-diphenyl-3-cyanoindene, mp 139–141 °C. The column was washed with 50% ether in hexane to give 10 mg of a pale yellow solid: mp 277 °C; NMR (CCl$_4$, CAT run) δ 6.9 (m, ca. 13 H, aromatic) and 5.3 ppm (s, 1 H, allylic); IR (KBr) 2230 cm^{-1}; mass spectrum (70 eV) *m/e* 293.

(d) **1e** (497 mg); 300 mL of benzene and 140 mL of methanol; 75-min irradiation. The oily residue, which contained some benzene, eventually crystallized, weight 523 mg. Its NMR showed only absorptions of **3** contaminated with benzene. This sample was chromatographed on a 1.4 × 25 cm column of silica gel slurry packed in 5% ether–hexane. The first six 50-mL fractions eluted with 5% ether–hexane contained 418 mg of a solid that was mostly (90+%) **3**. Three additional 50-mL fractions eluted with 50% ether–hexane contained 63 mg of a solid, the NMR of which showed four peaks between 4.8 and 5.4 ppm, all of about equal magnitude. One of them was due to **3**. The solid was not investigated further.

(e) **1e** (109 mg); 70 mL of benzene and 20 mL of CH$_3$OD; 15-min irradiation. The oily residue weighed 117 mg. The NMR between 0 and 6 ppm showed only **3** (90+%). The residue was chromatographed as above to yield 67 mg of **3** in the first six fractions. Six 50-mL fractions eluted with CHCl$_3$ yielded 31 mg of a yellow oil. Solid **3** was recrystallized from hexane to yield pure **3**, mp 139–141 °C. Quantitative analysis of the P and P + 1 peaks at *m/e* 293 and 294 showed 2.7% of one atom of deuterium.

Irradiation of Methyl 1,1-Diphenylindene-3-carboxylate (1c). (a) **1** (100 mg, 0.306 mmol); 150 mL of benzene; 30-min irradiation. The NMR spectrum of the residue showed that the only peaks present were those of methyl 1,2-diphenylindene-3-carboxylate and benzene. The product was suspended in hexane and filtered. Recrystallization from hexane did not raise the melting point. The ester weighed 78 mg (78%): mp 123–124 °C; NMR (CCl$_4$) δ 7.8 (m, 1 H, aromatic), 7.2 (m, 13 H, aromatic), 4.9 (s, 1 H, allylic), and 3.7 ppm (s, 3 H, methyl); IR (neat) 3090, 2965, 1710, and 1600 cm^{-1}; mass spectrum mol wt (calcd for C$_{23}$H$_{18}$O$_2$, 326.1306) 326.1317.

(b) **1** (100 mg); 150 mL of benzene; 2.5-h irradiation. The results were the same as in part (a).

(c) **1** (50 mg); 70 mL of benzene and 20 mL of CH$_3$OD; 15-min irradiation. The NMR spectrum of the residue indicated that both the 1,2-diphenyl and 2,3-diphenyl isomers were formed. The ratio of the two methyl group absorptions was 26:10, respectively. If the sum of the areas of these two peaks is taken to represent three protons, the allylic proton abosrption shows no decrease in area; i.e., it integrates to be one proton. The mass spectral analysis showed no deuterium incorporation within experimental error.

(d) **1** (100 mg); 150 mL of methanol; 15-min irradiation. The NMR spectrum of the residue showed only the absorption peaks of the two isomeric esters. The areas of the two methoxy singlets at 3.5 (2,3-diphenyl isomer) and 3.7 ppm (1,2-diphenyl isomer) were in the ratio of 2:3.

