295 (32,400), 282 (33,500), 273 (32,400); $\lambda_{\max}^{\mathrm{KBr}}$ 7.55 μ; R_f 0.08, 0.13, 0.21, 0.32.

Anal. Calcd for 61:39 $C_{30}H_{18}Br_2$–$C_{30}H_{18}Br_4$: C, 60.86; H, 3.07; Br, 35.97. Found: C, 60.53; H, 3.20; Br, 35.95.

The mass spectrum of mixture A (190° probe temperature) exhibited prominent peaks at 536, 538, 540 ($C_{30}H_{18}Br_2$, P), 456, 458 (P − HBr), 378 (P − 2Br), and 376 (P − 2HBr).

Preparative tlc of mixture A (11 mg) on silica gel afforded 4 mg of orange needles: mp 309–316°; $\lambda_{\max}^{\mathrm{KBr}}$ 5.97 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ 430 μ (4400), 335 (15,500), 321 (15,600), 305 (21,500), 267 (51,000); *m/e* 410.

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42. Found: C, 87.81; H, 4.41.

Chromatography of the hexane-soluble fraction afforded a yellow oil in 23% yield that was a mixture of two components: R_f 0.32, 0.38; $\lambda_{\max}^{\mathrm{Et_2O}}$ 327 mμ (sh, ϵ 11,500), 275 (43,400), 244 (35,800); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 4.5, 7.41 μ; *m/e* 536, 538, 540 ($C_{30}H_{18}Br_2$, P), 457, 459 (P − Br), 378 (base, P − Br_2).

Anal. Calcd for $C_{30}H_{18}Br_2$: C, 66.94; H, 3.37; Br, 29.69. Found: C, 66.52; H, 3.58; Br, 29.84.

Triyne **2** was also isolated in 19% yield.

Reduction of Mixture A.—Sodium, 13 g, was added in small portions to a suspension of 0.3 g (0.56 mmol) of mixture A in 80 ml of refluxing ethanol. After addition of the sodium was complete, the reaction mixture was heated to reflux for 3 hr, diluted with water, and worked up to afford 239 mg of a dark green gum, $\lambda_{\max}^{\mathrm{Et_2O}}$ 273 mμ ($E_{1\,\mathrm{cm}}^{\%1}$ 0.36). Chromatography of this on silica gel afforded 130 mg (61% yield) of a pale oil, $\lambda_{\max}^{\mathrm{Et_2O}}$ 273 mμ ($E_{1\,\mathrm{cm}}^{1\%}$ 0.2). Low voltage mass spectrometry indicated the following composition: mass 384 ($C_{30}H_{24}$), 35%; 386 ($C_{30}H_{26}$), 8%; 388 ($C_{30}H_{28}$), 15%; 390 ($C_{30}H_{30}$), 32%.

Reaction of 2 with Excess Bromine.—Addition of 2.0 g (12.0 mmol) of bromine in 18 ml of chloroform to a stirred solution of 500 mg (1.32 mmol) of **2** in 10 ml of chloroform at 0° gave, after 5-min stirring and work-up, 1.0 mg of a yellow gum. Trituration of the gum with ether afforded 0.66 g of an ether-insoluble yellow solid. Three recrystallizations of this from benzene–hexane afforded 171 mg (19% yield) of a tetrabromide (**4**) as yellow needles: dec pt 200°; $\lambda_{\max}^{\mathrm{MeOH}}$ 340–355 mμ (ϵ 5600), 261 (31,400); R_f 0.32.

Anal. Calcd for $C_{30}H_{18}Br_4$: C, 51.61; H, 2.60; Br, 45.79. Found: C, 51.54; H, 2.56; Br, 45.82.

Recrystallization of the combined mother liquors from the above recrystallization afforded 400 mg of yellow needles: mp 170–185° dec; $\lambda_{\max}^{\mathrm{MeOH}}$ 307 mμ (ϵ 23,200), 274 (30,600), 370 (sh, 2200), 320 (sh, 12,600), 294 (sh, 24,800), 282 (sh, 28,200); R_f 0.1, 0.22, 0.28, 0.33.

Anal. Calcd for 60:40 $C_{30}H_{18}Br_2$–$C_{30}H_{18}Br_4$: C, 60.81; H, 3.06; Br, 36.13. Found: C, 60.35; H, 3.17; Br, 36.45.

