

drous hexane. It is mandatory to keep an inert and dry atmosphere over solutions or solids during reactions, isolations, and crystallization.

The crude solids were usually used directly without further purification. The crude phosphinimines could be stored over KOH pellets in a vacuum desiccator without appreciable decomposition.

N-Methylcycloalkylaminotriphenylphosphonium Iodides (Table I, Compounds 1, 3, 5, 7).—The appropriate triphenylphosphinecycloalkylimine (3–4 g) and 15 ml of methyl iodide were refluxed in an inert atmosphere for 3 hr. To the solution, after cooling, was added sufficient anhydrous ether, whereupon a pale yellow precipitate was deposited. Purification was done by crystallization from chloroform–ether. Yields based on starting phosphinimine were usually high (Table I).

N-Ethylcycloalkylaminotriphenylphosphonium Iodides (Table I, Compounds 2, 4, 6, 8).—These compounds were obtained analogously except that 15 ml of anhydrous *t*-butyl alcohol was used as solvent.

N-Methylcycloalkyl- and N-Ethylcycloalkylammonium Hemioxalates. Hydrolysis of N-Methylcycloalkyl- and N-Ethylcycloalkylaminotriphenylphosphonium Iodides (Table II, Compounds 1–8).—A mixture of 3 g of the appropriate dialkylaminotriphenylphosphonium iodide (*ca.* 0.0055–0.007 mol) and 30 ml of 2% alcoholic potassium hydroxide solution was sealed under an inert atmosphere in a Jena glass pressure bottle and was heated on a steam bath for 3 hr. The bottle then was chilled and carefully opened. The reaction mixture which contained the free amine was saturated with NaCl and was extracted with ether. After combining all ether extracts and drying them over anhydrous sodium sulfate, they were filtered slowly with stirring into a solution of 2 g of anhydrous oxalic acid in 75 ml of dry ether. The white precipitate of hemioxalate which immediately formed was collected, washed with anhydrous ether, and finally purified by recrystallization from ethanol–ether.

Registry No.—Cyclopropylaminotriphenylphosphonium bromide, 24571-65-1; cyclopentylaminotriphenylphosphonium bromide, 24571-66-2; cycloheptylamino-triphenylphosphonium bromide, 24571-67-3; adamantylaminotriphenylphosphonium bromide, 24571-68-4; Table I—1, 24571-69-5; 2, 24571-70-8; 3, 24571-71-9; 4, 24571-72-0; 5, 24571-73-1; 6, 24571-74-2; 7, 24571-75-3; 8, 24571-76-4; 9, 24571-77-5; Table II—1, 24571-78-6; 2, 24571-79-7; 3, 24571-80-0; 4, 24571-81-1; 5, 24571-82-2; 6, 24571-83-3; 7, 24571-84-4; 8, 24571-85-5; 9, 24571-86-6.

Acknowledgment.—Partial financial support of this research through the U. S. Army Research Office, Grant DA-ARO-D-31-124-G122, and the National Institutes of Health, Grant CY-5841, is gratefully acknowledged.

Photodimerization of Some Thiophene Analogs of Chalcone

HANS WYNBERG, M. B. GROEN,
AND RICHARD M. KELLOGG

*Department of Organic Chemistry, The University
Bloemensingel, 10, Groningen, The Netherlands*

Received September 15, 1969

Since the early work of Stobbe^{1,2} concerning the photodimerization of chalcone (benzalacetophenone) and some of its derivatives, this reaction has attracted

surprisingly little attention.³ Recently⁴ we established that 1,2-dithienylethenes and 2-styrylthiophene, in contrast to stilbene,⁵ failed to undergo photochemical dimerization.⁴ It seemed of interest to see if the replacement of a phenyl by a thienyl ring in chalcone would also prevent dimerization. An additional motivation was provided by the fact that dimerization would yield cyclobutanes substituted with thiophene rings. This in turn would open the way to the synthesis of unusual cyclobutanes.⁶

Results

The heterocyclic chalcones 1–3 were readily prepared by the condensation of the appropriate aldehydes and ketones as described in literature.⁷

