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Phenylcinnamalones. II. Some Data Concerning the Preparative Reaction[1]

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Pyrolysis of α-phenyl-*trans*-cinnamic acid (Ia) in the presence of thionyl and sulfuryl chlorides yields phenylcinnamalone (14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (IIIa)). Two intermediates in this reaction appear to be α-phenyl-*trans*-cinnamoyl chloride (IIa) and 14b,14c-dihydro-5a-phenyl-10-(α-phenyl-*trans*-cinnamoxy)benz[*a*]indeno[2,1-*c*]fluoren-5-one (IVa). IVa also can be prepared directly from Ia using phosphorus trichloride in place of thionyl chloride. The 3,12-dichloro, 3,12-dimethyl, and 3,12-dimethoxy analogs of IIIa and the 3,12-dichloro and 3,12-dimethyl analogs of IVa can be prepared using similar techniques. The structures of these compounds and related derivatives were determined using chemical and spectral methods.

In a previous publication,[4] a procedure for the preparation of 14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (phenylcinnamalone, IIIa, see Scheme I) was reported along with a complete crystal and molecular structure proof. Since new procedures for the formation of carbon–carbon bonds are of great general interest and importance in organic chemistry, we have undertaken a detailed study of the reaction, its products, and its mechanism. This report will concern itself with the generality of the reaction and the nature of the reaction intermediates. The unusual chemistry of the phenylcinnamalone ring system (III) will be reported subsequently.

Results and Discussion

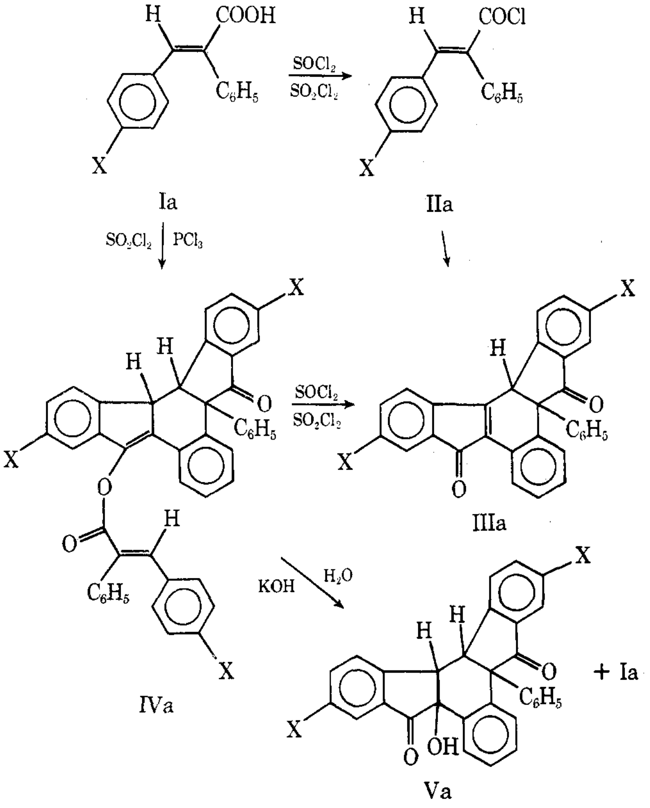
The preparative reaction involves a novel one-step reaction which results in the creation of four carbon–carbon bonds between two molecules of α-phenylcinnamoyl chloride (IIa) to yield a complex system of six fused carbocyclic rings. IIa is a known reaction intermediate, but it is not necessary to isolate IIa in order to make IIIa; rather it is more convenient to proceed directly from Ia to IIIa *via in situ* generation of IIa.

In order to clarify subsequent discussions involving proton magnetic resonance (pmr) spectra a brief review of the structure of IIIa as related to its pmr spectrum might be helpful.

Phenylcinnamalone was shown to have the structure of 14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (IIIa) (Figure 1).[4] The previously reported crystal and molecular structure data[4] allow a more complete interpretation of the pmr spectrum of IIIa than would ordinarily be possible. The spectrum displays a singlet at 4.68δ and two well-separated complex multiplets. One multiplet is centered at δ 7.40 and the other at δ8.40. The ratio of integration is 1:16:1, respectively. The singlet is clearly due to resonance of the methine proton of C_{14c}. The intense multiplet at δ7.40 may be reasonably assigned to the collective resonance of all but one of the 17 aromatic protons. Thus, the remaining multiplet must be due to resonance of a single aromatic proton. The shift of this multiplet, away from the bulk of aromatic resonance, toward the deshielded portion of the spectrum points to further strong deshielding. Such deshielding may be caused by a carbonyl group ortho to an aromatic proton.[5] Further, this effect is strongest when both the proton in question and the carbonyl group lie in the same plane. The crystallographic establishment of the coplanarity of the five-membered ring B and its carbonyl oxygen with benz ring A allow assignment of the multiplet at δ8.40 to the resonance of the proton of C_{11}.

If the reaction mixture from the preparation of IIIa is properly treated, a white compound (IVa) can be isolated. When the purified compound (IVa) is again subjected to

Scheme I[a]



$$\mathrm{Va} \xrightarrow[\mathrm{H_2O}]{\mathrm{NaOH}} \mathrm{IIIa}$$

$$\mathrm{Ib\text{-}d} \xrightarrow[\mathrm{SO_2Cl_2}]{\mathrm{SOCl_2}} \mathrm{IIIb\text{-}d}$$

$$\mathrm{Ib,c} \xrightarrow[\mathrm{SO_2Cl_2}]{\mathrm{PCl_3}} \mathrm{IVb,\ c}$$

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[a] Roman numeral legend: a, X = -H; b, X = -Cl; c, X = -CH_3; d, X = -OCH_3; e, X = -NO_2; f, X = -OH; g, X = -$NHCOCH_3$; h, X = NH_2.

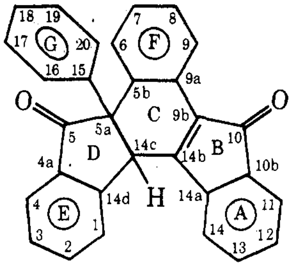


Figure 1. Diagram of phenylcinnalone (IIIa) showing the numbering system.

