# Chemistry of 1,2:5,6-Dibenzocyclooctatetraene Dianion

Thomas S. Cantrell*

*Chemistry Department, American University, Washington, D.C. 20016*

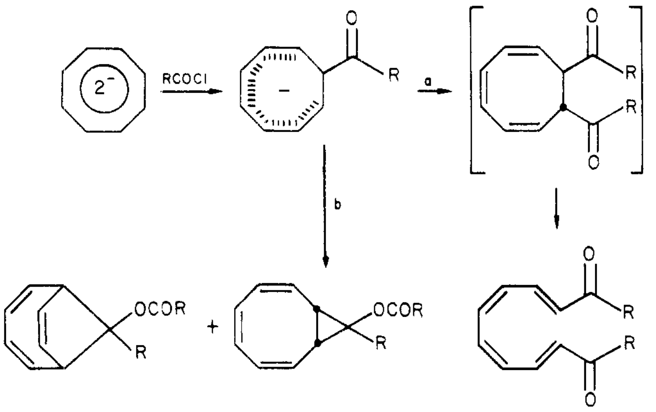
James V. Silverton

*Laboratory of Chemistry, National Heart, Lung, and Blood Institute, National Institutes of Health, Bethesda, Maryland 20205*

*Received May 14, 1979*

The reactions of *sym*-dibenzocyclooctatetraene dianion (2) with carbon dioxide, acetyl chloride, acetone, benzoyl chloride, acetaldehyde, diphenyldichloromethane, and benzyl chloride have been investigated. Carboxylation gave the predictable mixture of trans and cis $\alpha,\beta$-dicarboxylic acids, the latter in the form of its anhydride. Condensation with 1 mol of acetyl chloride led to the 1:1 product, ketone **10**, resulting from rapid intramolecular proton transfer in the intermediate monoanion, rather than intramolecular alkylation as in the parent nonannulated COT dianion. Reaction with acetone gave a 1:1 product, whereas the title dianion behaved as an electron source toward benzoyl chloride and the remaining substrates listed above. The structure of *cis*-bis[(benzoyl)oxy]stilbene, one of the two reduction products from **2** and benzoyl chloride, was established by single-crystal X-ray analysis. The X-ray results were used as a test of a new method of treating "unobserved" reflections.

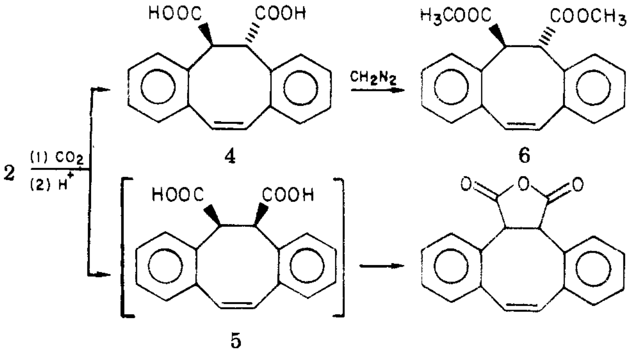
Cyclooctatetraene dianion was the first reported 10-electron monocyclic species to exhibit aromaticity.[1] The chemistry of cyclooctatetraene dianion is rich with fascinating processes which are interesting in themselves and which provide access to structurally interesting and useful products.[2] Alkylation is straightforward, yielding 1,2- and 1,4-products.[3] With acyl halides, COT dianion behaves as a dicarbanionic reagent to give (a) 1,8-diacylloctatetraenes, the result of electrocyclic ring opening of initially produced 1,2-diacyl-3,5,7-cyclooctatrienes and (b) bicyclic compounds of the type shown in eq 1.[4]



(1)

**1,2:5,6-Dibenzocyclooctatetraene.** Published investigations of the chemical behavior of 1,2:5,6-dibenzocyclooctatetraene (1) indicate that this derivative is much less prone than COT to undergo the diverse rearrangements that are so characteristic of COT.[5] Reaction with electrophiles such as bromine and chlorine occurs in a rather sedate manner to afford simple addition products. The dianion (2) of this bis-annulated derivative, also called *sym*-dibenzocyclooctatetraene, has been prepared by alkali metal reduction of the hydrocarbon; analysis of the $^1$H NMR spectrum of **2** indicates the existence of a ring

Scheme I



current and, hence, of a delocalized aromatic system.[6] Protonation of the dianion gave the expected 3,4-dihydrodibenzocyclooctatetraene. Electrochemical reduction in tetrahydrofuran gave only radical monoanions; in the absence of appropriate metal counterions the dianions were not formed.[7] Still other investigators found, however, that dianion formation did occur when electrochemical reduction was performed in dimethylformamide containing supporting electrolytes.[8]

It was deemed worthwhile by the present authors to examine the reactions of **2** with electrophiles. It seemed probable that the reaction course would prove to be different from that of the parent nonannualted COT dianion, since reaction in a 1,4-manner would result in disruption of the sextet of $\pi$ electrons of at least one of the two fused benzene rings, whereas vicinal reaction could lead to products retaining both of these $\pi$ systems intact, with consequent increased stability. There was also the enticing possibility that novel processes not observed with the parent system might ensue. In fact, one such new pathway was observed and is described, together with the other results obtained, herein.

*sym*-Dibenzocyclooctatetraene dianion (**2**, DBCOTDA) was generated in tetrahydrofuran by stirring 0.05–0.08 M solutions of DBCOT with excess potassium under argon

---

(1) Lloyd, D. "Carbocyclic Nonbenzenoid Aromatic Compounds"; Elsevier: New York, 1967; Chapter 7.

(2) Paquette, L. A. *Tetrahedron* **1976**, *32*, 2855–83.