Irradiation of 1,1-Diphenyl-3-acetylindene (1d). (a) **1** (100 mg, 0.323 mmol); 150 mL of benzene; 15-min irradiation. The 0–4.0-ppm region of the NMR spectrum of the pale yellow oil that remained showed only two singlets, at 2.0 (relative area 85, CH$_3$ of the 1,2-diphenyl isomer) and at 1.6 ppm (relative area 15, CH$_3$ of the 2,3-diphenyl isomer). The residue was stirred with 10 mL of hexane for about 5 min. The mixture was then filtered to remove some insoluble matter and the filtrate was allowed to stand in a lightly stoppered flask. After 2 days pale yellow aggregates of prisms of 1,2-diphenyl-3-acetylindene were formed. They weighed 33 mg (33%): mp 117–120 °C (remelted 169–171 °C); NMR (CCl$_4$) δ 7.7 (m, 1 H, aromatic), 7.2 (m, 13 H, aromatic), 4.9 (s, 1 H, allylic), and 2.0 ppm (s, 3 H, methyl); IR (neat) 3080, 3020, 1660, and 1565 cm^{-1}; mass spectrum mol wt (calcd for C$_{23}$H$_{18}$O, 310.1357) 310.1396.

(b) **1** (400 mg, 1.29 mmol); 150 mL of dry ether; 2-h irradiation. The NMR spectrum of the orange, solid residue showed principally one isomer. Two recrystallizations from ethanol of a portion of the solid produced pale yellow crystals of 2,3-diphenyl-1-acetylindene: mp 170–172 °C; NMR (CCl$_4$) δ 1.6 (s, 3 H, methyl), 4.8 (s, 1 H, allylic), and 7.2 ppm (m, 14 H, aromatic); IR (neat) 1690 cm^{-1}; mass spectrum (70 eV) *m/e* 310.

(c) **1** (200 mg); 150 mL of benzene; 30-min irradiation. The NMR spectrum of the residue showed five singlets at 2.3 (4%, unknown), 2.0 (40%, **3**), 1.8 (10%, unknown), 1.5 (30%, **4**), and 1.3 ppm (16%, **5**). The percentages were determined by assuming that the singlets were all caused by methyl groups and that their areas represented the relative amounts of the several products.

(d) **1** (50 mg); 70 mL of benzene and 20 mL of CH$_3$OD; 15-min irradiation. The NMR spectrum of the residue showed that 2,3-diphenyl-1-acetylindene made up 90 + % of the isomeric mixture. The mixture was found to contain 10.0% (±1%) atom of deuterium by mass spectral analysis of P and P + 1 of the *m/e* 310 parent. A duplicate run again gave a product that was almost entirely the 2,3-diphenyl isomer by NMR and which contained 11.9% of one atom of deuterium by mass spectral analysis.

Irradiation of 2,3-Diphenyl-1-methylindene (4b). **4** (100 mg, 0.354 mmol); 150 mL of benzene; 15-min irradiation; no Corex filter; air bubbled through the solution for 5 min prior to and for 5 min during the 15-min irradiation. The NMR spectrum of the yellow oil revealed only absorptions due to the indenophenanthrene derivative and benzene. However, not all of the crude product was soluble in carbon tetrachloride. The residue in approximately 1 mL of carbon tetrachloride was then placed over a 2.5 × 17.0 cm silica gel column slurry packed in hexane. The column was washed with 10% ether in hexane and 50-mL fractions were collected. The residue from each fraction was weighed and monitored by NMR. The third fraction contained 13*H*,13-methylindeno[1,2-*l*]phenanthrene as a pale yellow oil. Recrystallization from hexane produced prisms, 32 mg (32%): mp 141-143 °C; NMR (CCl_4) δ 7.5 (m, broad, 12 H, aromatic), 4.2 (quartet, 1 H, methine, $J = 7$ Hz), and 1.6 ppm (d, 3 H, methyl, $J = 7$ Hz); mass spectrum mol wt (calcd for $C_{22}H_{16}$, 280.1252) 280.1226.

Irradiation of 2,3-Diphenyl-1-cyanoindene (4e). (a) **4** (26 mg); 150 mL of benzene; 17-min irradiation. The NMR spectrum ($CDCl_3$) of the residue was identical with that of **3e**. A very small amount of this product was insoluble in $CDCl_3$ and was filtered from the solution.

(b) **4** (40 mg); 150 mL of benzene; 15-min irradiation; air bubbled through the solution for 5 min prior to and for 5 min during the irradiation. Most of the residue was insoluble in CCl_4 and hexane: mp 150-180 °C dec; NMR ($CHCl_3$) showed only aromatic absorption.

