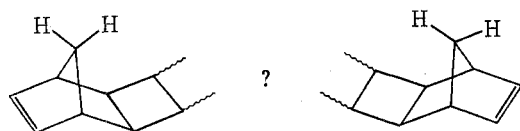


**Table II**  
Relative Concentrations of Products as Obtained from Gc

	Dimer	Trimer
Standard	87 ± 5	0.57 ± 0.04
Fortified expt	200 ± 10	2.50 ± 0.34



The final question as to how these two units are bonded to the central norbornyl fragment was solved by assuming that trimer originates from dimer plus monomer. Since this catalyst makes only exo,trans,exo dimer (I), it was logical to suspect that this dimer was the trimer precursor. Thus if I leads to IV and the two olefin moieties are identical, then exo,trans,exo,trans,exo must describe the stereochemistry of the trimeric compound. In order to test this hypothesis, two parallel experiments were run. Two sets of reaction tubes were charged with identical amounts of catalyst and norbornadiene. Then, to each of the second set of reaction tubes, 0.50 g of exo,trans,exo dimer was added. All the tubes were treated identically in degassing, irradiation, and analysis. The results are shown in Table II. The results of these experiments show a fourfold increase of trimer in the fortified case confirming that dimer I was converted to IV and thereby proving the stereochemistry of the trimer.

These results also prove that nickel catalyzed a mixed coupling between norbornadiene and a norbornene-type molecule.<sup>6</sup> The obvious difference between norbornene and the pseudo norbornene (dimer I) is the cyclobutane ring which must be activating the transannular olefin. This effect is being investigated further.

### Experimental Section

Glc analyses were performed on a Varian Model 1740 chromatograph using a 6 ft, 20% carbowax 20 M on 80–100 mesh Chromosorb W column. Nmr data were collected on Varian A-60 and HA-100<sup>7</sup> spectrometers.

**Correlation of Trimer Preparation and Fortified Experiment. Standard.** To three, 10 × 100 mm Pyrex test tubes containing 0.35 g (0.056 mmol) of bis(triphenylphosphine)dicarbonylnickel(0), 5.00 ml of freshly prepared norbornadiene was added using a vacuum line. These samples were degassed through three freeze-thaw cycles, sealed, and irradiated for 30 hr with Pyrex-filtered<sup>8</sup> light from a Hanovia 450-W mercury arc. The yields for Table II were garnered from glc data.

**Fortified.** To each of three test tubes prepared identically as above, 0.50 g (2.72 mmol) of exo,trans,exo dimer was added. These samples were analyzed and run simultaneously with the three standard samples.

**Preparation of Trimer.** In a typical experiment to prepare trimer IV a 450-W Hanovia mercury lamp equipped with a Pyrex filter, cooling jacket, and a "merry-go-round" sample holder was used to irradiate a sealed-degassed sample containing 6.5 ml of neat norbornadiene and 0.0465 g (7.28 × 10<sup>-2</sup> mmol) of (Ph<sub>3</sub>P)<sub>2</sub>Ni(CO)<sub>2</sub>. A total yield of 31% was obtained after 3 days of irradiation in which 93% was dimer I and 5% was trimer IV. There was a trace of another dimer which was not identified. Purification was effected through fractional sublimation giving white solid, mp 205–206°, m/e 276.

*Anal.* Calcd for C<sub>21</sub>H<sub>24</sub>: C, 91.25; H, 8.75. Found: C, 91.43; H, 8.84.

**Acknowledgment.** The authors are grateful to Cities Service Oil Company for partial support of this work.

**Registry No.**—I, 53166-41-9; IV, 53187-83-0; (Ph<sub>3</sub>P)<sub>2</sub>Ni(CO)<sub>2</sub>, 13007-90-4; norbornadiene, 121-46-0.