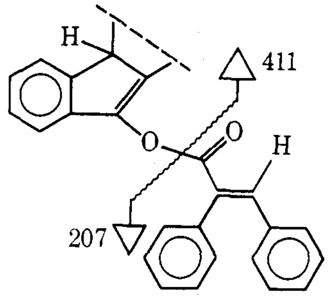


Figure 2. Partial structure of IVa showing one mode of α cleavage of the ester group.

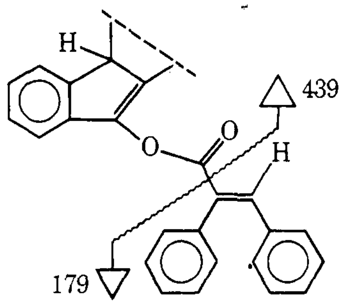


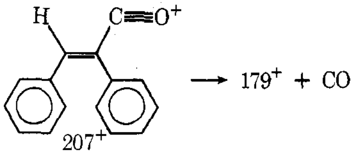
Figure 3. Partial structure of IVa showing the alternate mode of α cleavage.

the conditions for the preparation of IIIa, IIIa is formed. Also, if Ia is subject to reaction conditions identical with those employed to prepare IIIa but with phosphorus trichloride in place of thionyl chloride only IVa is formed.

The mass spectrum of IVa displayed its parent peak at *m/e* 618. Isotopic analysis indicated a molecular formula of $C_{45}H_{30}O_3$, in agreement with the elemental analysis. The infrared, mass, and pmr spectra are in agreement with the structure 14b,14c-dihydro-5a-phenyl-10-(α-phenyl-*trans*-cinnamoxy)benz[*a*]indeno[2,1-*c*]fluoren-5-one (IVa). IVa possesses the same ring system as phenylcinnamalone (IIIa). This is not inconsistent with the known convertibility of IVa to IIIa *via* repyrolysis using thionyl chloride.

The infrared spectrum of IVa has two strong, sharp absorptions attributable to the -CO-O- grouping. One peak located at 1220 cm^{-1} is moderately strong. The other at 1155 cm^{-1} is very strong. Two carbonyl bands are present at 1715 cm^{-1} and at 1730 cm^{-1}. The former is in agreement with the absorptions of the indone and indanone carbonyl groups of IIIa and thus attributable to the indanone carbonyl of IVa. The latter is reasonable for the ester carbonyl group of IVa. The rest of the spectrum bears a strong resemblance to that of IIIa.

The mass spectrum of compound IVa has a very complex fragmentation pattern. However, relationships in agreement with structure IVa are apparent. Strong peaks appear at *m/e 411* and 207. These are consistent with one mode of α cleavage of the ester group (Figure 2). The alternate mode of α cleavage of the ester would lead to fragments at *m/e* 439 and 179 (Figure 3). Only a very weak peak appears at *m/e* 439. A strong peak does appear at *m/e* 179. This fragment also could result from further fragmentation of 207. Fragments at *m/e* 395 (strong) and 223 (weak) are present in the spectrum. These are consistent with cleavage of the C_{10}–O bond (Figure 4). Relationships consistent with stepwise CH fragmentation are evident throughout the range of the spectrum. The low molecular weight portion of the spectrum displays peaks at both *m/e* 77 and 76, consistent with the presence of both phenyl groups and ortho fused phenylene rings.



The pmr spectrum of IVa provides, at once, information concerning: the placement and stereochemical nature of the α-phenylcinnamic ester group, the locations of both methine protons, and the stereochemical nature of the molecule as a whole. The spectrum displays a sharp singlet at δ8.28; an intense complex multiplet centered at δ7.60; a well-resolved multiplet centered at δ6.35; and a pair of coupled doublets, one centered at δ4.45 and the other at δ4.20 (J = 5 Hz). The respective ratio of intensities is 1:26:1:1:1.

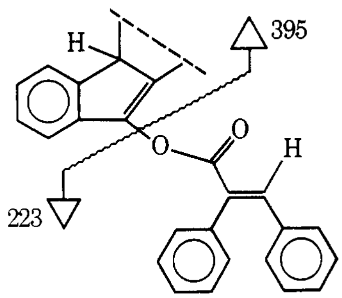


Figure 4. Partial structure of IVa showing cleavage of the C_{10}–O bond.

The pmr spectrum of α-phenyl-*trans*-cinnamic acid (Ia) possesses a singlet, due to resonance of its vinyl proton, at δ8.30. A vinyl proton of an ester of α-phenyl-*trans*-cinnamic acid would most probably give a similar chemical shift. Thus, the singlet at δ8.28, in the spectrum of IVa, can be so assigned. Further, several α-phenyl-para-substituted cinnamic acids, both cis and trans have been prepared. The pmr spectrum of each (Ia–e,g,h) displays a well-defined singlet which may be assigned to resonance of its vinyl proton. A comparison of these singlets may be made from the data in the Experimental Section. Deshielding of the vinyl protons of the trans isomers, as compared to the cis isomers, is evident. This deshielding is due to the proximity of the carbonyl group and the vinyl proton of the trans isomers. The cis configuration does not allow for such deshielding of the vinyl proton by the carbonyl group. Thus, the vinyl proton of the α-phenylcinnamic ester group of structure IVa, if cis, would not be expected to result in the observed chemical shift. The coupled doublets of the pmr spectrum of IVa can only arise from methine protons of adjacent carbons. Therefore, a structure such as 5,14c-dihydro-5a-phenyl-5-(α-phenyl-*trans*-cinnamoxy)benz[*a*]indeno[2,1-*c*]fluoren-10-one, which features the ester group substituted at C_5, cannot be correct. Such a structure also would be expected to be that of a highly colored compound since it would include an indone grouping. For similar reasons, a close structural variation, 10,14c-dihydro-5a-phenyl-10-(α-phenyl-*trans*-cinnamoxy)benz[*a*]indeno[2,1-*c*]fluoren-5-one, can be eliminated. The remaining possibility, 9b,10-dihydro-5a-phenyl-10-(α-phenyl-*trans*-cinnamoxy)benz[*a*]indeno[2,1-*c*]fluoren-5-one, cannot be eliminated on the above basis. However, resonance of the methine protons of carbons 9b and 10 would be expected to result in coupled doublets with well-separated chemical shifts. No such objection can be formulated against structure IVa, which is the only possibility not involving disruption of aromaticity or relocation of the phenyl group of carbon 5a. If structure IVa is correct, then all remaining peaks in the pmr spectrum must be due to resonance of aromatic protons. The complex multiplet centered at δ7.60 can be reasonably attributed to resonance of aromatic protons. However, the multiplet centered at δ6.35, if due to resonance of an aromatic proton, could only result from a shielded aromatic proton. Construction of framework molecular models of IVa indicates that in only one pair of enantiomers can such shielding reasonably occur. This case is illustrated schematically in Figure 5. The proton of carbon 1 lies in the positive pmr shielding zone of aromatic ring A. This pair of enantiomers is defined by cis fusion of rings D and C and by the methine protons of carbons 14b and 14c being cis to one another. Only one conformation of the pair of enantiomers in question places a proton in a positive pmr shielding zone. The molecular model of IVa reveals that severe nonbonded interaction would probably result if a change in this conformation were to occur. Thus, it could be concluded that the process of formation of IVa fixed the conformation and that the molecule must remain in it. The conformation of the five-membered ring D is the same as that of ring D of phenylcinnamalone, as revealed by X-ray crystallography.[4]