Concentrated solutions (*ca.* 35% wt/vol) in chloroform were irradiated in ordinary micro test tubes for 20 hr using 350 m μ ("dark light") lamps. In addition to large amounts of resinous material, insoluble in ethanol, colorless soluble compounds which turned out to be the cyclodimers 5–8 were also formed. 3-Phenyl-1-(2-thienyl)-2-propen-1-one (1) under the given conditions afforded the dimer 5 in 10% yield, mp 128–129.5° (from ethanol). Similarly, 1-phenyl-3-(2-thienyl)-2-propen-1-one (2) gave the cyclobutane derivative 6, mp 132–134° (from ethanol) in 6–10% yield; 1,3-di-2-thienyl-2-propen-1-one (3) furnished in 4% yield a mixture of dimers 7 and 8, mp 124–134° (from ethanol), in a ratio of about 10:1. The dimeric structure of the compounds was revealed by elemental analysis in combination with molecular weight determinations (osmometric in carbon tetrachloride) and by the spectroscopic properties. In order to elucidate the stereochemistry of the dimers the experiments of Stobbe^{1,2} were repeated. Irradiation of a concentrated solution of 1,3-diphenyl-2-propen-1-one (chalcone, 4) in chloroform in small quartz tubes for 20 hr afforded in 6% yield the dimer 9, mp 125–126.5° (from ethanol, lit.² 124–125°). The reaction was incomplete, however, since considerable starting material remained (as a *cis-trans* mixture) and no resinous polymer was found. When ordinary glass tubes were used, another dimer was formed in extremely low yield upon irradiation of a solution of chalcone for 20 hr. Almost all of the starting material was still present as a *cis-trans* mixture. This dimer 10 (mp 234–236°) was also reported by Stobbe. The dimerizations of 1 and 4 have also been carried out in the presence of iodine, taking longer irradiation times (*ca.* 48 hr). The yields were improved considerably by this procedure; 1 gave a 22% yield of 5, while 4 furnished the dimer 9 in 28% yield (Scheme I).

Discussion

On inspection of the mass spectra of the photodimers 5 and 6, it was found that the fragmentation pattern was compatible only with a head-to-head structure.

(3) We noted only the dimerization of nitrochalcones: I. Tănăsescu and F. Hudosan, *Acad. Repub. Pop. Rom., Bul. Stiint., Sect. Stiinte Tehnice Chim.*, **5**, 37 (1953); *Chem. Abstr.*, **50**, 14628 (1956); *Rev. Chim., Acad. Repub. Pop. Rom.*, **1** (2), 39 (1956); *Chem. Abstr.*, **52**, 2817 (1958).

(4) R. M. Kellogg, M. B. Groen, and H. Wynberg, *J. Org. Chem.*, **32**, 3093 (1967).

(5) G. Ciamician and P. Silber, *Ber.*, **35**, 4128 (1902).

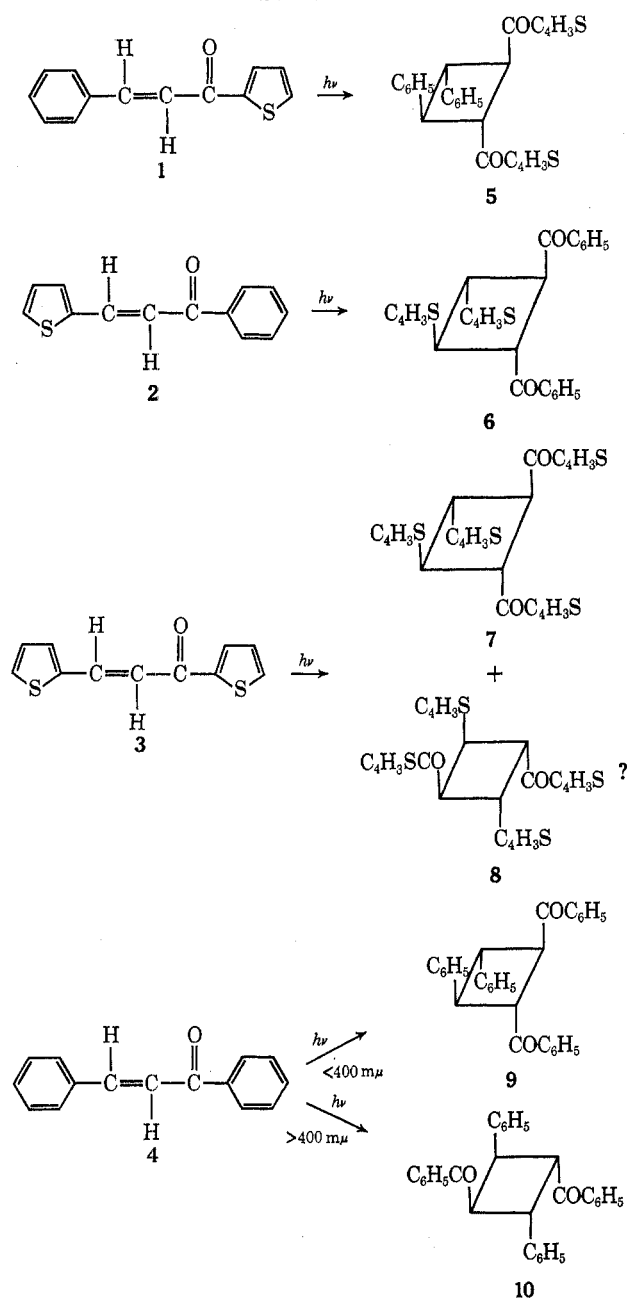
(6) Another route to cyclobutanes with thienyl substituents is the solid-state irradiation of β -(2-thienyl)acrylic acid: M. Lahav and G. M. J. Schmidt, *J. Chem. Soc. B*, 239 (1967).

