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Solution and Solid-State Photodimerization of Some Styrylthiophenes

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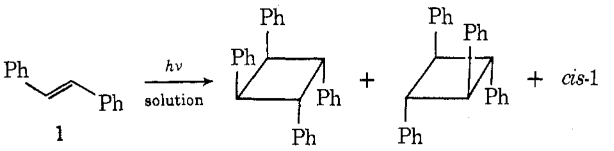
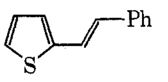
The Pyrex-filtered uv irradiation of *trans*-1-phenyl-2-(2-thienyl)ethene (4), *trans*-1-(2,4-dichlorophenyl)-2-(2-thienyl)ethene (7), and *trans*-1-(3,4-dichlorophenyl)-2-(2-thienyl)ethene (8) has been performed in the crystalline state and in benzene solution. The solid-state behavior is crystal lattice controlled: 4 and the two crystal modifications of 8 are light stable; 7 yields the topochemically expected mirror-symmetric dimer 9. Contrary to a previous report, 4 undergoes photodimerization in solution and one of the photoproducts has been assigned the centrosymmetric structure 23. The two dichloro derivatives also afforded solution photodimers and there is a striking substituent effect on their solution photobehaviors. The 2,4-dichloro isomer, 7, yields only the two dimers 9 and 11, both of cis,anti,cis stereochemistry. By contrast, the 3,4-dichloro isomer, 8, yields all four cyclobutane isomers possible from the union of trans monomers: two all-trans isomers, 16 and 17, and two cis,anti,cis isomers, 14 and 15. The photodimerization rates in benzene solution of 7, 4, 8, and *trans*-stilbene were in the ratio 1.0:2.1:2.4:15. Attention is drawn to a correlation between the monomer crystal structures and their solution photodimerization.

In the solid state *trans*-stilbene (1) is unreactive when irradiated[1] but in solution it yields the two photodimers, 2 and 3.[2] The absence of reaction in the solid can be ascribed to the lack of short intermolecular C=C double bond contacts in the crystal,[3] since substituted stilbenes whose crystal structures have such short spacings (parallel double bonds separated by 3.7–4.2 Å) do undergo solid-state photodimerization, affording the dimers predicted on the basis of the monomer lattices.[4] Irradiation of substituted stilbenes in solution generally yields mixtures of photodimers, although the stereochemistries of the products have been unambiguously established in only a few cases.[5]



1 2 3

In contrast to the above, it has been reported that irradiation of saturated benzene solutions of the thiophene analogs of 1, namely 4, 5, and 6, does not yield photodimers, although these molecules, like stilbene, photoisomerize to the cis isomers which, in turn, undergo photocyclization to unstable dihydrophenanthrene-like intermediates.[6] In the course of our investigation of the packing characteristics and photobehavior of dichloro-substituted molecules[7] we prepared 1-(2,4-dichlorophenyl)-2-thienyl-*trans*-ethene (7) and 1-(3,4-dichlorophenyl)-2-thienyl-*trans*-ethene (8). The solid-state photobehavior of 7 and 8, reported herein, conformed to topochemical expectations and we therefore investigated their solution photobehavior, as well as that of the previously investigated unsubstituted styrylthiophene, 4.



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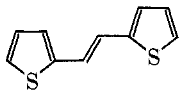

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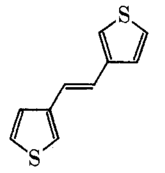

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In addition, this research sought to inquire into the possible correlation of solid-state photobehavior with solution photobehavior. There may well be such correlation in a photodimerization reaction in which the approach of two molecules in solution may be governed by intermolecular forces similar to those operative in the crystal. If preformed aggregates are important in the solution reaction we might also anticipate such a correlation. Evidence supporting a nonbonded *attractive* interaction between halogen atoms in organic molecules[7] made the dichloro derivatives 7 and 8 especially suitable subjects for this study.

Results and Discussion

Solid State. The crystallographic constants of the three stylthiophenes investigated are presented in Table I. The 2,4-dichloro derivative, 7, crystallizes in needles having a 4-Å axis and it was therefore expected to yield, on irradiation, the mirror-symmetric photodimer, 9; indeed, exposure (Westinghouse sun lamps, Pyrex filter) of solid 7 afforded 9 in high yield. The structure of 9 was suggested by spectral data and confirmed by oxidative degradation to the known tetrachloro-β-truxinic acid, **10a**,[8] whose dimethyl ester, **10b**, was identical with an authentic sample.

In addition to 9 the centrosymmetric dimer 11 was formed in small quantities on irradiation of crystalline 7, even at −20°. The presence of this nontopochemical product may be due to "local melting" and disruption of lat-

Table I
Crystallographic Constants of Styrylthiophenes and Their Centrosymmetric Photodimers

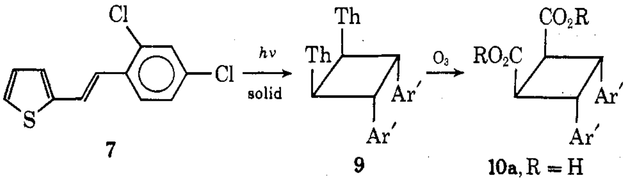
Compd	a, Å	b, Å	c, Å	β, deg	d_{calcd}, g/cm³	Z	Space group
1[a]	15.68	5.70	12.35	112		4	$P2_1/c$
4[b]	31.28	12.27	10.90		1.18	16	
7	10.74	3.98	27.15		1.50	4	$P2_12_12_1$
8 (form 1)	14.3	6.05	26.7		1.45	8	*Pbca*
8 (form 2)	12.86	11.5	7.72	94.5	1.48	4	$P2_1/c$
11	10.44	15.30	15.37	104.5	1.43[c]	4	$P2_1/c$
15	10.55	15.00	16.02	108	1.41	4	$P2_1/c$
23	16.30	6.1	20.45	102.8	1.25[d]	4	*Cc* or *C*2/*c*

[a] Reference 3a. [b] d_m = 1.23. The space group has not been established. The intensity data, according to the Weissenberg and precession photographs, show an orthorhombic symmetry *mmm*. The photographs however, exhibit a set of diffuse reflections. General conditions governing the diffraction data follow: *hkl*, for $k = 2n$, $h = 4n$; for $k = 2n + 1$ all reflections are present except for $4n + 2$; $0kl$, $l = 2n$ except for a small number of diffuse spots; $h0l$, $h = 8n$. These conditions suggest some kind of superstructure. [c] d_m = 1.42. [d] d_m = 1.28.