Hydrolysis of Tetrabromide 4.—A mixture of 64 mg (0.092 mmol) of **4** and 79 mg (0.47 mmol) of silver acetate in 8 ml of acetic acid was heated under reflux for 4 hr. Water (8 ml) was added and refluxing was continued for 7 hr. The reaction mixture was filtered and the filtrate was worked up to afford 48 mg of red needles: mp 220–230° dec (benzene–hexane); $\lambda_{\max}^{\mathrm{MeOH}}$ 446–466 mμ (ϵ 3400), 261 (51,700); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.87 μ; *m/e* 410.

Anal. Calcd for $C_{30}H_{18}O_2$: C, 87.78; H, 4.42. Found: C, 87.48; H, 4.34.

3-Bromo-2-phenylindenone.—This compound was prepared by heating under reflux a mixture containing 2.2 g (0.01 mol) of 2-phenyl-1,3-indandione in chloroform and 4.3 g (0.016 mol) of phosphorus tribromide. After work-up, the crude product was chromatographed on silica gel and crystallized from hexane to give 3-bromo-2-phenylindenone, mp 73–75° (lit.[16] mp 73–74°), as orange needles in 45% yield.

3,3′-Bi(2-phenyl-1-indenone) (**5**).—A mixture of 197 mg (0.7 mmol) of 3-bromo-2-phenylindenone and 1 g of copper powder[8] in 6 ml of dry dimethylformamide was refluxed under nitrogen for 1 hr. An additional 1 g of copper was added and heating was continued for 3 hr. After addition of 150 ml of water, the mixture was filtered and the filtrate was worked up to afford 157 mg of a red oil. Chromatography of this on silica gel gave 19 mg (13% yield) of red solid, crystallization of which from benzene–hexane afforded 4 mg of **5**: mp 215–232° dec; $\lambda_{\max}^{\mathrm{MeOH}}$ 450–465 mμ (ϵ 3400), 261 (52,200); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.87 μ; *m/e* 410.13178 [$C_{30}H_{18}O_2$ (P) requires 410.1307], 381.12863 [$C_{29}H_{17}O$ (P − HCO) requires 381.1279], 333.09107 [$C_{24}H_{13}O_2$ (P − C_6H_5) requires 333.0916], 273.09408 [$C_{22}H_{12}$ (P − 2CO − C_6H_5) requires 267.09390]. Comparison (ir, mass spectrum) of **5** with the diketone obtained by hydrolysis of tetrabromide **4** showed them to be identical.

Registry No.—**2**, 35324-43-7; **4**, 35324-44-8; **5**, 35324-45-9; 2,2′-diiododiphenylacetylene, 35324-46-0.

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Alkene Isomerization. An Improved One-Step Synthesis of *trans*-Cyclooctene[1]

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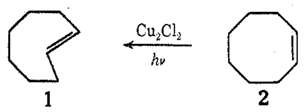
Ever since the pioneering work of Cope,[3] the unusual chemical properties of *trans*-cyclooctene (**1**) have attracted the attention of numerous chemists. In spite of the interest in this useful molecule, the published syntheses require a number of steps and/or proceed in low yield.[4] We would like to report a new procedure by which *trans*-cyclooctene (**1**) may be obtained in gram quanitities *via* one efficient light-induced step from its readily available isomer, *cis*-cyclooctene (**2**).



The isomerization of **2** was achieved by the irradiation of a stirred solution of Cu_2Cl_2 in a 2.6-fold excess of *cis*-cyclooctene at 2537 Å for 24 hr. Unisomerized **2** was removed *in vacuo* and the Cu(I) salts were successively extracted with aqueous ammonia and cyanide. Separation of **1** from **2** was accomplished by taking advantage of the former's solubility in aqueous silver nitrate.[4a] Liberation of the alkene from its silver complex afforded **1** in 19% yield (based on Cu_2Cl_2) in over 99% purity.