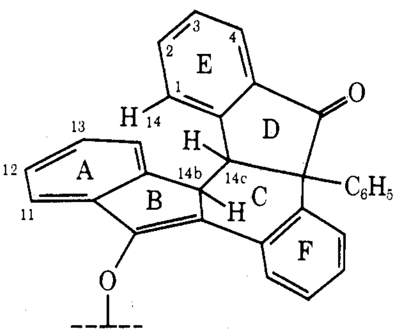
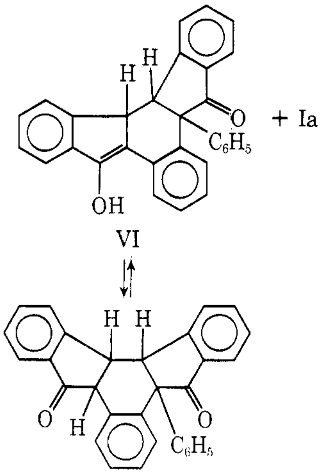


Figure 5. Partial schematic drawing of structure IVa showing the proton of carbon 1 in the positive pmr shielding zone of aromatic ring A.

When subjected to hydrolysis with aqueous ethanolic potassium hydroxide, IVa forms two major products. These are a white crystalline neutral compound (Va) and α-phenyl-*trans*-cinnamic acid (Ia). Spectral examination of Va indicates that its molecular structure is that of 14b,14c-dihydro-9b-hydroxy-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione.

The mass spectrum of Va displays its parent peak at m/e 428. Thus, the simple hydrolysis product (VI) or its tautomer (VII) are ruled out. Each would have parent peaks in their mass spectra at m/e 412. Isotopic analysis is in agreement with the molecular formula $C_{30}H_{20}O_3$, as is the elemental analysis.



VII

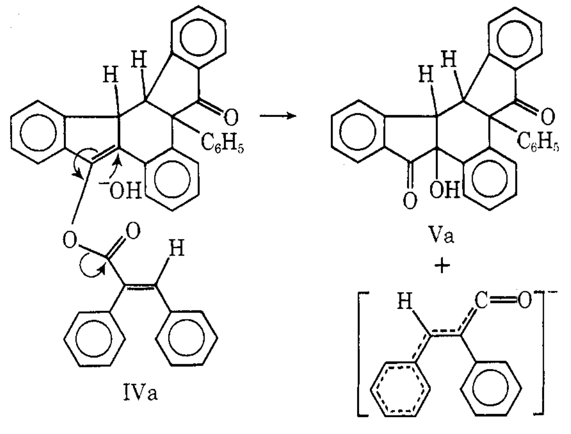
The infrared spectrum of Va possesses a strong absorption at 3450 cm^{-1}, indicative of the presence of a hydroxyl group. A very strong band appears at 1710 cm^{-1}, in agreement with the presence of indanone carbonyl groups.

The pmr spectrum of Va is very similar to that of the "white intermediate" (IVa). Va displays a pair of coupled doublets, one centered at δ4.25 and the other at δ4.55 (J = 6 Hz). These doublets compare favorably with those of the pmr spectrum of IVa, δ4.20 and δ4.45 (J = 5 Hz)). The presence of two adjacent methine protons on carbons 14b and 14c is thus indicated. A complex multiplet appears centered at δ6.55. Integration indicates it to be the result of resonance of two protons. One of the protons whose resonance might contribute to this multiplet could be the hydroxyl proton. No signal which can be easily assigned to this resonance otherwise appears in the spectrum. Presence of a hydroxyl group is firmly established *via* the infrared spectrum of Va. The other proton whose resonance is responsible for the balance of the multiplet could be the same shielded aromatic proton (that of C_1) of the precursor (IVa). Resonance of this proton resulted in a multiplet centered at δ6.35 in the pmr spectrum of IVa.

Construction of framework molecular models of Va reveals that introduction of a hydroxyl group at C_{9b} such that the fusion of rings B and C is cis would not substantially alter the position of the proton of C_1 with respect to aromatic ring A. Introduction of the hydroxyl group such that rings B and C were trans fused is unlikely on steric grounds. The pair of enantiomers resulting from such an introduction are characterized by the substituents of carbons 5a, 14c, 14b, and 9b being all cis to one another. As is the case with IVa, no other pair of enantiomers possesses a proton in a positive pmr shielding zone. The remainder of the peaks of the pmr spectrum of Va appear as an intense complex multiplet centered at δ7.50; integration is reasonable for the remaining aromatic protons.

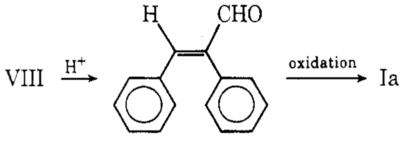
Structure Va is in agreement with the fact that Va can be converted to IIIa *via* prolonged reflux in 5% sodium hydroxide.

