

**Acknowledgment.**—The authors wish to express their appreciation for financial support of this work by the Purdue Research Foundation and the Public Health Service Research Grant No. CA-04536-11 from the National Cancer Institute.

### The [2 + 2] Photocycloadditions of Indene and 2- and 3-Chloroindenes

G. W. GRIFFIN\* AND U. HEPP

Department of Chemistry,  
Louisiana State University in New Orleans,  
Lake Front, New Orleans, Louisiana 70122

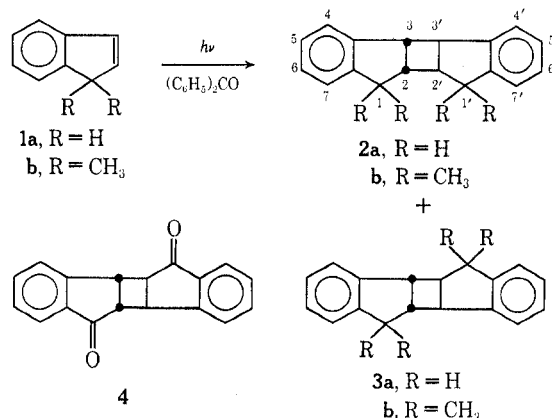
Received May 14, 1970

As a consequence of our continuing interest in the mechanism and stereochemistry of [2 + 2] photocycloadditions<sup>1</sup> and in the introduction of multiple trigonal centers into the resulting cyclobutyl products we have extended our previous studies of indenenes<sup>2</sup> to haloindene derivatives. It was anticipated that dimers and crossed cycloadducts of the latter substrates might be dehydrohalogenated or dehalogenated to unsaturated systems of potential theoretical interest. The photosensitized dimerization of indene **1a** was first reported by Schenck,<sup>3</sup> and the primary product (mp 110–112°) was shown in our laboratories to have the truxane structure **2a** with syn (head-to-head), trans stereochemistry by degradative ozonolysis to *cis,trans,cis*-tetracarboxycyclobutane and conversion to a truxone (in the formal sense an indenone dimer) of syn orientation.<sup>2a-c</sup> The same conclusion was reached independently by Bowyer and Porter by stereospecific oxidative conversion of the indene photodimer to the coumarin dimer of known syn, trans stereochemistry.<sup>4</sup>

Recently, McCullough has studied the direct and photosensitized dimerization of 1,1-dimethylindene (**1b**) and found that two dimers, the syn, trans and anti, trans isomers, **2b** and **3b**, respectively, are formed in a 5:1 ratio when acetophenone is employed as a photosensitizer.<sup>5</sup> The structures of the two dimers were assigned on the basis of nmr spectroscopy and it is noteworthy that the major product **2b** has syn, trans stereochemistry which is consistent with the results obtained with indene.

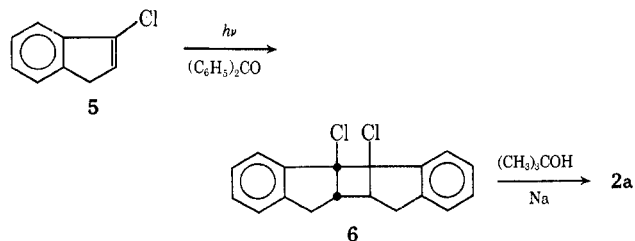
During a recent attempt to recover additional **2a** from the combined residues obtained from several irradiations

of indene by elution chromatography on silica gel, a previously unreported photodimer was isolated in low yield having a melting point of 142–143° consistent with



that reported for  $\alpha$ -truxane, the anti, trans isomer **3a**.<sup>4</sup> Upon oxidation of **3a** with sodium dichromate in glacial acetic acid, according to previously described techniques,<sup>4</sup> a truxone was obtained with mp 296–297° in agreement with the melting point reported for **4** obtained by cyclization of  $\alpha$ -truxillic acid.<sup>6,7</sup>