Irradiation of Methyl 2,3-Diphenyl-1-carboxylate (4c). **4** (300 mg, 9 mmol); 125 mL of cyclohexane; 30-min irradiation; no Corex filter. The NMR spectrum of a sample showed only unchanged starting ester. The irradiation was continued for an additional 30 min with air bubbling through the solution. The NMR spectrum of a sample showed only absorption due to methyl 13*H*-indeno[1,2-*l*]phenanthrene-13-carboxylate.[2] The oily residue remaining after the solvent had been evaporated was chromatographed on silica gel (1.2 × 45 cm) using chloroform as the eluting solvent. Fractions 4-6 (150 mL each) gave 100 mg of **5c**: mp 192-195 °C; NMR ($CDCl_3$) δ 3.5 (s, 3 H, methoxy), 5.02 (s, 1 H, methine), 7.25-7.95 (m, 8 H, aromatic), 8.17-8.80 (m, 4 H, aromatic).

Irradiation of 2,3-Diphenyl-1-acetylindene (4d). (a) **4** (100 mg, 0.323 mmol); 150 mL of benzene; 15-min irradiation; air was bubbled through the solution for 5 min prior to and for 5 min during the irradiation. The NMR spectrum of the residue showed the absorptions of 13*H*,13-acetylindeno[1,2-*l*]phenanthrene and benzene. Not all of the crude photolysis product was soluble in carbon tetrachloride. The residue was taken up in approximately 1 mL of carbon tetrachloride and placed on a 2.5 × 19.0 cm column of silica gel slurry packed in hexane. The column was eluted with 10% ether in hexane and 50-mL fractions were collected. Fractions 5 and 6 contained the cyclized product. The product was recovered as a pale yellow solid, 39 mg (39%), mp 163-166 °C. A portion of the material was recrystallized from methanol: mp 175-177 °C; NMR (CCl_4) δ 7.7 (m, broad, 12 H, aromatic), 5.0 (s, 1 H, methine), and 1.4 ppm (s, 3 H, methyl); IR (neat) 1695 and 1610 cm^{-1}; mass spectrum mol wt (calcd for $C_{23}H_{16}O$, 308.1200) 308.1185.

(b) **4** (140 mg); 50 mL of benzene and 14.3 mL of CH_3OD; 30-min irradiation. The NMR spectrum of the residue showed only **4** and a very small amount of **5**. The residue was recrystallized from methanol to yield yellow crystals, mp 169-171 °C. The intensity of the P + 1 peak in the mass spectrum of this compound indicated that the deuterium content (0.3%) was zero within experimental error.

Irradiation of 1,2-Diphenyl-3-cyanoindene (3e). (a) **3** (30 mg); 100 mL of benzene; 30-min irradiation; no Corex filter; air bubbled through the solution all during the irradiation. The residue remaining after the solvent had been removed was extracted with hot hexane to yield 21 mg of **3** (mp 138-140 °C) according to its NMR spectrum.

(b) **3e** (230 mg); 70 mL of benzene and 20 mL of CH_3OD; 15-min irradiation. The solid orange residue weighed 239 mg. The NMR of this solid showed only the absorption of **3** between 0 and 6 ppm, though the area of the methine peak at 5.1 ppm was small relative to the very strong absorption in the aryl region between 6 and 8 ppm. The mass spectrum was similar to that of pure **3** and showed no peaks above the parent region up to *m/e* 350. Quantitative analysis of the P and P + 1 peaks at *m/e* 293 and 294 showed 1.3% of one atom of deuterium. The sample was dissolved in hexane (and filtered to remove some hexane-insoluble material) and recrystallized to yield 64 mg of a solid with mp 137-139 °C.

Irradiation of 1,2-Diphenyl-3-acetylindene (3d). (a) **1d** (50 mg); 150 mL of benzene; 15-min irradiation. At this point the lamp was shut off and air was bubbled through the solution for 5 min. The air was left on for the first 5 min of another 15-min irradiation. The NMR spectrum of the oil remaining after the solvent had been removed showed mainly the absorption peaks of **3** (no **4** or **5** peaks were observed; there was very minor absorption at about 1.3 ppm).