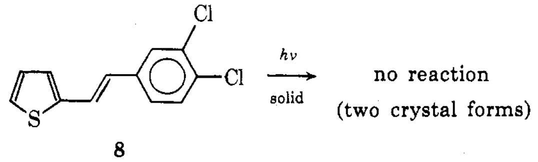
tice control with subsequent formation of the same products as derived from solution (see below). Alternatively, a stacking fault may be present in crystalline **7**, whose geometry allows formation of **11**; the reaction may then promote further propagation of such a dislocation.[4,9]

The 3,4-dichloro derivative, **8**, was found to be dimorphic, neither modification having a 4-Å axis. In the absence of full crystal-structure analyses one cannot make rigorous predictions of photobehavior; however, both forms may be expected either to give a photodimer of other than mirror symmetry or to be light stable; irradiation of both crystal modifications of solid **8** led to little reaction under conditions where **7** is largely converted to **9**. When solid **7** and **8** were irradiated at temperatures at which they gradually melted, the same photoproducts were obtained as described below for the solution experiments.

Exposure of solid **4** induces no detectable dimeric material, and we would therefore expect that there are no short, parallel C═C separations in the crystal of **4**; the cell constants of **4** do not reveal any short lattice-repeat distance.



7 **9** **10a**, R = H
b, R = CH₃



8

$\mathbf{4} \overset{h\nu}{\underset{\text{solid}}{\nrightarrow}}$ no reaction

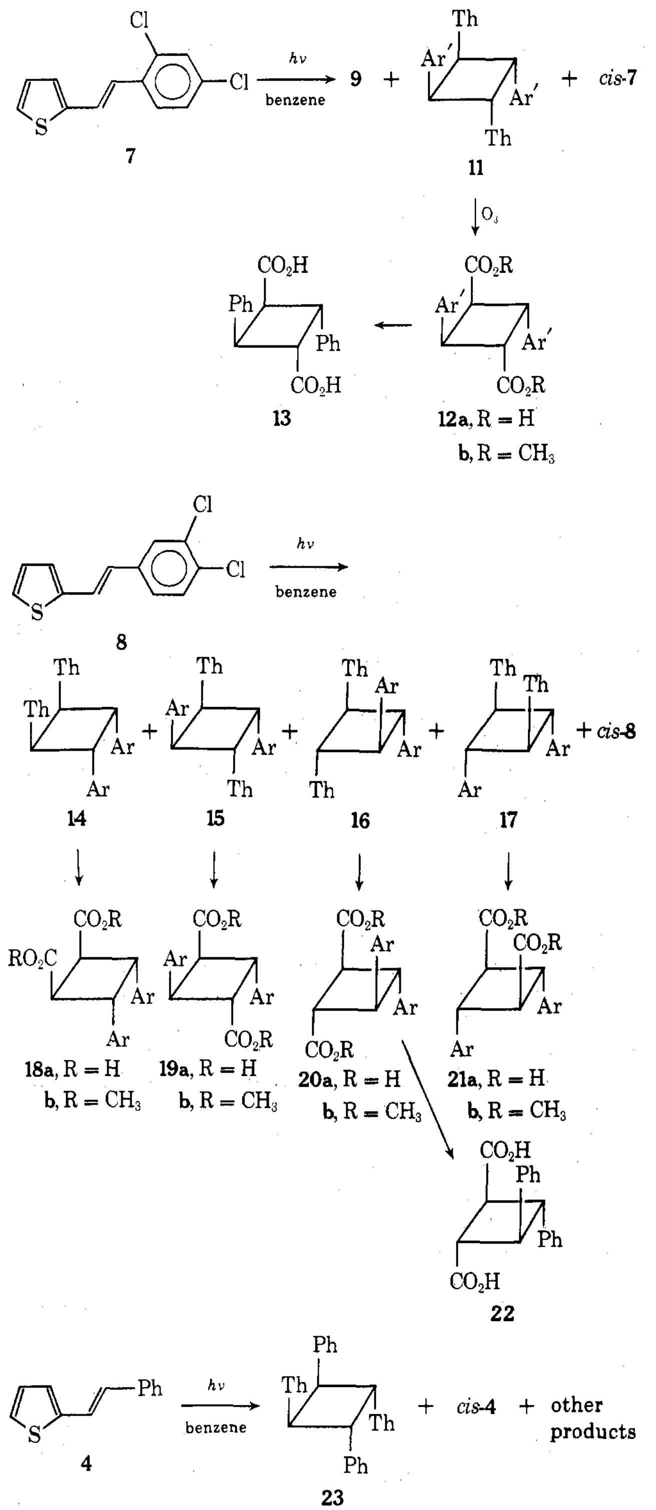
Solution. Irradiation of 2-styrylthiophene (**4**) in benzene solution through Pyrex led to photodimer formation. The nmr spectrum of the irradiated mixture contained a multiplet, δ 4.05–4.7, and a singlet, δ 3.72, in the cyclobutane region. One of the compounds responsible for the multiplet was isolated by column chromatography as a crystalline photodimer and, in view of the absence of a significant dithienyl ethene peak in the mass spectrum and because it matched, on tlc analysis, a sample obtained by the hydrogenative dechlorination of **11**, this dimer was assigned the structure **23**. The singlet at δ 3.72 is, by comparison with the cyclobutane signals in the spectra of the stilbene cis,anti,cis dimer **2** (δ 4.40) and the all-trans dimer **3** (δ 3.63), indicative of an isomer of all-trans configuration.