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- (4) D. R. Coulson, U.S. Patent 3,760,016.
- (5) All values for nmr resonance positions are reported in δ (ppm).
- (6) Attempts on our part to effect the same reaction with norbornene were unsuccessful.
- (7) Special thanks to the National Science Foundation for providing partial support for a HA-100 for the latter part of this work.
- (8) Appropriate filters were used to ensure that only the metal complex absorbed the light.
- (9) Spectra of dimers I, II, and III were obtained from compounds prepared in some of our previous studies.<sup>3h</sup>

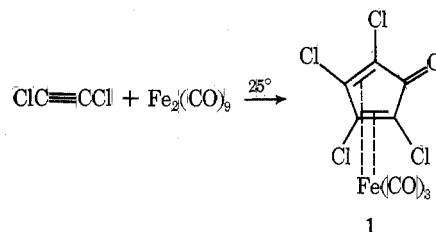
### Tetrachlorocyclopentadienoneiron Tricarbonyl

Carl G. Krespan

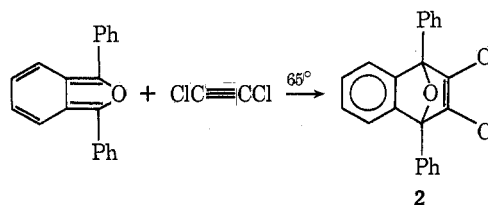
Contribution No. 2186 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received August 22, 1974

Few transition metal complexes of chlorocarbons are known and those with iron as the transition metal have been obtained indirectly by a series of metallation-halogenation reactions.<sup>1</sup> It has now been found that diiron nonacarbonyl reacts readily with dichloroacetylene to form tetrachlorocyclopentadienoneiron tricarbonyl (1) in moderate yield. The yellow-orange complex 1, isolated by chromatography on alumina, is sufficiently stable at its melting point of 101–102° to be melted and remelted without change, and crystalline samples were unchanged on handling in air. The compound is, however, photodegraded in solution, slowly by incidental light and rapidly by irradiation with a low-pressure ultraviolet lamp.



Dichloroacetylene, prepared by the solution method of Siegel, *et al.*,<sup>2</sup> was used as an approximately 20% solution in ether. No explosions were encountered during several such preparations, but suitable precautions against the possibility of violent detonation and toxic vapors should nevertheless be taken. Preparations of dichloroacetylene in ether were routinely monitored by gas chromatography. Although dichloroacetylene is not a reactive dienophile, it could be derivatized easily at atmospheric pressure by Diels-Alder addition to diphenylisobenzofuran to form adduct 2.



An attempt to generate tetrachlorocyclobutadiene from hexachlorocyclobutene and diiron nonacarbonyl gave no products readily elutable from alumina. Reaction of hexachlorocyclobutene with disodium iron tetracarbonyl resulted in a low yield of tetrachlorocyclobutadiene dimer, indicative of the intermediacy of tetrachlorocyclobutadiene, but no indication of a stable chlorocarbon complex with iron was found.

### Experimental Section

**Preparation of Dichloroacetylene.** Solutions of dichloroacetylene in ether were prepared by a literature procedure.<sup>2</sup> As claimed by these authors, the liquid phase synthesis seems to greatly reduce the danger of explosion during preparation, so that  $C_2Cl_2$ -ether solutions were prepared and allowed to react without incident in the present work. In view of the explosion and toxicity hazards, however, dichloroacetylene should be confined to the hood and proper shielding and protective clothing should be used.

A typical synthesis was carried out with a solution of 1000 g of 85% KOH pellets in 700 ml of glycol heated at 140° and stirred with a paddle stirrer. The system was kept under an inert atmosphere by a slow stream of nitrogen (100 cm<sup>3</sup>/min) while a mixture of 656 g (5.0 mol) of trichloroethylene and 370 g (5.0 mol) of ether was added at a rate of 3–5 ml/min over a period of 4–5 hr. Product was collected as formed in a receiver cooled at –80° and topped by a –15° condenser. When the addition was completed and the system purged with nitrogen, the liquid product was decanted from the ice, dried at 25°, and distilled through a Widmer column. The fraction with bp 33–35° was taken after a small foreshot containing volatile impurities was discarded. The  $C_2Cl_2$ -ether cut, 344 g, was assayed by gc with a column of 30% didecyl phthalate on 60–80 mesh Chromosorb W held at 50°. Ether has the shorter retention time on this column.