(b) **1** (50 mg); 90 mL of benzene; 15-min irradiation. The NMR spectrum of the residue showed singlets at 2.0 (**3**), 1.6 (**4**), and 1.45 ppm (**5**), the area of **3** being about three times that of the total of **4** and **5**. In addition there was a somewhat broader peak at 1.3 ppm (source unknown) with area about equal to that of **4** + **5**. This residue was irradiated again: 70 mL of benzene, 20 mL of CH_3OD; 10 min. The NMR spectrum showed a slight decrease in **3** at the expense of a small growth in the unknown peak at 1.3 ppm.

Thermal Isomerization of 2,3-Diphenyl-1-cyanoindene. A 20-mg sample of 2,3-diphenyl-1-cyanoindene was placed in a 25-mL distillation flask fitted with a nitrogen inlet capillary and evacuated via the side arm at aspirator pressure. The flask was then partially immersed in a Wood's metal bath preheated to 125 °C for 15 min. The pale yellow glass that remained was dissolved in boiling hexane. Colorless needles, 13 mg (65%), were formed, mp 138-140 °C. The NMR spectrum matched that of an authentic sample of 1,2-diphenyl-3-cyanoindene.

Thermal Isomerization of Methyl 1,2-Diphenylindene-3-carboxylate. In the manner described above 20 mg of methyl 1,2-diphenylindene-3-carboxylate was heated at 143 °C for 1 h. The residue was dissolved in boiling hexane. the pale yellow solid weighed 13 mg and showed singlet absorptions in the NMR at 3.5 and 3.7 ppm representing the methyl group absorptions of the 2,3-diphenyl and 1,2-diphenyl compounds, respectively. The ratio of the areas of the two absorptions was 3:1, respectively.

Base-Catalyzed Isomerization of Methyl 1,2-Diphenylindene-3-carboxylate (3c). A solution of 30 mg of methyl 1,2-diphenylindene-3-carboxylate and 100 mg of potassium acetate in 10 mL of anhydrous methanol was degassed by the freeze-thaw method at −196 °C. After 20 h at room temperature, 30 mL of water was added. The crystals that formed were filtered and dried in air. The product weighed 22 mg (74%): mp 150-152 °C; NMR (CCl_4) δ 7.2 (m, 14 H, aromatic), 4.8 (s, 1 H, allylic), and 3.5 ppm (s, 3 H, methyl); IR (neat) 3090, 2965, 1720, and 1600 cm^{-1}; mass spectrum mol wt (calcd for $C_{23}H_{18}O$, 326.1306) 326.1290.

Base-Catalyzed Isomerization of 2,3-Diphenyl-1-cyanoindene (4e). A solution of 30 mg of 2,3-diphenyl-1-cyanoindene and 100 mg of potassium acetate in 10 mL of anhydrous methanol was degassed as above. After 20 h at room temperature, 30 mL of water was added. The solid that formed was filtered and dried. It weighed 26 mg (87%), mp 126-130 °C. The NMR spectrum corresponded to that of 1,2-diphenyl-3-cyanoindene. One recrystallization from hexane raised the melting point to 139-140 °C.

Base-Catalyzed Isomerization of 1,2-Diphenyl-3-acetylindene (3d). A sample of **3** was prepared by irradiating 38 mg of **1** in benzene for 15 min. It was an oil and still contained about 20% unchanged starting material. A solution of this sample and 119 mg of potassium acetate in 10 mL of methanol was degassed as above and left at room temperature under argon for 30 min. Water was added and the mixture was extracted with ether. The ether was dried and evaporated to yield an oil which contained no **3** according to NMR. In addition to **4**, unreacted **1** was still present.

Base-Catalyzed Isomerization of 1,2-Diphenyl-3-methylindene (3b). A mixture of 0.5 mL of pyridine and 38 mg of 1,2-diphenyl-3-methylindene was placed in an NMR tube at room temperature and its spectrum was recorded at intervals for 90 h (for the final 24 h the tube was kept at 70 °C). The ratio of **3** to **4** (as measured by the relative areas of the two methyl doublets) stayed constant at about 1.1 after 36 h. A mixture of 15 mg of 3,4-diphenyl-1-methylindene in 0.5 mL of pyridine in an NMR tube was kept at room temperature for 52 h. The same ratio (1.0-1.1) was observed.