When 3-chloroindene (**5**)<sup>8</sup> is irradiated in benzene with benzophenone as a sensitizer a photodimer **6** is obtained (20–30%) which upon recrystallization from cyclohexane deposits in two crystal modifications (mp 169–170° and 179–180°). That the stereochemistry of **6**, the major dimeric product, is syn, trans was established by reductive dehalogenation with sodium in tetrahydrofuran containing *tert*-butyl alcohol which



gave exclusively **2a** in high yield.<sup>9</sup> The nmr spectrum of **6** (deuteriochloroform, 60 MHz) exhibits signals for the aromatic protons at  $\tau$  2.20 and 2.65 and multiplets for the remaining protons at  $\tau$  6.40–7.60. Clearly the preferred mode of dimerization observed for **5** is consistent with that found for **1a** and **1b**.

The crossed cycloaddition of indene to 2-chloroindene (**7**) was accomplished by Krauch and Metzner. While a syn orientation may be inferred for the adduct from the thermolysis product, namely 2,2'-biindenyl, a complete structural assignment was not reported.<sup>10</sup> We have investigated the benzophenone sensitized crossed cycloaddition of indene to 3-chloroindene (**5**). 3,3'-Dichlorotruxane (**6**) and small amounts of *syn,trans*-

\* To whom correspondence should be addressed.

(1) L. Due, R. A. Mateer, L. Brassier, and G. W. Griffin, *Tetrahedron Lett.*, 6173 (1968).

(2) A. G. Anastassiou, Ph.D. Thesis, Yale University, 1963; (b) A. G. Anastassiou, F. L. Setliff, and G. W. Griffin, *J. Org. Chem.*, **31**, 2705 (1966); (c) A. G. Anastassiou and G. W. Griffin, *ibid.*, **33**, 3441 (1968); (d) F. L. Setliff, A. G. Anastassiou, and G. W. Griffin, *ibid.*, **34**, 3047 (1969); (e) G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Lett.*, 2951 (1965).

(3) G. O. Schenck, W. Hartmann, S. P. Mannsfeld, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962). C. H. Krauch, W. Metzner, and G. O. Schenck, *Naturwissenschaften*, **50**, 710 (1963); Belgium Patent 630,110 (1963); *Chem. Abstr.*, **60**, 15801 (1964).

(4) J. Bowyer and Q. N. Porter, *Aust. J. Chem.*, **19**, 1455 (1966); *Chem. Abstr.*, **65**, 13643 (1966).

(5) (a) J. J. McCullough, *Can. J. Chem.*, **46**, 43 (1958). (b) A dimer of unknown structure was also obtained upon irradiation of 1,1-diphenylindene; however, it was shown to arise from the product of a rearrangement of the type we had reported earlier for 1,3,3-triphenylindene<sup>2a</sup> and not from 1,1-diphenylindene.<sup>5a</sup>

(6) (a) R. Stoermer and G. Foerster, *Chem. Ber.*, **52**, 1255 (1919); (b) E. H. White and H. C. Dunathan, *J. Amer. Chem. Soc.*, **78**, 6055 (1956).

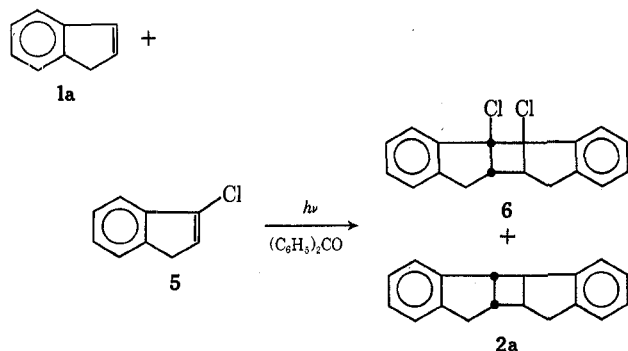
(7) Metzner and Wendisch have shown that the direct and photosensitized dimerization of indene gives **2a** (83%) and **3a** (9%) in addition to lower yields of the other possible isomeric truxanes, namely the *syn,cis* and *anti,cis* modifications (3 and 5%, respectively). See W. Metzner and D. Wendisch, *Justus Liebig's Ann. Chem.*, **730**, 111 (1969).