Structure Va could easily result from IVa *via* hydroxide ion attack at C_{9b}, cis to the proton at C_{14b}, with expulsion of ion VIII. Protonation of VIII followed by oxidation of the resultant α-phenyl-*trans*-cinnamaldehyde (IX) could yield the observed acid (Ia).


IVa

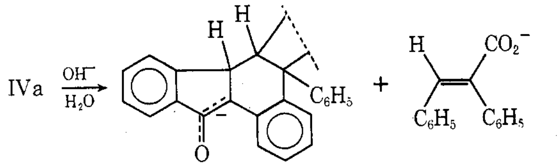
Va

VIII

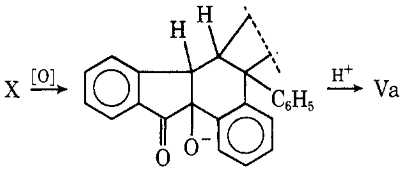


IX

Alternately, simple hydrolysis of the ester linkage of IVa would lead to the enolate anion X, plus the α-phenyl-*trans*-cinnamate ion. The enolate anion could then undergo autooxidation to XI, followed by protonation to yield the observed structure (Va). In view of the high yield of Ia (80%), the second process seems more likely. Oxidation of IX in basic media could occur *via* a Cannizzaro reaction. This type of reaction, however, would produce at maximum 50% of the carboxylic acid. Further, α,β-unsaturated aldehydes normally do not react *via* the Cannizzaro reaction.[6] In any case, structure Va is consistent with the analytical, spectral, and chemical data.



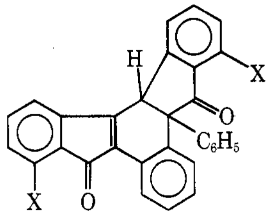
X

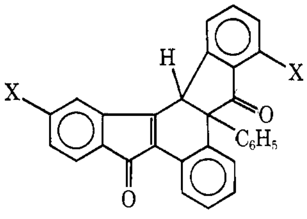


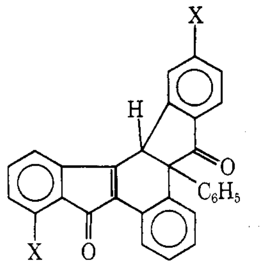
XI

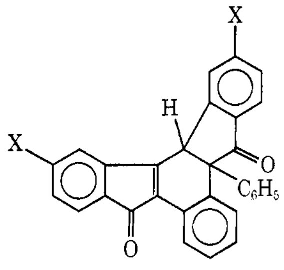
In order to test the generality of the preparative reaction, a series of para-substituted derivatives of α-phenylcinnamic acid (Scheme I; Ib–h) were prepared and subjected to the reaction conditions. Analogs of both phenylcinnamalone (IIIa) and the "white intermediate" (IVa) were prepared using thionyl chloride–sulfuryl chloride and phosphorus trichloride–sulfuryl chloride, respectively, as reagents.

The choice of Ib–h as starting materials was made for several reasons. First, it is possible that the five membered rings of either compound type (III or IV) are most probably formed as the result of condensation between an acid chloride (II) and one of the two ortho positions of the phenyl group β to the acid chloride function. If this is indeed the case, then only one analog of each compound type (III and IV) is possible when the β-phenyl group of the starting material is para substituted. With meta substitution of the β-phenyl group, any or all of four possible analogs could be formed. Examples of these are XII–XV.

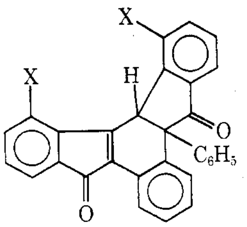

XII


XIII


XIV


XV

As with para substitution, ortho substitution of the β-phenyl group can lead to only one analog each of III and IV. The analog corresponding to III would be XVI. However, this substitution leaves only one ortho position of the β-phenyl group available for the five-membered ring forming reaction. Thus, the para-substituted acids were considered to be most suitable for initial attempts at analog formation.


XVI

Ib–g were readily prepared *via* Perkin condensation, employing triethylamine as the basic catalyst.[7a–d] Six acids (Ib–g) were prepared by this method from the corresponding para-substituted benzaldehydes and phenylacetic acid. All are known compounds.

From Ie, Ih was prepared by reduction with ammonium sulfide.[7e]

Pyrolysis of the various acids (Ib–h) yielded only three analogs, 3,12-dichlorophenylcinnamalone (IIIb), 3,12-dimethylphenylcinnamalone (IIIc), and 3,12-dimethoxyphenylcinnamalone (IIId). The yields (40–70%) compared favorably with the yield of the parent compound (IIIa). Attempts to prepare IIIe resulted in violent decomposition of the reaction mixture, and the reactions involving If and Ih yielded rubber-like polymers of unknown composition. Ig did not react appreciably as evidenced by recovery of most of the starting material.

In attempts to prepare analogs of IVa, only two analogs were obtained. IVb and IVc were prepared in yields of 40 and 35%, respectively. Again, reaction of Ie resulted in violent decomposition. The other acids were not reactive under the conditions employed which were identical with those for the preparation of IVa.

The structure of each of the analogs prepared was verified by spectral and analytical data. Elemental analysis of each analog (IIIb–d, IVb, and IVc) was consistent with the proposed structure.

Each of the analogs of IIIa displays a singlet in its pmr spectrum which may be reasonably attributed to resonance due to the lone methine proton of structures IIIb–d. The exact positions are as follows: $\delta 5.20$ for IIIb, $\delta 5.10$ for IIIc, and $\delta 5.00$ for IIId. The positions of these singlets compare well with the singlet due to resonance of the lone methine proton of IIIa ($\delta 4.68$). The pmr spectrum of IIIc displays a lone singlet at $\delta 2.65$ with six times the intensity of the singlet at $\delta 5.10$. This singlet may be reasonably assigned to the combined resonance of the six protons of the two methyl groups. The chemical shift of the singlet is representative of those due to resonance of protons of aromatic methyl groups.[5] The pmr spectrum of IIId displays a pair of closely spaced singlets of $\delta 4.25$ and 4.27. The combined intensity of these two peaks is six times that of the singlet of this spectrum at $\delta 5.00$. The chemical shifts of these singlets are consistent with those of singlets due to the resonance of the protons of known aromatic methoxy groups.[5] The remaining signals of each spectrum are consistent as being due to resonance of aromatic protons. However, the complex splitting patterns of these multiplets do not allow confirmation of the predicted positions of the substituent groups of the analogs.