Acknowledgment. Partial support of this work was provided by the Research Corporation. We especially thank Dr. Huh-

tanen for permission to use unpublished material from his dissertation.

References and Notes

(1) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1968).
(2) (a) K. L. Huhtanen, Ph.D. Dissertation, University of Kentucky, Lexington, Ky., 1969; (b) J. W. Wilson and K. L. Huhtanen, *Chem. Commun.*, 454 (1968).
(3) G. W. Griffin, A. F. Marcantonio, and H. Kristinsson, *Tetrahedron Lett.*, 2951 (1965).
(4) W. R. Roth, *Tetrahedron Lett.*, 1009 (1964).
(5) J. A. Berson and G. A. Aspelin, *Tetrahedron*, **20**, 2697 (1974).
(6) K. Alder, F. Pascher, and H. Vagt, *Chem. Ber.*, **75**, 1501 (1942).
(7) N. S. Isaacs, *Can. J. Chem.*, **44**, 415 (1966).
(8) (a) L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Am. Chem. Soc.*, **91**, 1578 (1969); (b) L. L. Miller and R. F. Boyer, *ibid.*, **93**, 650 (1971).
(9) J. Almy and D. J. Cram, *J. Am. Chem. Soc.*, **92**, 4316 (1970).
(10) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).
(11) W. R. Dolbier, Jr., L. McCullagh, D. Rolison, and K. E. Anapolle, *J. Am. Chem. Soc.*, **97**, 934 (1975).
(12) The intermediacy of a "pseudoisoindene"[7,13] is not excluded by any evidence here. However, its conversion to **3** or **4** would presumably be a concerted process[14a] and conclusions about the effects of substituents on the reaction would be substantially the same.
(13) J. A. Berson and M. Pomerantz, *J. Am. Chem. Soc.*, **86**, 3896 (1964).
(14) (a) M. J. S. Dewar, *Chem. Br.*, **11**, 97 (1975). (b) The observed relative stabilities of **3** and **4** can be rationalized by employing a combination of electronic and steric arguments as follows. In the absence of steric effects **4** would be the more stable isomer for all R groups. Steric interaction between the two phenyl groups prevents them from being coplanar and destabilizes **4** relative to **3**. Thus when R is a small conjugating substituent like cyano, **3** becomes the more stable isomer. When R is a large substituent like acetyl (presumably conjugated with the indene ring and coplanar with it in **3**) which can itself interact with the phenyl group on carbon 2 to destabilize **3**, **4** remains the more stable isomer. When R is methyl, a substituent of intermediate size, the two stabilities are evenly balanced.
(15) C. F. Koelsch and P. R. Johnson, *J. Am. Chem. Soc.*, **65**, 567 (1943).
(16) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", Wiley, New York, N.Y., 1961, Chapters 4 and 5.
(17) Reference 16, p 135.
(18) R. W. Schmid and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1453 (1954).
(19) O. E. Polansky and M. A. Grassburger, *Monatsh. Chem.*, **94**, 647 (1963).
(20) K. Fukui, K. Morokuma, C. Nagata, and A. Imamura, *Bull. Chem. Soc. Jpn.*, **34**, 1224 (1961).
(21) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1969: (a) p 184; (b) p 207; (c) pp 176–193.
(22) G. Bergson, *Acta Chem. Scand.*, **17**, 2691 (1963).
(23) A. M. Weidler, *Acta Chem. Scand.*, **17**, 2724 (1963).
(24) G. W. Borden, O. L. Chapman, R. Swindell, and T. Tezuka, *J. Am. Chem. Soc.*, **89**, 2979 (1967).
(25) L. B. Jones and V. K. Jones, *J. Am. Chem. Soc.*, **90**, 1540 (1968).
(26) L. Libit, *Mol. Photochem.*, **5**, 327 (1973).
(27) A. P. ter Borg, E. Razenberg, and H. Kloosterziel, *Chem. Commun.*, 1210 (1967).
(28) (a) N. D. Epiotis, *J. Am. Chem. Soc.*, **95**, 1206 (1973); (b) N. D. Epiotis, R. L. Yates, and F. Bernardi, *ibid.*, **97**, 4198 (1975); (c) J. Berson and L. Salem, *ibid.*, **94**, 8917 (1972).
(29) J. P. Freeman, *J. Org. Chem.*, **22**, 1608 (1957).
(30) C. F. Koelsch and C. D. LeClaire, *J. Org. Chem.*, **6**, 516 (1941).
(31) R. L. Shriner and W. R. Knox, *J. Org. Chem.*, **16**, 1064 (1951).
(32) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, p 149.
(33) C. F. H. Allen, J. W. Gates, Jr., and J. A. Van Allan in "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 353.
(34) C. F. Koelsch, *J. Am. Chem. Soc.*, **56**, 1338 (1934).
(35) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