Using 0.67 as the gc weight factor for ether, three determinations gave 0.87, 0.73, and 0.80 for an average value of 0.80 as the weight factor for dichloroacetylene. With these weight factors, the concentration of  $C_2Cl_2$  in the above preparation was found to be 19%. The conversion was 14% and the yield based on 276 g of unrecovered trichloroethylene was 33% (65.4 g) of  $C_2Cl_2$ .

**Tetrachlorocyclopentadienoneiron Tricarbonyl (1).** A mixture of 9.5 g (0.10 mol) of  $C_2Cl_2$  in ~50 ml of ether and 9.1 g (0.025 mol) of diiron nonacarbonyl was stirred at 25° for 1 day, by which time the initial moderate gas evolution had ceased. Gc indicated the  $C_2Cl_2$  to be more than half gone. Another 9.1 g (0.025 mol) of  $Fe_2(CO)_9$  was added and the mixture was stirred another day. Only a trace of  $C_2Cl_2$  remained. The dark mixture was filtered and the solid extracted several times with ether. Evaporation of the combined ether solutions to 50° (0.5 mm) gave a mixture of crystals and amorphous solid as residue. This residue was dissolved in dry benzene, filtered, and chromatographed on an 8.5 in. × 1.5 in. column of Woelm neutral alumina. Elution with 1:1 benzene-pentane rapidly removed 0.68 g (7%) of hexachlorobenzene, mp 223.5–225.5° after recrystallization from benzene, identified by comparison of its ir spectrum with that of a known sample.

Elution with tetrahydrofuran gave 1.5 g of yellow-orange crystals, mp 101–102°. Further elution with 3:1 tetrahydrofuran-methanol gave another 3.3 g of crystals, mp 100–102°, followed closely by a mixture of crystals and amorphous dark material. The combined crops of product, 4.8 g, are 27% tetrachlorocyclopentadienoneiron tricarbonyl. An analytical sample was recrystallized from pentane: mp 101–102°; ir (KBr) 4.73 and 4.85 (Fe–CO), 5.78 (sh) and 5.94 (conjugated C=O), 7.27,  $\mu$  (coordinated  $CCl=CCl$ ).

*Anal.* Calcd for  $C_8Cl_4FeO_4$ : C, 26.86; Cl, 39.64; Fe, 15.61; mol wt, 357.7. Found: C, 26.94; Cl, 39.39; Fe, 15.70; mol wt, 351 (vp osmometry, PhH at 37°).

**Diels-Alder Addition to Dichloroacetylene.** At 25–65°,  $C_2Cl_2$  undergoes Diels-Alder addition to only the most reactive dienes. Thus, no reaction was detected with tetraphenylcyclohexene at 65°, and a very slow oxygen-initiated polymerization to  $C_2Cl_2$ -diene- $O_2$  terpolymer occurred with 2,3-dimethylbutadiene at 35°. However, 1,3-diphenylisobenzofuran reacted readily with  $C_2Cl_2$  at 65°.

A solution of 1.35 g (0.005 mol) of 1,3-diphenylisobenzofuran and 1.9 g (0.02 mol) of  $C_2Cl_2$  in ~15 ml of ether and 50 ml of dry benzene was refluxed (65°) for 3 days, during which time the color lightened after 3–4 hr, and then darkened. Solvents were removed, the residue was extracted with hexane, and the hexane solution was concentrated to give 0.45 g of nearly colorless crystals, mp 134–135°. A second crop, 0.71 g, mp 132–134°, raised the total of 1.16 g (64%)

of 2,3-dichloro-1,4-diphenyl-1,4-epoxynaphthalene (2). A sample was recrystallized from hexane for analysis: mp 134.5–135°; ir (KBr) 3.26 (=CH), 6.22 and 6.67 (aromatic C=C), 9.0 and 9.9 (may be COC), 13 and 14  $\mu$  (mono- and disubstituted aromatic).