The infrared spectrum of each of the analogs of IIIa (IIIb–d) strongly resembles that of IIIa. These spectra are consistent with the proposed structures.

Both analogs of IVa (IVb and IVc) display pmr spectra consistent with the proposed structures. Both spectra display a pair of coupled doublets analogous to the coupled doublets of the spectrum of IVa. These doublets are consistent as being the result of resonance of the two adjacent methine protons of both analogs. The spectrum of IVb displays these centered at $\delta 4.35$ and $\delta 4.55$ ($J = 5.5$ Hz). The spectrum of IVc displays the coupled doublets centered at $\delta 4.20$ and 4.65 ($J = 6$ Hz). The analogous doublets of the spectrum of IVa appear centered at $\delta 4.20$ and 4.45 ($J = 5$ Hz). Both spectra also display a sharp singlet of analogous chemical shift to the singlet of the spectrum of IVa due to resonance of the vinyl proton of the α-phenyl-*trans*-cinnamoxy group substituted at C_{10}. The spectrum of IVb displays this singlet at $\delta 8.45$ and the spectrum of IVc displays the singlet at $\delta 8.60$. The spectrum of the parent compound (IVa) displays the singlet at $\delta 8.28$. Where there appears a complex multiplet ($\delta 6.35$) in the pmr spectrum of IVa, both spectra of the analogs (IVb and IVc) display what appear to be well resolved doublets. The spectrum of IVb displays the doublet centered at $\delta 6.55$ ($J = 9$ Hz). The spectrum of IVc displays the doublet centered at $\delta 6.40$ ($J = 8$ Hz). Assuming that these doublets in the spectra of the analogs result from resonance of the protons analogous to the proton of IVa which is responsible for the multiplet at $\delta 6.35$ of the spectrum of IVa, then this simplification of splitting pattern may be interpreted with regard to a change in substitution. The multiplet of the spectrum of IVa has been assigned to resonance due the aromatic proton of C_1 (see Figure 5). The pmr multiplet due to resonance of this proton may be coupled to the protons at the positions: C_2, C_3, and C_4. Replacement of a proton at any of these positions with a substituent group should simplify the splitting of the signal due to resonance of the proton of C_1. The coupling constants of the doublets of the pmr spectra of the analogs of IVa are indicative of coupling of ortho aromatic protons.[5] Indeed, they are much too large to be the result of coupling of meta aromatic protons ($J = 2$–3 Hz) or para aromatic protons ($J = 1$ Hz). Thus, substitution at the C_2 position may be ruled out since a proton must occupy this position in order to justify the observed coupling constants of the doublets in question. If substitution at the C_4 position is the case, then one might expect the doublets to be further split into a four-peak multiplet with a secondary coupling constant of 2–3 Hz. Or, if substitution at the C_3 position is the case, as in the proposed structures (IVb and IVc), then a four-peak multiplet with a secondary coupling constant of only 1 Hz would be expected. However, since neither of these possibilities is, in fact, observed, then a choice of C_3 or C_4 substitution must be based on a guess. The most likely possibility is easiest to rationalize. One hertz splitting is most likely to be unimportant or masked by low resolution. Therefore, the choice of C_3 substitution is more likely than C_4 substitution. This interpretation of the pmr spectra of the analogs of IVa reinforces the argument presented earlier for the assignment of the proton of C_1 as responsible for the multiplet at $\delta 6.35$ in the spectrum of IVa. IVc shows a multiplet at $\delta 2.00$ which integrates properly for the protons of the substituent methyl groups. The remaining signals of both spectra are intense complex multiplets, which are reasonable as resulting from resonance of aromatic protons.

The infrared spectra of both IVb and IVc display all the principal bands present in IVa.

In summary, our data at this point in the study seem to show that the structures assigned to IIIa–d, IVa–c, and Va are correct. Further, type II compounds are almost certainly intermediates in the formation of IIIa, IVa, and their analogues. Also IVa probably is precursor to IIIa. It is possible that IVa may not lie on the reaction coordinate between IIa and IIIa, and since no kinetic data are available, it is not possible to state with certainly that IVa is a precursor of IIIa. However, it should be noted that when Ia or IIa are subjected to the preparative reaction conditions for IVa in phosphorus trichloride–sulfuryl chloride, no IIIa is formed. Further, IIIa can be prepared from IVa in the thionyl chloride–sulfuryl chloride mixture (IIIa is stable to these reaction conditions while IVa is not), and when IIIa is prepared from Ia or IIa, IVa is a by-product.

The preparative reactions as observed to date seem to work best when the para substituent of the β-phenyl group is electron donating with respect to the aromatic ring. However, successful reactions for the preparation of type

III compounds were not observed when electron-donating substituents possessing potentially reactive hydrogen atoms were employed, nor did the reaction yield the desired product when the highly electronegative nitro group was the substituent. These same observations were made with respect to the preparation type IV compounds, and in addition it was not possible to obtain a successful reaction when the substituent was a methoxy group. It should be pointed out that these generalizations regarding substituent effects may not really be definitive because only seven substituents other than hydrogen have been utilized to date.

The detailed nature of the reaction mechanism is at present unknown to us. However, the process does involve the copious condensation of hydrogen chloride. Wawzonek, Hansen, and Zigman[8] have reported the preparation of phenylcinnamalone (IIIa) and an isomer thereof by the Diels–Alder addition of 2-phenylindenone (generated *in situ*) to itself followed by dehydrogenation of an intermediate somewhat similar in nature to Va. Earlier, it had occurred to us that perhaps 2-phenylindenone was a precursor of IIIa, but we have been unable to isolate 2-phenylindenone from the reaction mixture, and we were unable to prepare either 2-phenylindenone or IIIa from intramolecular condensation of IIa utilizing typical Friedal-Crafts catalysts such as aluminum chloride. Thus, at this time, we do not feel that 2-phenylindenone is an intermediate in the reactions described herein.