This photosensitized isomerization probably succeeds because the greater stability of the *trans*-cyclooctene–Cu_2Cl_2 complex shifts the equilibrium in favor of isomerization. Although other workers have employed Cu_2Cl_2 in the isomerization of alkenes which form stable complexes,[5] our work has demonstrated that prior synthesis and isolation of the Cu(I)–olefin complex is unnecessary. Thus, in addition to its convenience, our procedure allows isomerization of alkenes

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which do not form readily isolable complexes[6] in good yield.[7] Even alkenes which form relatively stable complexes may be isomerized *via* our procedure with clearly superior results. For example, 1,5-*cis,cis*-cyclooctadiene (**3**) can be converted to 1,5-*cis,trans*-cyclooctadiene (**4**) in 30–40% yields. It is interesting to note, however, that Cu_2Br_2 was much less effective than Cu_2Cl_2.

Although the precise role of the Cu(I) salts cannot be specified at this time, we have made several pertinent observations. Irradiation of **1** in pentane in the presence of Cu_2Cl_2 gave an 80:20 mixture of **2** and **1**, respectively. As a result we conclude that the isomerization is reversible and that **1** and **2** and their respective complexes are in equilibrium under conditions of irradiation. It is known that Cu_2Br_2–olefin complexes have an absorption maximum at approximately 245 nm.[8] Irradiation of **2** under our conditions but in the absence of Cu_2Cl_2 failed to produce detectable **1**.[9] Irradiation in the presence of Cu_2Cl_2 at 2537 Å with a low-pressure lamp was far more effective than irradiation with an intense unfiltered broad spectrum medium-pressure lamp. We believe, therefore, that the complex itself is the probable primary absorbing species.

Our results suggest that, in principle, photosensitized cis–trans isomerization should be practical in any case where the respective complexes are on significantly different stability. A wide range of metals and ligands should be investigated in order to extend the generality of these isomerizations.

Experimental Section

Irradiations at 2537 Å were done in a Southern New England Ultraviolet Co. (Middletown, Conn.) "Rayonet" Model RS preparative photochemical reactor. Irradiation at longer wavelengths was carried out using a Hanovia 550-W medium pressure quartz mercury arc lamp equipped with a water-cooled Pyrex immersion well (Ace Glass Co., Vineland, N. J.). Infrared spectra were obtained with a Perkin-Elmer (Norwalk, Conn.) Model 137 Infracord. Analytical gas chromatographs were obtained on a Varian Associates (Palo Alto, Calif.) Aerograph Hy-Fi Model 600-D analytical gas chromatograph using 6 ft × 0.125 in. columns. Peak areas were measured by disc integration.

***trans*-Cyclooctene (1).**—A 60-ml quartz irradiation tube was charged with 25 ml of *cis*-cyclooctene (**2**), (0.18 mol) and 7.0 g of freshly prepared[10] cuprous chloride (0.07 mol). The tube was fitted with a condenser and mercury bubbler and the entire apparatus was flushed with nitrogen. With all the cuprous chloride had dissolved in the olefin, the magnetically stirred mixture was irradiated at 2537 Å for 24 hr. The solution was then evaporated at 1.0 mm to a thick oil. To this oil was added concentrated ammonia and pentane, and it was shaken, decolorized with sodium cyanide, and separated. The aqueous layer was then extracted twice with pentane, and all pentane solutions were combined, dried over $MgSO_4$, and concentrated by distillation to *ca.* 50 ml. The solution was then extracted with 20% aqueous $AgNO_3$ and the aqueous layer was washed once with pentane. Treatment of the aqueous layer with concentrated ammonia followed by three pentane extractions yielded *trans*-cyclooctene in 99% purity (gc, Carbowax 20M). The extracts were dried over $MgSO_4$, concentrated by distillation using a wire gauze column, and finally evaporated at 0°, yield 1.4 g (19% based on Cu_2Cl_2 used) of *trans*-cyclooctene. The infrared spectrum of this material was identical with that of authentic *trans*-cyclooctene. Degassing the reaction mixture failed to change the yield.

Irradiation of *trans*-Cyclooctene (1) with Cuprous Chloride.—To the 60-ml quartz tube arranged as before were added 1.0 g (9.0 mmol) of *trans*-cyclooctene, 2.0 g (0.021 mol) of freshly prepared cuprous chloride, and 10 ml of pentane. The apparatus was flushed with nitrogen and irradiated, with vigorous magnetic stirring, at 2537 Å for 33 hr. Work-up consisted of adding the entire mixture to concentrated ammonia, decolorizing with sodium cyanide, and extracting three times with pentane. Analysis of the pentane extracts by gas chromatography (Carbowax 20M) showed that 80% of the material had been converted back to *cis*-cyclooctene (**2**). Distillation of the pentane extracts, using a wire gauze column, to *ca.* 25 ml, drying over $MgSO_4$, evaporation at 0° to an oil, and distillation of the oil at 55–60° (29 mm) gave 0.95 g (95%) of a mixture of the two cyclooctene isomers. Only traces of any other material were found by gc analysis.