Since the styryl thiophene **4** does afford photodimers, its photobehavior is at least qualitatively analogous to that of trans-stilbene (**1**). The photodimerization of **4** is, however, considerably less efficient than that of the phenyl compound **1**. This rate difference, and the difference of the rates of the solution photodimerizations of the dichloro compounds **7** and **8**, cannot be discussed until a variety of additional information is available. Even the multiplicity(ies) of the excited state(s) responsible for dimerizations remains to be established for the thiophene compounds discussed herein; *trans*-stilbene has been shown to photodimerize *via* its lowest singlet state.[1a]

Irradiation through Pyrex of **7** in benzene solution led to the formation of the same mirror dimer **9** obtained in the solid and a second dimer, having the centrosymmetric configuration **11** on the basis of its nmr spectrum; the same cis,anti,cis geometry as in **9** is indicated, since the midpoints of the symmetrical cyclobutane AA′BB′ multiplets in both compounds fall at almost the same point in the spectrum,[4a,10] and the aromatic signals in both are shifted upfield owing to mutual shielding of the cis 1,2-diaryl groups, a feature that would be lacking in a dimer of all-trans configuration.

The structure of **11** was confirmed by ozonolysis of the dimer to give the tetrachloro-α-truxillic acid **12a**, which was hydrogenatively dechlorinated to give α-truxillic acid (**13**), identical (melting point, ir) with an authentic sample.

However, the irradiation of the isomeric 3,4-dichloro derivative, **8**, under identical conditions to those used for **7** resulted in the formation of *four* dimeric photoproducts whose nmr spectra all displayed symmetrical cyclobutane signals; these products are assigned structures **14**, **15**, **16**, and **17**. The formation in comparable yield of all four possible cyclobutane-type photodimers that can result without isomerization from 1,2-disubstituted trans ethenes is uncommon.[4a,5,11] The four nmr spectra fall into two groups, those of **14** and **15** having their symmetrical cyclobutane AA′BB′ multiplets centered at δ 4.41, while those of **16** and **17** have multiplets centered at δ 3.60–3.63; the spectra of the former show similar characteristics to the pair **9** and **11**. The assignment of head-to-head and head-to-tail constitution is provided by the mass spectra of the four, all of which show molecular ions, *m/e* 508, and, as base peaks, half molecular ions, *m/e* 254, all containing the characteristic isotope pattern expected for a species containing four chlorine or two chlorine atoms, respectively. The head-to-head configuration of **14** and **16** is appar-



Th = 2-C_4H_3S; Ar′ = 2,4-$C_6H_3Cl_2$; Ar = 3,4-$C_6H_3Cl_2$

ent from the peaks in their mass spectra due to cleavage perpendicular to the direction of monomerization, *m/e* 316 ($C_6H_3Cl_2CH{=}CHC_6H_3Cl_2$) and 192 ($C_4H_3SCH{=}CHC_4H_3S$); these signals are absent in the mass spectra of **15** and **17**.

An interesting stereochemical point with regard to the direction of ring splitting of the cyclobutane is revealed by comparison of the fragmentation patterns of the two head-to-head dimers **14** and **16**. In the dimer of all-trans configuration, **16**, the intensity ratio of the dithienylethene to the half-molecular ion is 0.32, whereas in the cis,anti,cis dimer **14**, this ratio is only 0.04. This can be explained both by the greater aryl-aryl repulsion in **14** relative to **16** as well as by the greater stability of the expected trans species from **16** compared to the cis species from **14**.

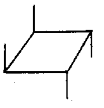
The structure assignments were corroborated by degradation of all four dimers of **8**. Ozonolysis of **14** led to the known tetrachloro-β-truxinic acid **18a**[8] while ozonolysis of **15** led to the tetrachloro-α-truxillic acid **19a** whose dimethyl ester **19b** showed a single $-OCH_3$ signal at δ 3.42 characteristic of methyl esters of α-truxillic acid derivatives.[12] The ozonolysis of **16** and **17** afforded two new diacids, **20a** and **21a**, respectively, whose dimethyl esters, **20b** and **21b**, displayed OCH_3 signals at δ 3.77 and 3.75, respectively. Confirmation of the stereochemical assignment of **16** was obtained by hydrogenative dechlorination of **20a** to give δ-truxillic acid **22**.[11b]

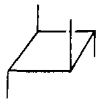
The crystallographic constants of the centrosymmetric dimers were measured in the hope that crystallographic and molecular centers of symmetry would coincide, as is often observed,[2a,13] and would therefore prove or confirm structure assignments. However, the results, presented in Table I, do not allow any structural conclusions to be drawn.

In order to obtain a quantitative estimate of the relative dimerizing efficiencies of these materials as well as a comparison to the hydrocarbon analog, *trans*-stilbene (**1**), degassed solutions, 0.3 *M* in benzene, of each were irradiated in a rotating turntable apparatus for varying periods and the total amount of dimer formed was estimated by integration of the cyclobutane proton signals in the nmr spectra using a known quantity of *n*-octadecane as a standard. The initial rates, relative to the slowest reaction, are as follows: **7**:**4**:**8**:**1** = 1.0:2.1:2.4:15.

To summarize the photochemical results, we find that styrylthiophenes do photodimerize in solution and, if the molecular juxtaposition within the crystal lattice is appropriate, in the solid as well. The photoproduct structures have been established, but additional work is called for in order to identify the electronic multiplicity of each dimer precursor and to compare the rates of competing process (*e.g.*, trans → cis isomerization, deactivation) with photodimerization. Although evidence for aggregation has not yet been sought, we anticipate that photodimerization in these materials will be strongly aggregation dependent.[11a] The only evidence of concentration or solvent effects which we can present so far is the change in product ratio when 3,4-dichlorostyrylthiophene is irradiated in the melt and in 0.4 *M* benzene solution (the ratio of cis,anti,cis dimers, **14** and **15**, to all-trans dimers, **16** and **17**, changes from *ca.* 1:1 in the melt to 2.5:1 in solution).