Experimental Section

All infrared spectra were recorded in potassium bromide wafers using a Perkin-Elmer 237 spectrophotometer. Pmr spectra (Varian A-60A spectrometer) were recorded at 37° unless otherwise noted. Melting points were taken on a Reichert polarizing hot stage. Elemental analyses were done by Gailbraith Laboratories, Knoxville, Tenn. Mass spectra were taken by Morgan and Shaeffer, Montreal, Canada.

α-Phenyl-*trans*-cinnamic acid (Ia) (mp 172–173°) was purchased from the Aldrich Chemical Co. and was recrystallized twice from water or ethanol–water before use. Thionyl chloride, sulfuryl chloride, and phosphorus trichloride were purchased from Eastman Organic Chemicals, were of practical grade, and were used as received. Phenylcinnanalone (IIIa) was prepared as reported previously.[4]

Preparation of α-Phenyl Para-Substituted Cinnamic Acids (Ib–g). The acids were prepared using the general directions of Ketcham and Jambotkar.[7c] All pmr spectra were taken in DMSO-d_6 at 37° unless otherwise indicated. **α-Phenyl-*trans*-*p*-chlorocinnamic acid (Ib),** after five recrystallizations from acetic acid–water, had mp 210–211° (lit.[7c] 202–203°): pmr δ[9a] 7.50 (m, 9), 8.00 (s, 1). **α-Phenyl-*trans*-*p*-methylcinnamic acid (Ic),** after four recrystallizations from acetic acid–water, had mp 179–181° (lit.[7c] 177–178°): pmr δ 2.22 (s, 3), 7.70 (m, 9), 8.40 (s, 1), 12.40 (broad, 1). **α-Phenyl-*trans*-*p*-methoxycinnamic acid** (Id), after three recrystallizations from glacial acetic acid had mp 191–193° (lit.[7c] 189–190°): pmr δ 3.55 (s, 3), 7.20 (m, 9), 7.95 (s, 1), 11.50 (broad, 1). **α-Phenyl-*trans*-*p*-nitrocinnamic acid** (Ie), after recrystallization from glacial acetic acid, had mp 206–209° (lit.[7c] 208–210°): pmr δ 7.50 (m, 9), 8.20 (s, 1), 11.75 (s, 1). **α-Phenyl-*cis*-*p*-nitrocinnamic acid,** recrystallized from toluene, had mp 140–142° (lit.[7c] 141–143°): pmr δ 7.10 (s, 1), 8.00 (m, 9), 12.70 (broad, 1). **α-Phenyl-*trans*-*p*-acetamidocinnamic acid** (Ig), recrystallized from water–ethanol, had mp 251–253° (lit.[7c] 250–252°): pmr δ 2.13 (s, 3), 7.60 (m, 9), 8.20 (s, 1), 10.55 (s, 1). **α-Phenyl-*trans*-*p*-hydroxycinnamic acid** (If), after recrystallization from acetic acid, melted with decomposition at 223° (lit.[7c] 220–222 dec).

Using the method of Hey and Orbond[7e] **α-Phenyl-*trans*-*p*-aminocinnamic acid** (Ih) was obtained. The pure amino acid was recrystallized from toluene and had mp 211–213° (lit.[7e] 210–211°): pmr δ 4.50 (s, 2), 6.25 (d, 2), 6.70 (d, 2), 7.20 (m, 5), 7.70 (s, 1) (acetone-d_6) in DMSO-d_6 8.10 (s, 1). The cis isomer was prepared by the same method. The mp of yellow needles recrystallized from toluene was 165–166° (lit.[7e] 160–162°): pmr δ 6.75 (d, 2), 6.95 (s, 1), 7.40 (m, 10–11) (DMSO-d_6, 120°).

Preparation of 3,12-Dichloro-14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (3,12-Dichlorophenylcinnamalone, IIIb). Five grams (0.019 mol) of Ib was dissolved in 48 ml of thionyl chloride with 2 ml of sulfuryl chloride added. This mixture was refluxed for 30 min, after which time the excess thionyl chloride was removed by distillation. The resultant mixture was then heated slowly until vigorous reaction took place (140–160°). The temperature rapidly rose to 200°. This temperature was maintained for 5 min, resulting in a dark red oil, which solidified upon cooling. The red glass was recrystallized (glacial acetic acid) to yield 40% of bright red crystals, mp 265°. *Anal.* Calcd for $C_{30}H_{16}O_2Cl_2$: C, 75.17; H, 3.35; Cl, 14.82. Found: C, 75.26; H, 3.13; Cl, 14.70. Infrared:[9b] 3050 w, 1710 s, 1595 w, 1575 w, 1490 w, 1470 m, 1435 w, 1415 m, 1360 w, 1295 w, 1245 w, 1220 w, 1205 w, 1170 m, 1125 w, 1110 w, 1050 vw, 905 w, 830 w, 820 w, 800 m, 780 w, 770 m, 765 w, 740 m, 725 w, 700 m, 655 cm^{-1} w. Pmr: δ 5.20 (s, 1), 7.90 (m, 15) (DMSO-d_6).

Preparation of 3,12-Dimethyl-14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (3,12-Dimethylphenylcinnamalone, IIIc). Five grams (0.021 mol) of Ic was dissolved in the thionyl chloride–sulfuryl chloride reagent, and the pyrolysis reaction and purification were carried out as described above. The yield of bright red prisms, mp 279–282°, was 48%. *Anal.* Calcd for $C_{32}H_{22}O_2$: C, 87.64; H, 5.06. Found: C, 87.34; H, 5.18. Infrared: 3050 w, 2925 w, 1710 s, 1600 w, 1580 w, 1525 vw, 1490 m, 1440 m, 1375 vw, 1290 m, 1265 vw, 1240 vw, 1220 vw, 1160 m, 1125 w, 1110 w, 1055 w, 955 vw, 940 vw, 830 w, 800 m, 775 w, 765 m, 760 w, 730 w, 705 m, 650 cm^{-1} w. Pmr: δ 2.65 (s, 6), 5.10 (s, 1), 7.80 (m, 12), 8.40 (m, 2), 9.10 (m, 1) ($CDCl_3$).