(8) E. A. Braude and L. A. Evans, *J. Chem. Soc.*, 3337 (1955).

(9) P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Amer. Chem. Soc.*, **90**, 7271 (1968).

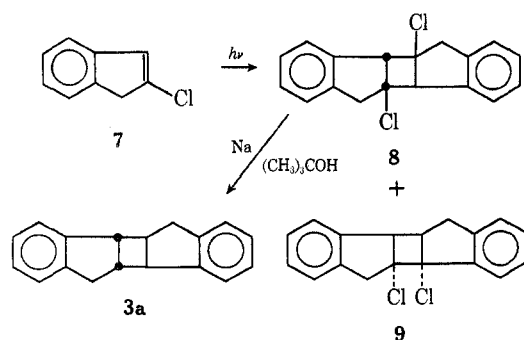
(10) C. H. Krauch and W. Metzner, *Chem. Ber.*, **98**, 2762 (1965).

truxane (2a) were obtained when equimolar amounts of the two components were irradiated. No crossed cycloadducts of 1a and 5 could be detected among the



reaction products even in the case where a tenfold excess of indene was employed although under these circumstances 2a then becomes the principal product. The reasons for the apparent reluctance of indene to participate in crossed cycloadditions with 5 are presently under study.

While the photodimerization of 2-chloroindene (7)<sup>11</sup> previously had been investigated no definitive structural assignments were made.<sup>12</sup> In agreement with



Metzner's original work,<sup>12</sup> we have found that irradiation of 7 in benzene affords two dimers ( $\sim 1:1$ ) of mp 173 and 115°. We assign the anti,trans structure 8 to the high melting isomer on the basis of reduction with sodium in tetrahydrofuran containing *tert*-butyl alcohol which gives the anti,trans-truxane 3a. It is apparent on theoretical grounds that the head-to-head configuration should be favored in a triplet (presumably stepwise) cycloaddition process and this is generally the case (*vide supra*). In view of the competitive formation of the head-to-tail isomer 8 from 7 we felt it advisable to augment our chemical results with X-ray data. These confirm that the molecule is indeed centrosymmetric.<sup>13</sup>

Under reductive conditions similar to those employed with 8, the lower melting isomer 9 gives a complex mixture of products. The absence of *syn,trans*-truxane 2a among the reduction products suggests that the adduct has cis stereochemistry in agreement with Metzner's

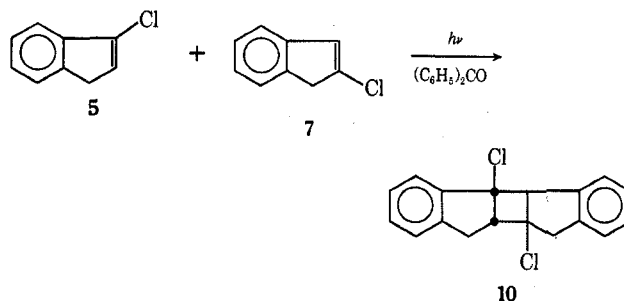
(11) C. M. Sutter and G. A. Lutz, *J. Amer. Chem. Soc.*, **60**, 1360 (1938).

(12) (a) W. Metzner, Ph.D. Thesis, University of Bonn, Germany, 1966. We wish to thank Dr. Metzner for kindly providing us with a copy of this document. (b) In a recent report<sup>7</sup> Metzner alludes to the isolation of three cyclodimers upon irradiation of 7 although no further data are presented.

(13) L. M. Trefonas and R. L. R. Towns, personal communication. Preliminary crystallographic work and density measurements on 8 indicate a space group of P21/c with two molecules per unit cell. Since the multiplicity for this space group is four molecules per unit cell, the molecule itself must sit on a center of symmetry. The unit cell lattice constants are  $a = 8.40 \text{ \AA}$ ,  $b = 9.37 \text{ \AA}$ ,  $c = 8.92 \text{ \AA}$ ,  $\beta = 91.3^\circ$ .

original proposal.<sup>12</sup> An X-ray crystallographic study on 9 is presently in progress.