(7) C. Weijand and F. Strobel, *Ber.*, **68**, 1839 (1935).

(1) H. Stobbe and A. Hensel, *Ber.*, **59**, 2254 (1926).

(2) H. Stobbe and K. Bremer, *J. Prakt. Chem.*, **123** [2], 1 (1929).

SCHEME I



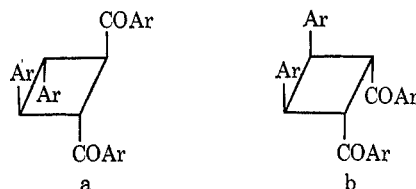
One of the main fragments of **5** is the stilbene positive ion (m/e 192). We were not able to get a mass spectrum of the product formed from **3**, since it decomposed in the inlet system to the monomer **3**. Nmr data are summarized in Table I.

TABLE I
NMR SPECTRA OF THE DIMERS

Compd	Chemical shifts of cyclobutane protons ^a		
	Multiplet A	Multiplet B	Singlet
5	5.60	5.94	
6	5.47	5.82	
7	5.62	5.82	
8			5.31
9	5.38	5.97	
10			5.06

^a All spectral are recorded in CDCl_3 solution with TMS as an internal standard. Chemical shifts are given in parts per million on the τ scale.

The nmr spectra of **5** and **6** showed two symmetrically arranged multiplets, characteristic for an AA'BB' system, which requires either a plane or a twofold axis of symmetry in the molecule. The products formed from **3** had an additional small broad singlet, the integration ratio multiplets:singlet being about 10:1. The nmr and mass spectral data leave for the major products two equally possible structures as depicted in A and B below. Two other structures, namely with both aryl



groups *cis* to the adjacent aryl groups, although in principle possible, are very unlikely.

The photodimer **9** formed from chalcone has been shown by independent synthesis⁸ to have the C_2 symmetric head-to-head structure A. Its nmr spectrum showed exactly the same pattern as the compounds **5**, **6**, and **7**. Moreover, the low field parts of the multiplets of **9** and **6**, caused by the protons adjacent to the aryl groups, have almost equal chemical shifts. The same is true for the high-field parts of **9** and **5** caused by the protons adjacent to the aryl groups. These facts suggest strongly that **5**, **6**, and **7** have the same stereochemical configuration as the chalcone dimer **9**, although strictly spoken the structure B cannot be ruled out completely. The structure of the minor product, **8**, is not at all certain. We propose, however, a structure similar to that of the second chalcone dimer **10**, which is consistent with our findings that both **8** and **10** show singlets for the cyclobutane protons in the nmr spectrum. We believe that the addition of iodine to the reaction mixture causes a suppression of the *trans* to *cis* isomerization. This, in turn, inhibits polymerization of the *cis* form of the starting material.

Although the reactions described in this paper can be expected to proceed *via* triplets, we have not done experiments to prove or disprove this. The dependence of the product formation in the case of chalcone itself on the reaction conditions and especially on the wavelength suggests that the actual mechanism is quite complex.