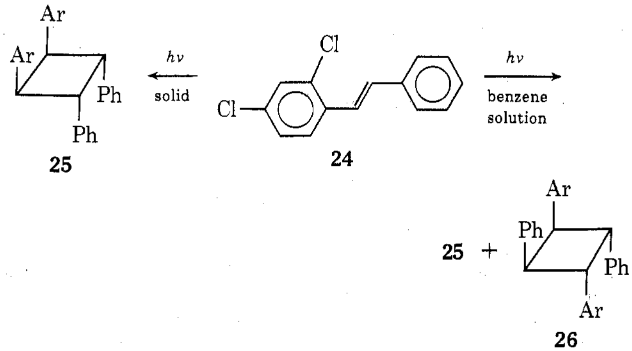
The most striking aspect of this investigation is the dramatic substituent effect on the photobehavior of the 2,4-dichloro- and 3,4-dichloro derivatives of *trans*-styrylthiophene. The 2,4-dichloro isomer **7** yields only *two* dimers, both of the cis,anti,cis geometry (A), while the 3,4-dichloro isomer **8** affords all four of the possible cyclobutane photoproducts resulting from union of two trans olefins, two isomers of all-trans configuration (geometry B) and two of cis,anti,cis configuration (geometry A).

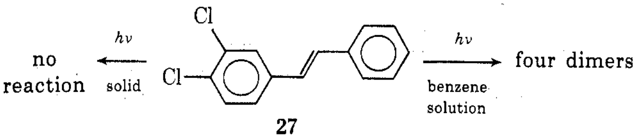

A


B

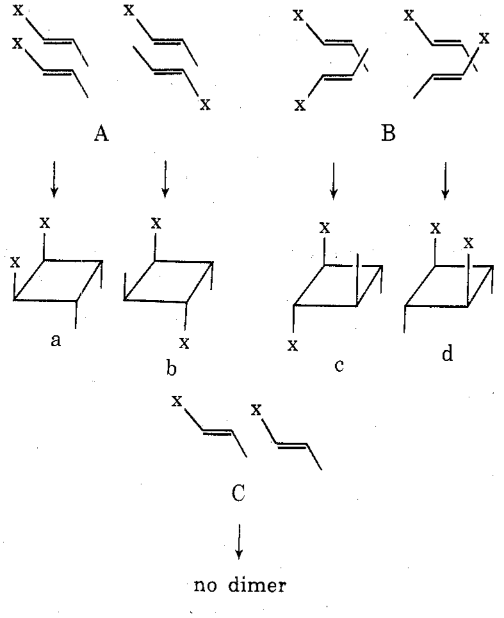
It is interesting to recall that 2,4-dichloro-*trans*-stilbene (**24**) behaves analogously to the corresponding thiophene compound **7** both in its solid-state and in its solution photobehavior. Irradiation of the solid (short 4-Å axis as in **7**) affords the topochemical dimer **25**, while irradiation in solution yields the two cis,anti,cis photodimers **25** and **26**.[4a]

The suggestion that this similarity between the identically substituted thiophene and phenyl compounds is indeed due to the substitution pattern is strongly supported by our preliminary results on the solution and solid-state photobehavior of 3,4-dichloro-*trans*-stilbene (27). This material is exactly analogous in behavior to 3,4-dichlorostyrylthiophene. Solid 27 lacks a 4-Å axis and is light stable, while irradiation of 27 in solution affords *four* photodimers all having symmetrical nmr spectra and assigned structures analogous to 14–17.





At the outset of this paper we suggested that it might be possible in such systems as are here described to find a correlation between the crystal lattice of the monomers and their solution photodimerization. We consider first three kinds of solution precrystal aggregate geometries. (Alternatively, these can be considered as approach geometries of an excited-state species with a ground-state monomer): (i) a highly overlapped molecular juxtaposition A, either parallel or antiparallel; (ii) an arrangement with only close double bond overlap B, also of either head-to-head or head-to-tail; and (iii) arrangements C in which double bond–double bond overlap is not present. Cycloaddition from geometry A affords the two cis,anti,cis cyclobutane isomers a and b while B affords the all-trans dimers c and d. Geometry C cannot lead to dimer formation.



No crystalline arrangements corresponding to B have been found in any of the more than 100 solid trans olefins whose crystallographic properties or solid-state photochemistry have been studied.[14] However, the intermolecular arrangements A are very common, as are the arrangements C. Thus, we can ask whether materials which crystallize with a parallel or antiparallel A structure will differ in their solution photobehavior from those which crystallize in one of the C-type structures. In the admittedly limited number of materials which have been studied thus far, the following correlation emerges: 1,2-diaryl-*trans*-ethenes crystallizing in photoreactive A-type lattices afford two solution photodimers, of structure a and b, while materials crystallizing in the light-stable C-type lattices afford, on irradiation in solution, four photodimers, a, b, c, and d.

This correlation presently rests on the six compounds 1,[15] 4, 7, 8, 24, and 27, and we await further examples before judging its validity and defining the scope of its applicability. A reasonable interpretation is that materials which favor crystal structures with highly overlapped molecules will tend to aggregate in this fashion in solution as well (or, alternatively, will favor molecular approaches, of the A type). Compounds for which good molecular overlap is not a high-priority requirement in their crystal structures, C-type lattices, will in solution show no distinct preference for any particular intermolecular geometry and afford all four possible photodimers.