The benzophenone crossed cycloaddition of 2-chloroindene (7) with 3-chloroindene (5) in benzene proceeds in low yield and a single crystalline adduct is isolated



which tentatively has been assigned the *syn,trans* structure 10 on the basis of the nmr spectrum (deuteriochloroform), which shows signals at  $\tau$  2.69 (aromatic, 8 protons) and broad singlets at  $\tau$  5.60, 6.41, and 6.66 (aliphatic, 6 protons) characteristic of the *syn,trans* skeletal structure. X-Ray data are presently being obtained on 10 as part of a continuing extensive crystallographic study of fused cyclobutyl systems in collaboration with Professor R. Davis, University of Texas, Austin, Texas.

Perturbational molecular orbital calculations similar to those reported by Feuer, Herndon, and Hall<sup>14</sup> have been conducted on several systems including those reported herein and will be reported in a subsequent communication.

#### Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. Nmr spectra were obtained at 60 MHz on a Varian A-60 spectrometer using tetramethylsilane as the internal standard. Infrared spectra were recorded with a Perkin-Elmer Model 337 grating spectrophotometer. The mass spectra were determined with a Hitachi Perkin-Elmer RMU-6 spectrometer at an ionizing voltage of 70 eV. Elemental analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tenn.

**Dimerization of Indene (1a). Isolation of anti,trans-Truxane (3a).**—The benzophenone sensitized dimerization of indene (1a) was conducted repeatedly according to the method of Schenck and coworkers<sup>3,7</sup> and the oily residues obtained after isolation of the major product, *syn,trans*-truxane (2a, mp 110°), were chromatographed on silica gel (Woelm grade I) using *n*-hexane as the eluent. A crystalline fraction was isolated which upon recrystallization from acetone melted at 142–143°. A mixture melting point determination employing an authentic sample of 3a showed no depression.

**Oxidation of anti,trans-Truxane (3a) to anti,trans-Truxone (4).**—To 2 g (8.7 mmol) of 3a dissolved in 12 ml of glacial acetic acid was added 16 g (54 mmol) of sodium dichromate and the resulting mixture was heated under reflux for 4 hr and subsequently quenched in water and the solid material was collected on a filter. Recrystallization from acetone gives a solid [1.5 g, mp 296–297° (lit.<sup>4</sup> 294–295.5°)].

**syn,trans-3,3'-Dichlorotruxane (6). Photodimerization of 3-Chloroindene (5).**—A solution of 2.3 g (15 mmol) of freshly distilled 3-chloroindene [bp 108–109° (16 mm)] in 5 ml of benzene containing 0.2 g of benzophenone was irradiated for 8 hr.<sup>15</sup>

(14) J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, **24**, 2575 (1968), and W. C. Herndon, personal communication.

(15) All irradiations were conducted in serum capped Pyrex vessels using either (a) a Hanovia 450-W high pressure mercury lamp (type 79A36) at 0°, or (b) an RPR-100 Rayonet chamber reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 RPR 8-W lamps (3500 Å) at 35°, or (c) a preparative Rayonet RPR 208 unit fitted with 8 RUL 3500-Å lamps.

The solvent and residual 3-chloroindene (1.1 g) were then removed by distillation; the residue was triturated with ether and recrystallized from ether-cyclohexane to give 490 mg (21%) of white crystalline dimer.

Further purification was achieved by vacuum sublimation [150° (1 mm)] and subsequent recrystallization from cyclohexane. Two crystalline modifications of the dichlorotruxane [(a) (mp 169–170°, and (b) (180–181°)] deposited from cyclohexane which were separated mechanically. The infrared spectra determined in potassium bromide were very similar, while in solution they are identical as are the nmr spectra (deuteriochloroform)  $\tau$  2.19 and 2.65 (m, 8, aromatic) and 6.40–7.60 (m, 6, aliphatic).

*Anal.* Calcd for  $C_{18}H_{14}Cl_2$ : C, 71.77; H, 4.68; Cl, 23.43. Found: C, 71.82; H, 4.80; Cl, 23.16 (determined on lower melting isomer).