Experimental Section

The irradiation experiments were carried out in a Rayonet reactor equipped with 350 $m\mu$ ("dark light") lamps. Nmr spectra were taken with a Varian A-60 instrument using tetramethylsilane (TMS) as an internal standard. Melting points were determined with a Koffler hot-stage apparatus and are uncorrected. Mass spectra were taken with an AEI MS-902 instrument.

trans,trans,trans-1,2-Diphenyl-3,4-di-2-thienylcyclobutane (**5**). A.—A solution of 7 g of **1** in 20 ml of chloroform was irradiated for 20 hr in ordinary micro test tubes. The solvent was evaporated and the residue was treated with hot ethanol. The ethanol solution was decanted leaving a resinous residue. This procedure was repeated twice. On standing for several days, a colorless precipitate was formed which was recrystallized from ethanol. The yield of **5** was 0.7 g (10%), mp 128–129.5°. The mass spectrum showed peaks at m/e 428, 410, 317, 214, and 180.

Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{O}_2\text{S}_2$: C, 72.87; H, 4.71; S, 14.96; mol wt, 428.6. Found: C, 72.74, 72.89; H, 4.73, 4.50; S, 14.90, 15.22; mol wt (osm), 425.0, 427.9.

B.—To a solution of 18 g of 1 in 60 ml of chloroform, a crystal of iodine (0.2 g) was added and the solution was irradiated for 48 hr. Work-up as described above gave 4.0 g (22%) of product, mp 127–128.5°.

trans,trans,trans-1,2-Dibenzoyl-3,4-di-2-thenoylcyclobutane (6).—A solution of 8 g of 2 in 20 ml of chloroform was irradiated for 20 hr. The same procedure as in the previous experiments furnished 0.45 g (6%) of the product 6, mp 132–134° (from ethanol). In a second run the irradiation time was prolonged to 48 hr. The product was obtained in 10% yield, mp 130–132°. The mass spectrum showed peaks at *m/e* 428, 410, 323, 214, and 192.

Anal. Calcd for C₂₆H₂₀O₂S₂: C, 72.87; H, 4.71; S, 14.96; mol wt, 428.6. Found: C, 72.80, 72.90; H, 4.82, 4.79; S, 14.82, 14.95; mol wt (osm), 416.9, 424.1.

trans,trans,trans-1,2-Di-2-thienyl-3,4-di-2-thenoylcyclobutane (7) and *trans,cis,trans*-1,3-Di-2-thienyl-2,4-di-2-thenoylcyclobutane (8).—A solution of 8 g of 3 in 25 ml of chloroform upon irradiation for 20 hr furnished 0.3 g (4%) of a mixture of 7 and 8, mp 124–134°. No attempts were made to separate the mixture. The mass spectrum showed only peaks with *m/e* of 220.

Anal. Calcd for C₂₂H₁₆O₂S₄: C, 59.97; H, 3.67; S, 29.11; mol wt, 440.6. Found: C, 60.14, 59.99; H, 3.57, 3.70; S, 29.04, 28.90; mol wt (osm), 437.4, 431.7.

trans,trans,trans-1,2-Dibenzoyl-3,4-diphenylcyclobutane (9).—A solution of 17 g of 4 in 50 ml of chloroform was irradiated in small quartz tubes for 20 hr. Work-up in the usual way afforded 1.0 g (6%) of product, mp 125–126.5° (lit.² 124–125°). By prolonging the irradiation time and adding a crystal of iodine, the yield of 9 could be improved to 28%.

trans,cis,trans-1,3-Dibenzoyl-2,4-diphenylcyclobutane (10).—A solution of 7 g of 4 in 20 ml of chloroform was irradiated in ordinary micro test tubes for 20 hr. After evaporation of the solvent, a yellow oil was obtained consisting mainly of starting material (*cis-trans* mixture). Ethanol was added and, on standing, starting material crystallized. It was removed by filtration. From the mother liquor 10 mg (0.15%) of 10 crystallized eventually, mp 234–236° (lit.² 225–226°).

Registry No.—5, 24825-03-4; 6, 24825-04-5; 7, 24825-05-6; 8, 24825-06-7; 9, 24825-07-8; 10, 24825-08-9.

1,5-Hydrogen Migrations in Bicyclic Carboxaldehydes

DAVID L. GARIN

Department of Chemistry, University of Missouri at St. Louis, St. Louis, Missouri 63121

Received January 23, 1970

Cyclopropyl ketones have been reported to undergo thermal and photochemical rearrangements to homoallylic ketones (1 → 2).^{1,2} We have observed that analogous reactions occur in bicyclic carboxaldehydes, 3 (*n* = 1, 2), where 1,5-hydrogen migration is possible, leading to δ²-cycloalkenyl acetaldehydes, 4 (*n* = 1, 2).