Experimental Section

Melting points, measured on a Fisher-Johns apparatus, are uncorrected. Ir spectra were determined on a Perkin-Elmer Infracord spectrophotometer in KBr pellets, unless otherwise indicated. The nmr spectra were recorded on a Varian A-60 spectrometer in deuteriochloroform. Chemical shifts are reported in δ units downfield from internal tetramethylsilane (TMS); the multiplicity, number of hydrogens, coupling constants, and proton assignments are given in parentheses. When accurate integration was required the average of four to six readings on a digital integrator attachment was made. The mass spectra were recorded on an Atlas MAT CH4 mass spectrometer at 70 eV. The mass spectral data are presented using the following format: *m/e* (relative abundance), fragment assignment, molecular formula. All chlorine-containing fragments show the expected isotope patterns corresponding to the number of chlorine atoms present.

Solids were irradiated, unless otherwise stated, in Petri dishes with Pyrex covers using Westinghouse sun lamps at a distance of *ca.* 30 cm. Samples were irradiated at 40 or 8°, the latter by placing the irradiation apparatus in a cold room. Solutions were irradiated in benzene (Fluka, for uv spectroscopy) in Pyrex ampoules, after being deaerated by passing a stream of benzene-saturated argon through and then sealing under argon. Thin layer chromatographic (tlc) analyses were performed on silica gel HF_{254} using methylcyclohexane as eluent. Spots were indicated by fluorescence (Mineral-light UVS-12) and/or iodine vapor. Column chromatography was performed using the dry-column method[16] with Merck 0.05–0.20-mm silica gel in a ratio of 20–30 times the weight of the sample. Ozonolyses were performed with a Welsbach ozonator Model T-408. Powder photographs were taken with a "Guinier" Nonius camera using Cu Kα radiation.

Preparation of phosphonates was accomplished (Michaelis-Arbuzov reaction[17]) in 80–90% yield by heating the benzyl chlorides and triethyl phosphite for 16 hr. Diethyl benzylphosphonate had bp 110–118° (0.5 mm); diethyl 3,4-dichlorobenzylphosphonate had bp 142° (0.5 mm); diethyl 2,4-dichlorobenzylphosphonate was used directly without distillation.

Preparation of 1-Aryl-2-thienylethenes. *trans*-1-Phenyl-2-(2-thienyl)ethene (4) was prepared, as were compounds 7 and 8, by the method of Seus and Wilson.[18] The product was purified by sublimation, mp 113–115° (lit.[18] mp 112–113°) (monomorphic from methylcyclohexane, ethyl acetate, or ethanol and by sublimation), ir (Nujol) 975, 965 cm^{-1} (trans HC=CH). ***trans*-1-(2,4-Dichlorophenyl)-2-(2-thienyl)ethene** (7) was prepared from diethyl 2,4-dichlorobenzylphosphonate and 2-thienoaldehyde. The product separated as an oil and was extracted from the aqueous DMF solution with *n*-hexane (2 × 100 ml). The hexane extract was dried (sodium sulfate) and evaporated to give a 45% yield of crude product which was purified by crystallization (75% recovery) from ethanol-methanol to give colorless needles; mp 61.5-62°; ir 948, 958 cm^{-1} (trans HC=CH); uv λ_{max} (MeOH) 330 nm (ϵ 2.5 × 10^4).

Anal. Calcd for $C_{12}H_8Cl_2S$: C, 56.48; H, 3.16; Cl, 27.79; S, 12.57. Found: C, 56.28; H, 3.02; Cl, 27.95; S, 12.75.

Single crystals of 7 were grown from ethanol and placed in sealed Lindemann glass capillaries coated with Mercurochrome to prevent photoreaction while taking X-ray photographs. ***trans*-1-(3,4-Dichlorophenyl)-2-(2-thienyl)ethene (8)** precipitated from the reaction of diethyl 3,4-dichlorobenzylphosphonate and 2-thienoaldehyde in 60% yield and was crystallized from 2-propanol to give colorless crystals (45% overall yield): mp 96-97°; ir 955, 970 cm^{-1} (trans CH=CH); nmr δ 6.9-7.6; mass spectrum: *m/e* 254 (rel intensity) (100, molecular ion, $C_{12}H_8Cl_2S$), 218 (36, M − HCl, $C_{12}H_7ClS$), 184 (66, M − Cl_2, $C_{12}H_8S$), 139 (22), 109 (16).

Anal. Calcd for $C_{12}H_8Cl_2S$: C, 56.48; H, 3.16; Cl, 27.79; S, 12.57. Found: C, 56.57; H, 3.16; Cl, 27.64; S, 12.73.

Compound 8 is dimorphic; form I, shiny, colorless plates, was grown from carbon tetrachloride, 2-propanol, or 1-butanol; form II, colorless needles, was obtained from ethyl acetate, methylcyclohexane, acetone, acetic acid, or methanol.

Irradiation of *trans*-1-Phenyl-2-(2-thienyl)ethene (4). Solid State. The sample remained solid and no dimerization was observed after 1 month of exposure at 40° or 8°; however, the upper, exposed layer gradually darkened. (This process is faster at 40°).

Solution. A 0.85 *M* benzene solution of 4 was irradiated for 1 month. Nmr analysis showed cyclobutane signals at δ 4.05-4.7 (m), corresponding to a cis,anti,cis structure, and 3.72 (s) due to an all-trans structure, in the ratio 2.5:1. A second sample of 4, 1.5 g (8.0 mmol), in 15 ml of benzene, was irradiated as above and then chromatographed with petroleum ether (bp 40-60°) containing increasing amounts of ethyl acetate as eluent. First 750 mg (50%) of *cis*-1-phenyl-2-(2-thienyl)ethene (colorless oil) was eluted followed by 330 mg (22%) of a mixture of *cis*- and *trans*-4. The next component to elute was 150 mg (10%) of yellow oil which, upon treatment with aqueous ethanol, deposited 40 mg of **1,*trans*-3-diphenyl-*trans*-2,*cis*-4-dithienylcyclobutane (23)** as colorless crystals: mp 110°; nmr δ 6.7-7.37 (m, 16 H, aromatic) and 4.90-4.15 (AA′BB′, 4 H, cyclobutane); mass spectrum *m/e* (rel intensity) 372 (0.016, molecular ion, $C_{24}H_{20}S_2$), 188 (6), 187 (15), 186 (100, monomer, $C_{12}H_{10}S$), 185 (25), 184 (10). The oily residue (100 mg) showed several nmr signals in the cyclobutane region: δ 3.75 (s, all-trans dimer), 4.15-4.65 (m) (peak shape suggests more than one dimer). The last component to elute was an unidentified dark oil (50 mg) having no cyclobutane nmr signals.