Generation and Properties of 4,9- and 3,8-Methano[11]annulenylidenes

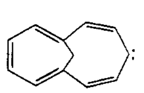
W. M. Jones,* R. A. LaBar,[2] U. H. Brinker,[2,3] and P. H. Gebert[1]

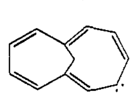
Contribution from the Department of Chemistry, University of Florida, Gainesville, Florida 32611.

Received October 1, 1976

Abstract: The two carbocyclic aromatic carbenes, 4-9-methano[11]annulenylidene (**1**) and 3,8-methano[11]annulenylidene (**2**), have been generated by decomposition of the corresponding ketone tosylhydrazone salts and the sodium salts of the tosylhydrazones of 3- and 2-formyl-1,6-methano[10]annulene (**5** and **14**). The latter reactions are believed to involve carbene–carbene rearrangements which proceed with a high degree of regioselectivity. The facility of rearrangement of these carbenes as compared with other arylcarbenes is discussed. In the absence of substrates 4,9-methano[11]annulenylidene (**1**) dimerizes to give fulvalene **8**. In the presence of styrenes or dimethyl fumarate it adds to give spirocyclopropane adducts and in the presence of 1,2-cyclononadiene and phenylacetylene it gives 1:1 adducts that are assigned structures that would result from rearrangement of initially formed spirocyclopropane adducts. These properties are all very similar to those of cycloheptatrienylidene which places **1** in the category of the so-called "nucleophilic" carbenes (a term for which a new definition is suggested). In contrast to **1**, 3,8-methano[11]annulenylidene (**2**) gives neither a fulvalene in the absence of substrates nor spirocyclopropanes in their presence. Without substrate it gives two isomeric dimethylenecyclobutane products which have structures that can be accounted for by the dimerization of an allene intermediate or initial formation of a fulvalene followed by a 22 π electron electrocyclic ring closure. The stereochemistry of the products is not consistent with a Woodward-Hoffmann controlled ring closure. Generation of **2** in the presence of styrene or dimethyl fumarate gives no isolable adducts. However, in the presence of phenylacetylene, 1,2-cyclononadiene, or 1,1-diphenylethylene, 1:1 adducts are formed. These are assigned structures that could result from either cycloaddition of the substrate and an allene intermediate or rearrangement of an initially formed spirocyclopropane.

As a continuation of our research on carbocyclic aromatic carbenes[4-8] and carbene-carbene rearrangements[9-12] we have now studied some of the chemistry of **1** and **2**,[13] two of the five possible methano[11]annulenylidenes. These intermediates have been generated from both the tosylhydrazone salts of the ketones **3**[14] and **10**[15] (Schemes I and II) and carbene–carbene rearrangement of the arylcarbenes **7** and **15**. **1** and **2** constitute the only recorded examples of carbocyclic aromatic carbenes in which the vacant orbital of the singlet state is an integral component of a non-cross-conjugated (such as benzocycloheptatrienylidene) 10 π electron system.


1


2

Generation of the Carbenes. 4,9-Methano[11]annulenylidene (**1**) was generated by pyrolysis of the tosylhydrazone salts of the ketone **3** and the aldehyde **4**. The ketone was synthesized using a nine-step sequence developed by Vogel.[14] Synthesis of

Jones et al. / 4,9- and 3,8-Methano[11]annulenylidenes