*Anal.* Calcd for  $C_{22}H_{14}Cl_2O$ : C, 72.34; H, 3.86; Cl, 19.41. Found: C, 72.69; H, 4.17; Cl, 19.43.

Cyclopentadiene did not react with  $C_2Cl_2$  in 1 day at 25°, but Diels-Alder addition was observed at 100° for 15 hr. Distillation of the 100° reaction mixture gave, in addition to tars, a low yield of 2,3-dichlorobicycloheptadiene<sup>3</sup> codistilling at ca. 68° (22 mm) with dicyclopentadiene. The components of the mixture were identified by ir, nmr, and gc-mass spectrometry.

**Tetrachlorocyclobutadiene Dimer.**<sup>4</sup> A number of highly chlorinated olefins were exposed to diiron nonacarbonyl and to disodium iron tetracarbonyl. In some cases, little interaction occurred at 25–50°. In others, any iron-chlorocarbon complexes which may have been formed were readily decomposed.

Reaction of  $Fe_2(CO)_9$  with hexachlorocyclopentadiene occurred readily at 25° to give 19% of decachlorodicyclopentadienyl as the only product isolated by chromatography. A related compound with no allylic chlorine, 5,5-dimethoxytetrachlorocyclopentadiene, did not react readily with  $Fe_2(CO)_9$  at 50°. Similarly, the diene system in tetrachloro- $\alpha$ -pyrone did not appear to react with  $Fe_2(CO)_9$  at 25–50°, and hexachlorocyclobutene reacted poorly.

A more nucleophilic reagent, disodium iron tetracarbonyl, reacted with hexachlorocyclopentadiene at 0–25° with formation of a black, amorphous insoluble solid. With hexachlorocyclobutene, disodium iron tetracarbonyl reacted exothermically to give (after chromatography and recrystallization) 5% of tetrachlorocyclobutadiene dimer, mp 160.5–161.5°, after recrystallization from methylene chloride-hexane.

*Anal.* Calcd for  $C_8Cl_8$ : C, 25.31; Cl, 74.69. Found: C, 25.72; Cl, 74.24.

The ir spectrum corresponded to that reported in the literature,<sup>4</sup> as did the melting point.

**Registry No.**—1, 53336-51-9; 2, 53336-59-7; dichloroacetylene, 7572-29-4; diiron nonacarbonyl, 20982-74-5; 1,3-diphenylisobenzofuran, 5471-63-6; hexachlorocyclopentadiene, 77-47-4; disodium iron tetracarbonyl, 14878-31-0; tetrachlorobutadiene dimer, 53336-52-0.

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### Synthesis of 1,4-Dihydro-1,4-dimethyl-1,4-epoxynaphthalene and Conversion to 1,4-Dimethyl-1,2,3,4-tetrahydronaphthalene and *o*-Diacylbenzene<sup>1</sup>

Melvin S. Newman,\* Hemalata M. Dali,<sup>2</sup> and William M. Hung<sup>3</sup>

*Department of Chemistry, The Ohio State University, Columbus, Ohio 43210*

*Received August 29, 1974*

Compounds of the type 1,4-dihydro-1,4-epoxynaphthalene (1) are of synthetic interest because they can be synthesized from the reaction of a benzyne with a furan<sup>4</sup> and transformed into a variety of naphthalene derivatives in good yields by relatively simple experimental procedures. For example, the parent 1 (R = R' = H) was reduced to the tetrahydro derivative 3 (R = R' = H), which on treatment with methanolic acid yielded naphthalene 4 (R = R' = H) in 90% yield.<sup>5</sup> Obviously, a variety of 1-monosubstituted and 1,4-disubstituted naphthalenes are accessible by this route. By more involved chemistry, the availability of the