Irradiation of *trans*-1-(2,4-Dichlorophenyl)-2-(2-thienyl)ethene (7). Solid State. Irradiation at 8° using a Corning filter (color specification no. 3-73, code no. 5543, for $\lambda > 405$ nm, or color specification no. 5-60, code no. 5543, for $520 > \lambda > 350$ nm) led to formation of a strong tlc spot corresponding to 9 (see below) and weak spots corresponding to *cis*-7, 11, and "polymer" (R_f 0). Irradiation at 8° through a Pyrex filter caused darkening of the product and a considerable increase in the amount of "polymer;" irradiation at 40° or exposure to sunlight caused the sample to turn brown and melt after 1 day. Tlc analysis of these samples revealed spots corresponding to *cis*-7, *trans*-7, 9, 11, and "polymer" (R_f 0). A 2.5-g sample of 7, irradiated in sunlight for 2 days, was chromatographed and eluted with *n*-hexane; 20-ml fractions were collected. Fractions 6-12 afforded 550 mg (22%) of *cis*-7 [nmr δ 6.4 (1 H, cis HC=CH, J = 12 Hz), 6.75-7.55 (aromatic multiplet, 7 H)] followed by a mixture of *cis*- and *trans*-7, 400 mg (16%). Fractions 35-60 gave, upon concentration, 560 mg (22%) of colorless crystals, mp 189-191°. Recrystallization from ethyl acetate afforded pure **1,*trans*-3-di(2,4-dichlorophenyl)-*trans*-2,*cis*-4-dithienylcyclobutane (11):** mp 194°; nmr δ 6.75-7.5 (m, 12 H, aromatic) and 4.45-5.0 (AA′BB′, 4 H, cyclobutane); mass spectrum *m/e* (rel intensity) 508 (0.014, molecular ion, $C_{24}H_{16}Cl_4S_2$), 254 (100, M/2, $C_{12}H_8Cl_2S$), 218 (20, M/2 − HCl, $C_{12}H_7ClS$), 184 (30, M/2 − Cl_2, $C_{12}H_8S$).

Anal. Calcd for $C_{24}H_{16}Cl_4S_2$: C, 56.48; H, 3.16; Cl, 27.79; S, 12.57. Found: C, 56.45; H, 2.95; Cl, 27.68; S, 12.68.

Fractions 64-72 contained 440 mg (18%) of a yellow oil from which, **1,*cis*-2-di(2,4-dichlorophenyl)-*trans*-3,*trans*-4-dithienylcyclobutane (9)** crystallized upon standing. Two recrystallizations from ethanol gave a colorless solid: mp 196-197°; nmr δ 6.85-7.3 (m, 12 H, aromatic) and 4.30-5.0 (AA′BB′, 4 H, cyclobutane); mass spectrum *m/e* (rel intensity) 508 (0.02, molecular ion, $C_{24}H_{16}Cl_4S_2$), 316 (0.6, ArCH=CHAr, $C_{14}H_8Cl_4$), 254 (100, M/2, $C_{12}H_8Cl_2S$), 218 (11, M/2 − HCl, $C_{12}H_7ClS$), 192 (4.6, ThCH=CHTh, $C_{10}H_8S_2$), 184 (82, M/2 − Cl_2, $C_{12}H_8S$).

Anal. Calcd for $C_{24}H_{16}Cl_4S_2$: C, 56.48; H, 3.16; Cl, 27.79; S, 12.57. Found: C, 56.28; H, 3.36; Cl, 27.52; S, 12.61.

Dehalogenation of 11. A solution of 11 (200 mg) in 80 ml of methanol containing 200 mg of KOH and 160 mg of 10% Pd/C was warmed to gentle reflux while passing through a stream of hydrogen gas. Periodic tlc analysis indicated that the reaction was proceeding very slowly and was still incomplete after 4 weeks. At this point tlc analysis (benzene-methylcyclohexane, 1:4) showed traces of starting material and four additional, less mobile spots, the final one having an R_f value identical with that of 23. Additional attempts at reaction shifted the product distribution in the direction of this spot, implying that the intermediate three spots were tri-, di-, and monochloro derivatives, but in no case was 23 isolated.

Solution. A 0.1 *M* solution of 7 in benzene or in *n*-hexane was irradiated for 18 days. Tlc analysis showed *cis*-7 as the major component in addition to dimers 9 and 11, in approximately equal quantities, 7, and a spot with R_f 0.

Ozonolysis of 9. A 180-mg sample of 7, irradiated at 8° using a blue Corning filter, code no. 5543, was dissolved in 30 ml of acetic acid, and 1% ozone was bubbled through the ice-cooled solution for 12 min followed by an oxygen stream for 30 min. One milliliter of 30% H_2O_2 was added and the mixture was kept for 24 hr and then warmed with 5% Pd/C to destroy the peroxides present. After filtration, the solvents were evaporated to give 2,2′,4,4′-tetrachloro-β-truxinic acid (10a), which was esterified (diazomethane) and the product was passed over a short column of silica, using benzene as eluent, to afford pure dimethyl 2,2′,4,4′-tetrachloro-β-truxinate (10b), mp 111-113°, identical (melting point and ir) with an authentic sample.