**Dehalogenation of *syn,trans*-3,3'-Dichlorotruxane (6).**—To a solution of 0.20 g (0.67 mmol) of the dichlorotruxane 6 dissolved in a mixture of 10 ml of tetrahydrofuran and 3 ml of *tert*-butyl alcohol at 0° was added in small portions (1.0 g, 43.5 mg-atoms) of finely divided sodium metal under nitrogen. After 72 hr the solution was warmed to 25° and the excess sodium metal collected on a filter. The filtrate was then quenched by pouring onto ice, the organic material extracted repeatedly with ether, and the combined ethereal extracts were dried over anhydrous magnesium sulfate. Upon concentration of the ethereal solution, a white crystalline material (mp 110–111°) separated which was shown to be identical with *syn,trans*-truxane 2a by infrared and nmr spectroscopy.

**Attempted Photocycloaddition of 3-Chloroindene (5) to Indene (1a).**—A mixture of 7.5 g (50 mmol) of 3-chloroindene and 5.8 g (50 mmol) of indene dissolved in 25 ml of benzene containing 1.0 g of benzophenone was irradiated<sup>15a</sup> for 10 hr at 10°. The oil remaining after removal of solvent and unreacted indenenes from the brown irradiation mixture was chromatographed over silica gel using mixtures of *n*-hexane and ether as the eluting solvent. *syn,trans*-3,3'-Dichlorotruxane (6) (2.2 g, 29%) and *syn,trans*-truxane (2a) (40 mg, 0.7%) were isolated. No crossed dimer was detected in this case or under a variety of different reaction conditions in which the solvent, light source, and temperature were changed (–30–40°). Acetophenone also was employed as a solvent in an attempt to sensitize the reaction without success.

**Dimerization of 2-Chloroindene (7).**—A modification of the method described by Metzner<sup>7</sup> was employed for the dimerization of 2-chloroindene (7). A benzene solution (100 ml) of 7.5 g (55 mmol) of freshly distilled 2-chloroindene [bp 95–98° (11 mm),  $n_D^{20}$  (1.5824)]<sup>11</sup> containing 2 g of benzophenone were irradiated<sup>15c</sup> in a Pyrex vessel for 25 hr. After removal of the solvent and excess 2-chloroindene under vacuum the residue was chromatographed on silica gel using hexane ether (20:1) as the eluent mixture. The two crystalline fractions were isolated and recrystallized from methanol to give two dimers, mp 115° (1.1 g, 14.5%) and 173° (1.0 g, 13.5%) (lit.<sup>7</sup> 115 and 173–174°).

**Dehalogenation of the Isomeric Dichlorotruxanes Obtained from 2-Chloroindene (7).**—To a solution of 200 mg (0.67 mmol) of each of the 2-chloroindene dimers in 12 ml of tetrahydrofuran containing 3 ml of *tert*-butyl alcohol at 0° was added 0.8 g of sodium metal. The mixture was stirred for 50 hr at 0–5° under nitrogen. An additional 0.1 g of sodium metal and 1 ml of *tert*-butyl alcohol were then added; the resulting mixture was allowed to warm to room temperature over a period of 2–3 hr. The reaction mixture after removal of excess sodium by filtration was poured onto ice, the aqueous phase extracted repeatedly with ether, and the combined organic phases dried over anhydrous magnesium sulfate. The residues obtained after removal of solvent were purified by elution chromatography on silica gel.

The 2-chloroindene dimer 8 (mp 172°) upon dechlorination afforded 130 mg (84.5%) of a crude product which was purified by recrystallization from methanol to give a hydrocarbon (mp 141°) shown to be identical with *anti,trans*-truxane (3a) by mixture melting point and infrared and nmr spectroscopy.

The reduction of the 2-chloroindene dimer 9 (mp 115°) gave a more complex mixture of reduction products. The absence of *syn,trans*-truxane (2a) among the products was demonstrated by tlc; however, insufficient material was available to achieve separation and unambiguous structural characterization of any product.