Injection of the *endo* isomers of 3 (*n* = 1, 2) into a vapor phase chromatograph (vpc) at 190° with the injection port heated to 230° produces a single volatile compound identified as the corresponding cycloalkenyl acetaldehyde, 4 (*n* = 1, 2).³ The *exo* isomers are inert under these conditions.

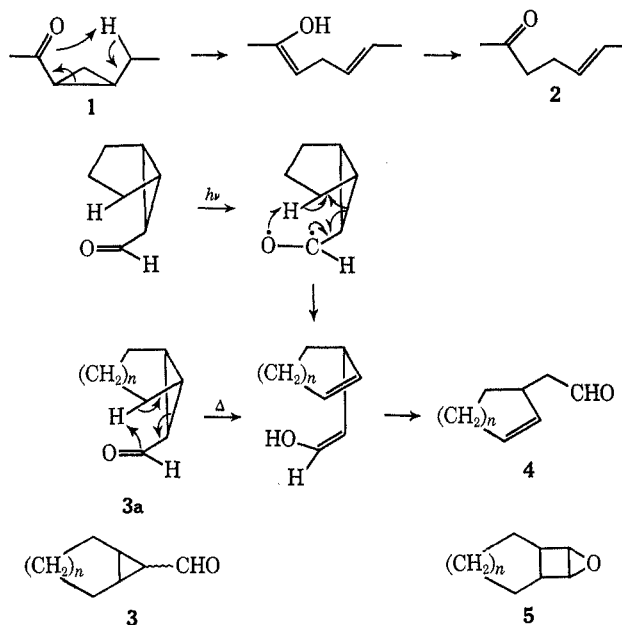
(1) R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, **89**, 1404 (1967). This article contains an excellent discussion of and leading references to the thermal rearrangement of cyclopropyl ketones, carboxaldehydes, and carboxylate esters.

(2) W. G. Dauben, L. Schutte, and R. E. Wolf, *J. Org. Chem.*, **34**, 1849 (1969).

(3) D. L. Garin, *ibid.*, **34**, 2355 (1969).

The dropwise addition of the *endo* isomer of 3 (*n* = 1) onto a column of glass beads at 300° under helium gas flow gives a crude pyrolysate whose nmr spectrum is identical with that of 4 (*n* = 1). The *exo* isomer of 3 (*n* = 1) remains unchanged at temperatures as high as 400° suggesting that the reaction is not proceeding in a stepwise fashion involving the initial cleavage of the cyclopropyl bond. The necessity for the proximity of the carbonyl group and a γ hydrogen has been demonstrated in a similar bicyclic system where initial thermal rearrangement to a cycloalkenyl acetaldehyde is postulated.⁴ The thermal instability of *endo*-3 (*n* = 1, 2) may account for its absence and the presence of 4 (*n* = 1, 2) among the products of the thermal rearrangement of the cyclobutene epoxides, 5 (*n* = 1, 2).³

The irradiation of a 1% ethereal solution of 3a (*n* = 1) with 3000 Å light gives 4 (*n* = 1) in ca. 30% yield. Similar irradiation of *exo*-3 (*n* = 1) gives a complex mixture of products which does not contain significant amounts of 4 (*n* = 1). Initial rupture of the cyclopropyl bond would give a common intermediate. An intramolecular γ hydrogen abstraction (Norrish "type II"), leading to the formation of 4, can only occur in the *endo* isomer. It appears that this pathway is favored when possible.²



Experimental Section⁵

Bicyclic Carboxaldehydes (III).—The *endo* isomers of 3 (*n* = 1, 2) were synthesized by known procedures.^{6,7} The *exo* isomers of 3 (*n* = 1, 2) were synthesized by epimerization of the *endo* isomers.⁷ The aldehydic protons of the *exo* and *endo* isomers have different chemical shifts in their nmr spectra providing a

(4) F. Bickelhaupt, W. L. DeGraaf, and G. W. Klumpp, *Chem. Commun.*, 53 (1968).

(5) A Perkin-Elmer R-20 spectrometer was used for nmr measurements in CDCl₃ using TMS as internal standard. Wilkens A-700 (Autoprep) instruments were used for vpc analyses and separations utilizing silicone gum rubber (SE-30) and fluorosilicone (QF-1) as stationary phase materials.

(6) R. T. LaLonde and M. A. Tobias, *J. Amer. Chem. Soc.*, **86**, 4068 (1964); D. L. Garin, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1964.

(7) D. L. Garin, Abstracts, 149th National Meeting of the American Chemical Society, Houston, Texas, 1970, Orgn 137 (submitted for publication).