Irradiation of *cis*-Cyclooctene (2) without Cuprous Chloride.—A 60-ml quartz tube equipped with magnetic stirring was charged with 25 ml (20 g, 0.18 mol) of *cis*-cyclooctene. The apparatus was flushed with nitrogen and irradiated at 2537 Å for 24 hr. Analysis by gas chromatography (Carbowax 20M) of the irradiated solution showed no evidence of isomerization. Repeating the experiment with 8 g (10 ml, 0.09 mol) of *cis*-cyclooctene dissolved in 40 ml of pentane again gave no evidence of isomerization.

***cis,trans*-1,5-Cyclooctadiene (4).**—This compound can be prepared from the di-μ-chlorobis(*cis,cis*-1,5-cyclooctadiene)dicopper(I) complex using published procedures (13% yield).[5] A more convenient preparation consisted of adding 5.0 g (0.046 mol) of commercial *cis,cis*-1,5-cyclooctadiene (**3**) followed by 200 ml of reagent grade pentane, 5.0 g (0.05 mol) of commercial cuprous chloride, and 300 ml more of pentane to a 1.5-l. quartz irradiation vessel fitted with a condenser leading to a mercury bubbler. The entire apparatus was flushed with dry nitrogen and the vigorously stirred suspension was irradiated at 2537 Å for 24 hr. The solid material was then filtered off and stored in the dark under N_2 at room temperature. Approximately 45 g of this material (the result of five runs) was worked up by shaking it with pentane and concentrated ammonia until all the solid had dissolved. To the mixture was then added ice and sufficient sodium cyanide to decolorize the solution. The solution was then shaken again and separated. The aqueous layer was then extracted twice more with pentane, and the pentane solutions were combined and dried over $MgSO_4$. Analysis of this solution by gas chromatography (SE-30) showed approximately equal amounts of *cis,cis*-1,5-cyclooctadiene and *cis,trans*-1,5-cyclooctadiene along with a small amount (*ca.* 1%) of *trans,trans*-1,5-cyclooctadiene. The solution was then concentrated by distillation, using a wire gauze column, to *ca.* 200 ml. To this solution was added an equal amount of water containing sufficient $AgNO_3$ (usually 10–13 g was required) to eliminate the product peak from a gas chromatogram of the pentane solution. The aqueous layer was then washed once with pentane and to it was added excess concentrated ammonia in order to liberate the olefin. The mixture was extracted three times with pentane, and the pentane solutions were combined, dried over $MgSO_4$, and concentrated to about 100 ml by distillation of the pentane through a wire gauze column. Analysis of this solution by gas chromatography showed 99% pure *cis,trans*-1,5-cyclooctadiene (**4**) and integration data gave a yield of 8–10 g (30–40%).

Irradiation of *cis,cis*-1,5-Cyclooctadiene (3) with Cuprous Bromide.—A mixture of 7.25 g (0.05 mol) of cuprous bromide, 200 ml of pentane, 5 g (0.046 mol) of *cis,cis*-1,5-cyclooctadiene, and 300 ml more of pentane was placed in a 1.5-l. quartz irradiation vessel. The apparatus was arranged and flushed with nitrogen as before. Using vigorous magnetic stirring, the mixture was irradiated at 2537 Å for 26.0 hr. The reaction mixture was filtered to give 7.4 g of irradiated solid. Working up the solid in the usual way with ammonia and sodium cyanide followed by gc analysis (SE-30) showed that 40% of the complexed material had been converted to *cis,trans*-1,5-cyclooctadiene (**4**), the remainder being starting material. The actual yield, however, of *cis,trans*-cyclooctadiene was 0.045 g (0.9%) from gc data.

Registry No.—*trans*-Cyclooctene, 931-89-5.

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[10] W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1960, pp 142–143. Commercial curpous chloride is also satisfactory.