**Photocycloaddition of 3-Chloroindene (5) to 2-Chloroindene (7).**—An equimolar mixture of 3-chloroindene (1.2 g, 8.0 mmol) and 2-chloroindene (1.2 g, 8.0 mmol) dissolved in *n*-hexane (~30 ml) containing 0.16 g of benzophenone was irradiated for 12 hr.<sup>15a</sup> Upon work-up according to procedures previously described a dimer (mp 190°) was isolated (100 mg): nmr (deuteriochloroform)  $\tau$  2.69 (m, 8, aromatic), 5.80, 6.41, and 6.6 (s, br, 6, aliphatic).

**Registry No.**—1a, 95-13-6; 5, 25894-22-8; 6, 25894-23-9; 7, 18427-72-0; 8, 25894-25-1; 9, 25957-54-4.

**Acknowledgment.**—We wish to thank the National Science Foundation (Grant GP 9434) and the National Institutes of Health (Grant GM14667) for support of this work. We are also grateful to Astrid Heep for technical assistance.

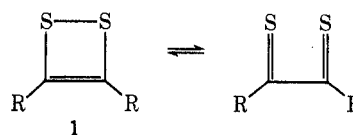
### Monothiobenzil<sup>1,2</sup>

DONALD C. DITTMER\* AND GEORGE E. KUHLMANN

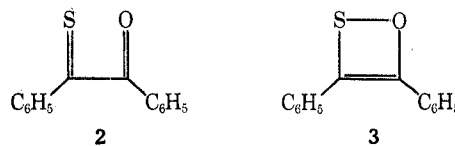
Department of Chemistry, Bowne Hall,  
Syracuse University, Syracuse, New York 13210

Received March 16, 1970

Considerable interest has been shown recently in the interaction of two sulfur atoms or a sulfur and an oxygen atom when they are situated near each other.<sup>3</sup> The interaction of two sulfur atoms on adjacent carbon atoms has been considered theoretically,<sup>4a</sup> and 1,2-



dithietes (1) appear to have some relative stability.<sup>4b</sup> Several molecules with very short S–O intramolecular distances have been investigated.<sup>5</sup> In monothiobenzil,<sup>6</sup> (2), a possibility exists for interaction of sulfur and oxygen, leading in the extreme case to an oxathiete structure, 3.



\* To whom correspondence should be addressed.

(1) This work was aided by the National Science Foundation, Grant GP-5513, for which we are grateful.

(2) For complete details, see G. E. Kuhlmann, Ph.D. Thesis, Syracuse University, 1968.

(3) Y. Mollier, F. Terrier, and N. Lozac'h, *Bull. Soc. Chim. Fr.*, 1778 (1964); G. Claesson and J. Pedersen, *Tetrahedron Lett.*, 3283 (1967); N. Lozac'h and J. Vialle, "The Chemistry of Organic Sulfur Compounds," Vol. 2, N. Kharasch and C. Y. Meyers, Ed., Pergamon Press, London, 1966, p 276; E. I. G. Brown, D. Leaver, and T. J. Rawlings, *Chem. Commun.*, 83 (1969).

(4) (a) G. Bergson, *Ark. Kemi*, 19, 181, 265 (1962); H. E. Simmons, D. C. Blomstrom, and R. D. Vest, *J. Amer. Chem. Soc.*, 84, 4756 (1962); W. Schroth, *Tetrahedron Lett.*, 195 (1965). (b) C. G. Krespan, B. C. McKusick, and T. L. Cairns, *J. Amer. Chem. Soc.*, 82, 1515 (1960).

(5) P. L. Johnson and I. C. Paul, *ibid.*, 91, 781 (1969); J. A. Kapecki and J. E. Baldwin, *ibid.*, 1120 (1969).

(6) D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *ibid.*, 89, 2793 (1967); D. C. Dittmer, G. E. Kuhlmann, and G. C. Levy, *J. Org. Chem.*, 35, 3676 (1970). Although a satisfactory elemental analysis for monothiobenzil could not be obtained, its conversion to a dioxime and hydrogen sulfide establishes its structure.