Preparation of 3,12-Dimethoxy-14c-hydro-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (3,12-Dimethoxyphenylcinnamalone, IIId). By the procedure described above, 5 g (0.020 mol) of α-phenyl-*trans*-*p*-methoxycinnamic acid was converted to IIId. One recrystallization from glacial acetic acid yielded 50% of dark purple crystals, mp 291–293°. *Anal.* Calcd for $C_{32}H_{22}O_4$: C, 76.95; H, 4.94. Found: C, 77.06, H, 5.12. Infrared: 3000 (broad) w, 1700 s, 1600 w, 1480 m, 1460 w, 1445 w, 1425 m, 1375 vw, 1330 w, 1280 m, 1245 m, 1225 w, 1200 vw, 1180 vw, 1170 vw, 1130 w, 1055 w, 1025 m, 860 w, 830 w, 800 m, 770 m, 750 m, 740 w, 725 w, 710 m, 705 m, 650 cm^{-1} w. Pmr: δ 4.25 (s, 3), 4.27 (s, 3), 5.00 (s, 1), 7.80 (m, 13), 8.50 (m, 1), 9.20 (m, 1) ($CDCl_3$).

Preparation of the "White Intermediate" (14b,14c-Dihydro-5a-phenyl-10-(α-phenyl-*trans*-cinnamoxy)benz[*a*]indeno[2,1-*c*]fluoren-5-one) (IVa). The same procedure that was used in the preparation of IIIa–d was employed except that phosphorous trichloride was used in place of thionyl chloride. The exothermic reaction started at about 120°. Five grams (0.022 mol) of Ia yielded 60% of off-white crystals, mp 249–251° (glacial acetic acid). To obtain a sample of high purity for the purpose of obtaining spectral data IVa was recrystallized from methanol in a Soxhlet extractor. Fine white crystals, mp 253–254°, separated from the methanol solution. *Anal.* Calcd for $C_{45}H_{30}O_3$: C, 87.36; H, 4.88. Found: C, 87.10; H, 5.12. Infrared: 3050 w, 1730 s, 1715 s, 1620 w, 1600 w, 1495 w, 1445 w, 1360 w, 1320 w, 1280 w, 1220 m, 1155 s, 1125 w, 1080 w, 1065 w, 1030 vw, 1005 vw, 955 m, 915 vw, 905 vw, 765 m, 755 m, 720 m, 715 m, 705 m, 695 m, 660 w. Pmr: δ 4.20 (d, 1), 4.45 (d, 1), 6.35 (m, 1), 7.60 (m, 26), 8.28 (s, 1) (CS_2). Mass spectrum: (*m/e*) 618 (P), 600, 572, 484, 411, 410, 396, 395, 379, 378, 365, 363, 352, 350, 333, 319, 318, 317, 291, 289, 224, 223, 222, 207, 179.

When the mother liquor from the crystallization of IIIa[4] was drowned in water, crude IVa was obtained which was purified as described immediately above. IVa obtained in this fashion gave no depression of the melting point upon admixture with IVa prepared in phosphorous trichloride. Also, the infrared spectra of both samples were identical.

Preparation of 3,12-Dichloro-14b,14c-dihydro-5a-phenyl-10-(α-phenyl-*trans*-*p*-chlorocinnamoxy)benz[*a*]indeno[2,1-*c*]fluoren-5-one (IVb). IVb was prepared in the same manner as IVa using 5 g (0.019 mol) of Ib. Final purification was effected by extraction with methanol as above. Colorless crystals (40%), mp 277–278°, were obtained. *Anal.* Calcd for $C_{45}H_{27}O_3Cl_3$: C, 74.85; H, 3.76; Cl, 14.73. Found: C, 74.57; H, 3.54; Cl, 14.55. Infrared: 3050 w, 1725 s, 1710 s, 1620 m, 1600 m, 1490 m, 1470 m, 1420 w, 1380 vw, 1360 vw, 1300 w, 1280 w, 1260 w, 1225 m, 1210 m, 1145 s, 1110 w, 1095 m, 1080 w, 1055 vw, 1030 vw, 1020 m, 1005 w, 980 vw, 960 vw, 945 vw, 925 vw, 875 vw, 855 m, 845 m, 790 m, 765 m, 760 m, 745 w, 730 w, 720 w, 705 m, 680 w, 660 cm^{-1} w. Pmr: δ 4.35 (d, 1), 4.55 (d, 1), 6.55 (d, 1), 7.7 (m, 23), 8.45 (s, 1) ($CDCl_3$).

Preparation of 3,12-Dimethyl-14b,14c-dihydro-5a-phenyl-10-(α-phenyl-*trans*-*p*-methylcinnamoxy)benz[a]indeno[2,1-*c*]fluoren-5-one (IVc). IVc was prepared and purified as was IVa.

White crystals (35%), mp 298–300°, were obtained. *Anal.* Calcd for $C_{48}H_{36}O_3$: C, 84.91; H, 5.65. Found: C, 85.03; H, 5.58. Infrared: 3060 w, 3025 w, 2915 w, 2860 w, 1725 s, 1705 s, 1615 m, 1605 m, 1490 w, 1440 w, 1380 vw, 1360 vw, 1315 w, 1280 w, 1230 m, 1205 m, 1180 w, 1175 w, 1140 s, 1075 vw, 1060 w, 1030 vw, 1005 vw, 980 vw, 960 vw, 930 w, 870 vw, 860 w, 820 m, 805 m, 770 w, 760 m, 755 m, 745 m, 700 m, 655 cm^{-1} w. Pmr: δ 2.00 (m, 9), 4.20 (d, 1), 4.65 (d, 1), 6.40 (d, 1), 7.4 (m, 23), 8.60 (s, 1) (DMSO-d_6).