Ozonolysis of 11. Dimer 11 (400 mg), was dissolved in 40 ml of methylene chloride and cooled to −45°. Ozone (1%), was bubbled in for 25 min followed by oxygen for 0.5 hr. The solution was allowed to warm to room temperature and then 50 ml of acetic acid and 10 ml of 50% H_2O_2 were added. The mixture was kept for 24 hr and then warmed with 5% Pd/C to decompose the excess peroxides. Filtration and evaporation to dryness left 230 mg (68%) of 2,2′,4,4′-tetrachloro-α-truxillic acid (12a), mp >290°, ir 1695 cm^{-1} COOH. The methyl ester was prepared by refluxing overnight a solution of 40 mg of 12a in 30 ml of methanol containing two drops of thionyl chloride. Evaporation of volatile material left dimethyl 2,2′,4,4′-tetrachloro-α-truxillate (12b): mp 175-176°; nmr δ 7.3-7.5 (m, 6 H, aromatic), 3.95-4,95 (AA′BB′, 4 H, cyclobutane), and 3.4 (s, 6 H, methyl).

Dehalogenation of 12a. A solution of 12a (120 mg) in 50 ml of 4% aqueous NaOH containing 50 mg of 10% Pd/C was hydrogenated at atmospheric pressure for 20 hr. The catalyst was filtered off and the solution was acidified with HCl to precipitate α-truxillic acid (13), ir identical with that of an authentic sample.

Irradiation of *trans*-1-(3,4-Dichlorophenyl)-2-(2-thienyl)ethene (8). Solid State. Both crystalline forms of 8 show identical behavior on irradiation. After 1 month of exposure at 8° the surface layer darkens slightly, but tlc analysis shows no dimer spots, only a spot with R_f 0. On irradiation at 40° both forms darken and gradually melt; after 20 days both forms have melted entirely and display three strong tlc spots corresponding to the four dimers [14 (R_f 0.095); 15 (R_f 0.13); 16 and 17 appear together (R_f 0.17)] as well as *trans*-8 (R_f 0.32) and traces of *cis*-8 (R_f 0.38). Based on nmr analysis, the ratio of all-trans configurated dimers, 16 and 17, to the cis,anti,cis configurated dimers, 14 and 15, in such a melt-irradiated sample is *ca.* 1:1. The photodimers were isolated from a melt-irradiated sample of 8 because of the small quantity of cis monomer present and because of the larger dimer content compared to a sample irradiated in benzene solution.

Form I (4.9 g) was irradiated at 40° for 1 month and then chromatographed (*n*-hexane elution) to give the following fractions: (a) the cis isomer of 8 as an oil, nmr δ 6.4 (d, 1 H, J = 12 Hz, cis HC=CH); (b) mixture of *cis*- and *trans*-8; (c) 1.4 g (28%) of *trans*-8; (d) dimers 16 and 17, 1.4 g (28%), which upon treatment with *n*-hexane gave 900 mg (18%) of **1,*trans*-2-di(3,4-dichlorophenyl)-*cis*-3,*trans*-4-dithienylcyclobutane (16)** which was recrystallized from CH_2Cl_2-EtOH to give colorless crystals [mp 142-143°; nmr δ 6.83-7.50 (m, 12 H, aromatic) and 3.42-3.85 (AA′BB′, midpoint at 3.63, 4 H, cyclobutane); mass spectrum *m/e* (rel intensity) 508 (0.036, molecular ion, $C_{24}H_{16}Cl_4S_2$), 316 (0.27, ArCH=CHAr, $C_{14}H_8Cl_4$), 254 (100, M/2, $C_{12}H_8Cl_2S$), 218 (8.6, M/2 − HCl, $C_{12}H_7ClS$), 192 (32, ThCH=CHTh, $C_{10}H_8S_2$), 184 (15, M/2 − Cl_2, $C_{12}H_8S$), 139 (2.8), 109 (1.3)].

Anal. Calcd for $C_{24}H_{16}Cl_4S_2$: C, 56.48; H, 3.16; Cl, 27.79; S, 12.57. Found: C, 56.60; H, 3.25; Cl, 27.87; S, 12.38.

The filtrate, after chromatography and several crystallizations from MeOH and EtOH, gave 170 mg of **1,*cis*-3-di(3,4-dichlorophenyl)-*trans*-2,*trans*-4-dithienylcyclobutane (17)**: mp 102–103.5°; nmr δ 6.83–7.58 (m, 12 H, aromatic) and 3.55–3.75 (A_2B_2, midpoint at 3.63, 4 H, cyclobutane); mass spectrum *m/e* (rel intensity) 508 (0.0054, molecular ion, $C_{24}H_{16}Cl_4S_2$), 254 (100, M/2, $C_{12}H_8Cl_2S$), 218 (14, M/2 − HCl, $C_{12}H_7ClS$), 184 (25, M/2 − Cl_2, $C_{12}H_8S$), 139 (6), 109 (2.3). Fraction e was a mixture of **15**, **16**, and **17**, 650 mg (13%). Fraction f was **1,*trans*-3-di(3,4-dichlorophenyl)-*trans*-2,*cis*-4-dithienylcyclobutane (15)**, 160 mg (~3%), which crystallized from MeOH: mp 84–86.5°; nmr δ 6.67–7.45 (m, 12 H, aromatic) and 4.00–4.83 (AA′BB′, midpoint at 4.41, 4 H, cyclobutane); mass spectrum *m/e* (rel intensity) 508 (0.15, molecular ion, $C_{24}H_{16}Cl_4S_2$), 254 (100, M/2, $C_{12}H_8Cl_2S$), 218 (21, M/2 − HCl, $C_{12}H_7ClS$), 184 (36, M/2 − Cl_2, $C_{12}H_8S$), 139 (8.6), 109 (33). Fraction g was a mixture of photodimers **14** and **15**, 460 mg (9%). Fraction h was **1,*cis*-2-di(3,4-dichlorophenyl)-*trans*-3,*trans*-4-dithienylcyclobutane (14)**, 270 mg (5.5%), an almost colorless oil which failed to crystallize: nmr δ 6.67–7.73 (m, 12 H, aromatic) and 4.20–4.65 (AA′BB′, midpoint at 4.41, 4 H, cyclobutane); mass spectrum *m/e* (rel intensity) 508 (0.022, molecular ion, $C_{24}H_{16}Cl_4S_2$), 316 (0.31, ArCH=CHAr, $C_{14}H_8Cl_4$), 254 (100, M/2, $C_{12}H_8Cl_2S$), 218 (15, M/2 − HCl, $C_{12}H_7ClS$), 192 (3.8, ThCH=CHTh, $C_{10}H_8S_2$), 184 (23, M/2 − Cl_2, $C_{12}H_8S$), 139 (5.6), 109 (4.2).