Alkaline Hydrolysis of the "White Intermediate" IVa. Preparation of 14b,14c-Dihydro-9b-hydroxy-5a-phenylbenz[*a*]indeno[2,1-*c*]fluorene-5,10-dione (Va). One gram (0.0016 mol) of IVa was dissolved in 40 ml of 1,4-dioxane by warming. To this solution was added a mixture of 3 g of potassium hydroxide dissolved in 20 ml of 95% ethanol. After 3 hr of reflux, the resultant solution was poured into 300 ml of water. Extraction of the aqueous solution with ether yielded upon evaporation of the ether 0.35 g (50%) of a pale-yellow solid (Va). Recrystallization from glacial acetic acid gave a white solid, mp 271–273°. *Anal.* Calcd for $C_{30}H_{20}O_3 \cdot H_2O$: C, 82, 83; H, 4.93. Found: C, 82.54; H, 4.63. Infrared: 3460 s, 3080 w, 3060 w, 3010 w, 2930 w, 1710 s, 1605 m, 1580 w, 1490 m, 1470 m, 1445 m, 1325 m, 1315 m, 1295 m, 1290 m, 1280 m, 1260 w, 1235 w, 1195 w, 1140 s, 1090 w, 1080 vw, 1065 vw, 1040 m, 1035 w, 1005 s, 960 w, 935 w, 905 w, 900 vw, 885 w, 870 m, 850 vw, 830 vw, 780 s, 770 s, 755 m, 740 s, 715 s, 710 s, 690 s, 650 cm^{-1} s. Pmr: δ 4.25 (d, 1), 4.55 (d, 1), 6.55 (m, 2), 7.5 (m, 16) (DMSO-d_6, 150°). Mass spectrum: (m/e) 428 (P), 427, 426, 410, 400, 382, 381, 353, 352, 283, 282, 266, 265, 254, 253, 222, 206, 77, 76. Isotopic analysis:[9c] Calcd for $C_{30}H_{20}O_3$: P, 100; (P + 1), 32.7; (P + 2) 5.7. Found: P, 100; (P + 1), 32.9; (P + 2), 5.8.

The aqueous solution, following ether extraction, was acidified with concentrated HCl to yield a pale yellow solid. Recrystallization from glacial acetic acid gave a white crystalline solid (0.25 g, 75%), mp 169–171°, which did not depress the melting point of authentic Ia and had an infrared spectrum identical with Ia.

Conversion of Va to Phenylcinnamalone (IIIa). Va (200 mg, 0.00046 mol) was dissolved in 10 ml of 1,4-dioxane. To this solution at reflux was added 20 ml of 5% sodium hydroxide. After reflux for 48 hr the solution was blue. Acidification of the solution changed the color from blue to orange, and an orange solid separated. Recrystallization (glacial acetic acid) gave an orange solid (30 mg, 16%), mp 255–256°. Upon mixture of this solid with IIIa no depression of the melting point was observed. The infrared spectra of the orange product and of IIIa were identical.

Preparation of Phenylcinnamalone (IIIa) from IVa. Two grams (0.0032 mol) of IVa was subjected to the same conditions employed to prepare IIIa.[4] The yield of IIIa obtained was 1.00 g (76%). The product was identified as IIIa by mixture melting point determination and comparison of infrared spectra.

Preparation of Phenylcinnamalone (IIIa) from α-Phenyl-*trans*-cinnamoyl Chloride (IIa). IIa was prepared by reported methods[10] and by refluxing Ia with the thionyl chloride–sulfuryl chloride or phosphorus trichloride–sulfuryl chloride mixtures for 30 min exactly as in the preparations described for IIIa and IVa. However, the reactions were stopped prior to the pyrolysis step and the products (IIa) were crystallized and recrystallized from hexane or petroleum ether to give yields of IIa (mp 39–40°, lit.[10b] 39–41°) ranging from 65 to 85%. Upon mixing IIa prepared by reported techniques[10] with IIa prepared using the prepyrolysis procedures, no depression of the melting point was observed.

When equivalent molar quantities of IIa were substituted for Ia in the preparation of IIIa[4] or IVa, the products were formed in comparable yields.

Registry No.—Ia, 91-48-5; Ib, 19319-36-9; Ic, 20432-19-3; Id, 13938-24-4; Ie, 19319-30-3; Ie cis analog, 19319-33-6; Ig, 52873-62-8; Ih, 52873-63-9; Ih, cis analog, 52873-64-0; IIa, 51388-67-1; IIIa, 18585-55-2; IIIb, 52873-65-1; IIIc, 52873-66-2; IIId, 52873-67-3; IVa, 52873-68-4; IVb, 52921-07-0; IVc, 52873-69-5; Va, 52873-70-8.

References and Notes

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(2) (a) Brookhaven National Laboratory; (b) Clarkson College of Technology; (c) Carnegie-Mellon University.

(3) Taken in part from the dissertations submitted by Drs. Brown, Donaruma, Kropf, and Stansfield in partial fulfillment of the requirements for the Ph.D. degree.

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Pyrolytic and Photochemical Fragmentation of 1,1-Dimethyl-2-phenyl-1-silacyclobutane

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An efficient synthesis of 1,1-dimethyl-2-phenyl-1-silacyclobutane (I) is reported. Gas-phase pyrolysis of I at 500° yields *cis*- and *trans*-1,1,3,3-tetramethyl-2,4-diphenyl-1,3-disilacyclobutane. The mass spectrum of I is discussed. Photolysis of I in methanol yields 3-phenylpropyldimethylmethoxysilane.

There has been considerable recent interest in reactive intermediates that may possess a formal carbon–silicon double bond.[1-11] These intermediates were first generated by pyrolysis of various silacyclobutanes.[1] More recently photolysis of 1,1-diphenyl-1-silacyclobutane[8] or pentaphenylmethyldisilane[5] has been shown to lead to reactive intermediates possessing a formal carbon–silicon double bond.

The nature of the carbon–silicon double bond is of considerable interest. Substituent effects have often been used to explore the nature of reactive intermediates. The effect of various groups bonded to the silyl center on the ease of pyrolysis of silacyclobutanes to an alkene and a reactive intermediate possessing a carbon–silicon double bond has been reported.[1] Thus, for example, 1,1-dichloro-1-silacyclobutane was stable until 750° whereas 1,1-dimethyl-1-silacyclobutane decomposed at 550° under conditions that were otherwise comparable.[1-3] The products in both cases were ethylene and the 1,3-disilacyclobutane formed by head-to-tail dimerization of the reactive carbon–silicon