Solution. After irradiation of a 0.4 *M* benzene solution of **8** for 1 month at 40° *ca.* one-third had been transformed to the cis isomer and *ca.* 15% had undergone dimerization; the ratio of cis,anti,cis dimers (**14** and **15**) to all-trans dimers (**16** and **17**) was *ca.* 2.5:1.

Ozonolysis of 14. The dimer (70 mg) was treated as in the case of **9** above. Work-up afforded diacid **18a**, which was esterified (methanol, thionyl chloride) to give dimethyl 3,3′,4,4′-tetrachloro-β-truxinate (**18b**): mp 107–108° (lit.[8] mp 106.5–107°); ir identical with that of an authentic sample; nmr δ 6.6–7.35 (m, 6 H, aromatic), 3.75–4.45 (AA′BB′, midpoint at 4.1, 4 H, cyclobutane), and 3.75 (s, 6 H, methyl).

Ozonolysis of 15. Ozonolysis as above afforded **19a**, which was directly esterified to give dimethyl 3,3′,4,4′-tetrachloro-α-truxillate (**19b**): mp 191–193° (from methanol); nmr δ 7.0–7.5 (m, 6 H, aromatic), 3.6–4.6 (AA′BB′, midpoint at 4.1, 4 H, cyclobutane), and 3.42 (s, 6 H, methyl).

Ozonolysis of 16. The dimer (380 mg), ozonolyzed according to the procedure used for **11**, gave 175 mg (50%) of **20a**, mp 255–261°. A portion of **20a** was esterified ($MeOH-SOCl_2$) and afforded dimethyl 3,3′,4,4′-tetrachloro-δ-truxinate (**20b**): nmr δ 7.0–7.6 (m, 6 H, aromatic), 3.25–3.8 (AA′BB′, midpoint at 3.53, 4 H, cyclobutane), and 3.77 (s, 6 H, methyl). The remainder of **20a** was hydrogenated, as described for **12a**, and afforded δ-truxinic acid **22**, which was crystallized from benzene-acetic acid, mp 175–177° (lit.[11b] mp 175°). The dimethyl ester of **22** was prepared and crystallized from methanol, mp 76–77° (lit.[11b] mp 76°).

Ozonolysis of 17. The dimer was ozonolyzed by the method used for **9** and gave **21a** which was directly esterified ($MeOH-SOCl_2$) to give dimethyl 3,3′,4,4′-tetrachloro-ε-truxillate (**21b**): mp 166–167.5° (methanol); nmr δ 7.0–7.55 (m, 6 H, aromatic), 2.85–4.25 (A_2B_2, midpoint at 3.55, 4 H, cyclobutane), and 3.75 (s, 6 H, methyl).

Determination of Rates. Solutions (3.0 ml) of **1**, **4**, **7**, and **8**, respectively, in benzene (Fluka, for uv spectroscopy) in identical Pyrex tubes were degassed by three freeze-evacuate-thaw cycles on a vacuum line and then flame sealed *in vacuo*. The tubes were exposed for varying times to identical radiation conditions in a Rayonet type RS Merry-Go-Round photochemical reactor equipped with lamps having maximum emission at 350 nm. The tubes were opened, the solvent was evaporated, and a weighed quantity of *n*-octadecane was added to the residue. Integration of the cyclobutane region, δ 3.5–5, and *n*-octadecane region, δ 1.4–0.7, allowed calculation of the total dimer content by the following relationship: milligrams of dimer = (milligrams of *n*-octadecane)(area of cyclobutane signals/area of *n*-octadecane signals)(38/4)(molecular weight of cyclobutane/molecular weight of *n*-octadecane).

Results obtained were (compound, molarity of solution, milligrams of material irradiated, irradiation time in hours, milligrams of dimer formed, rate in mmol $l.^{-1}min^{-1}$): *trans*-stilbene (**1**), 0.30, 162, 3.83, 10.8, 0.087; **1**, 0.30, 162, 9.6, 22.2, 0.071; **1**, 0.30, 162, 27.3, 38.2, 0.043; *trans*-styrylthiophene (**4**), 0.29, 163, 61.3, 24.7, 0.012; **4**, 0.29, 163, 90.0, 32, 0.0106; **7**, 0.29, 218, 61.3, 15.8, 0.0057; **8**, 0.29, 218, 27.3, 25.2, 0.020; **8**, 0.29, 218, 61.3, 37.8, 0.0135.

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Registry No. **1**, 103-30-0; *cis*-**4**, 23516-73-6; *trans*-**4**, 26708-50-9; *cis*-**7**, 42829-18-5; *trans*-**7**, 42829-19-6; *cis*-**8**, 42829-20-9; *trans*-**8**, 42829-21-0; **9**, 42829-22-1; **11**, 42829-23-2; **12a**, 42829-24-3; **12b**, 42829-25-4; **14**, 42829-26-5; **15**, 42829-27-6; **16**, 42829-28-7; **17**, 42829-29-8; **18b**, 42903-89-9; **19b**, 42829-30-1; **20a**, 42829-31-2; **20b**, 42829-32-3; **21b**, 42829-33-4; **23**, 42829-34-5; diethyl benzylphosphonate, 2768-31-2; diethyl 3,4-dichlorobenzylphosphonate, 42822-50-4.

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