(3) Conrow, K. H.; Bak, D. A. *J. Org. Chem.* **1966**, *31*, 3958–62.

(4) Cantrell, T. S.; Shechter, H. *J. Am. Chem. Soc.* **1967**, *89*, 5867–77.

(5) (a) Cava, M. P.; Erickson, B. W.; Pohl, R. J.; Fraenkel, G. *Tetrahedron* **1962**, *18*, 1005–12. (b) Avram, M.; Dinulescu, I. G.; Dinu, D.; Mateesu, G.; Nenitzescu, C. D. *Ibid.* **1963**, *19*, 309–19.

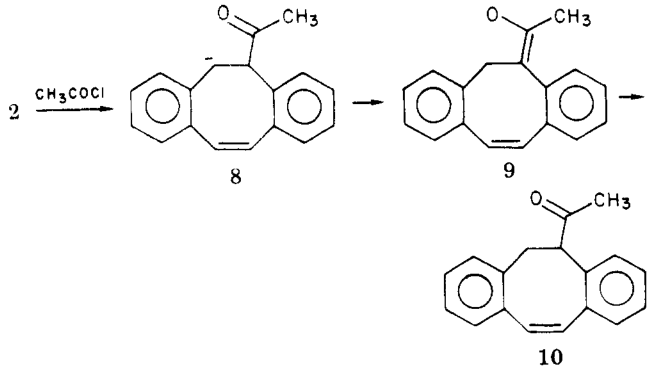
(6) (a) Katz, T. J.; Yoshida, M.; Siew, L. C. *J. Am. Chem. Soc.* **1965**, *87*, 4516–21. (b) Gunther, H.; Gunther, M. E.; Mondeska, D.; Schmickler, H. *Justus Liebigs Ann. Chem.* **1978**, 165–76.

(7) Anderson, L. B.; Paquette, L. A. *J. Am. Chem. Soc.* **1972**, *94*, 4915–22.

(8) Kojima, H.; Bard, A. J.; Wong, H. N. C.; Sondheimer, F. *J. Am. Chem. Soc.* **1976**, *98*, 5560–2.

0022-3263/79/1944-4477$01.00/0

Scheme II

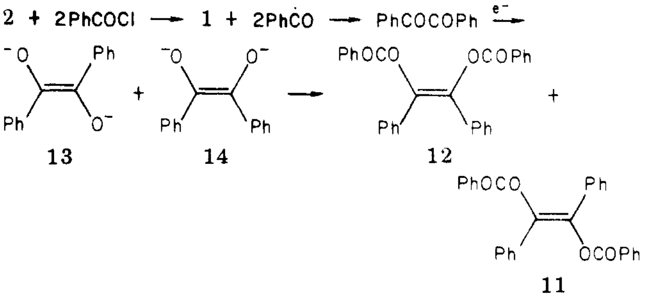


at 0–10 °C. Protonation of dark red solutions of **2** thus obtained by addition of methanol or THF–$H_2O$ gave 3,4-dihydro-1,2:5,6-dibenzocyclooctatetraene, in agreement with the results of Katz et al.[6a] Carbonation of solutions of **2** (Scheme I) produced a mixture of the dicarboxylic acids **4** and **5**. Extraction of the reaction mixture with aqueous base and acidification of the extracts gave first **7**, the anhydride of **5** (44%), and, after concentration of the extracts, the more soluble trans dicarboxylic acid **4**, mp 217 °C, in 27% yield. For characterization, the very slightly soluble **4** was converted via diazomethane to the dimethyl ester **6**, mp 172 °C. The structure of **6** was evident from its NMR spectrum, which exhibited signals at $\delta$ 7.2 (8 H, m), 7.0 (2 H, s), 4.95 (2 H, s), and 3.72 (6 H, s), and from the mass spectral parent peak at *m/e* 322.

Prior to actual isolation of the diacid **4**, the anhydride **7** was obtained as a gum which slowly crystallized. Attempts to isolate the free cis dicarboxylic acid (**5**) were fruitless, a property in accordance with the structural assignment. The great propensity for spontaneous anhydride formation on the part of similar rigid cis 1,2-dicarboxylic acids, e.g., *cis*-dimethylmaleic acid, has been observed by others.[9] Compound **7** was characterized via its infrared, NMR, and mass spectra (see Experimental Section).

In contrast to the multiple reaction paths exhibited by nonannulated cyclooctatetraene dianion upon treatment with acyl halides,[4] reaction of **2** with acetyl chloride (Scheme II) gave only the 1:1 adduct **10** (46%), whose structure was apparent from its spectral properties, including an ABX pattern in the $^1H$ NMR spectrum (at $\delta$ 4.38, 3.69, and 3.12 ($J_{AM}$ = 6.8, $J_{AX}$ = 11.4, $J_{MX}$ = 14 Hz)), an IR carbonyl band at 1709 cm$^{-1}$, and an ultraviolet maximum consistent with a *cis*-stilbene chromophore (UV $\lambda_{max}$ 249 nm, $\epsilon$ 5200). Product **10** most likely arises as shown, via an initial monoacylation of **2** to form the monocarbanion **8** which, instead of undergoing intramolecular alkylation, as does COTDA, prefers the intramolecular proton transfer shown, yielding enolate ion **9**, which after aqueous workup furnishes ketone **10**. This behavior of **2** is evidently a reflection of the greater basicity and lower stability of **2**, compared to the case for cyclooctatetraene dianion, and consequently, the lower stability and greater reactivity of monoanion **8**, as compared to the case for the corresponding monoanion derived from acylation of nonannulated COT. The reaction of COT dianion itself was repeated and the reaction mixture was carefully examined for the presence of monoacylcyclooctatrienes analogous to the dibenzo compound **10**. The search proved to be fruitless.

Scheme III



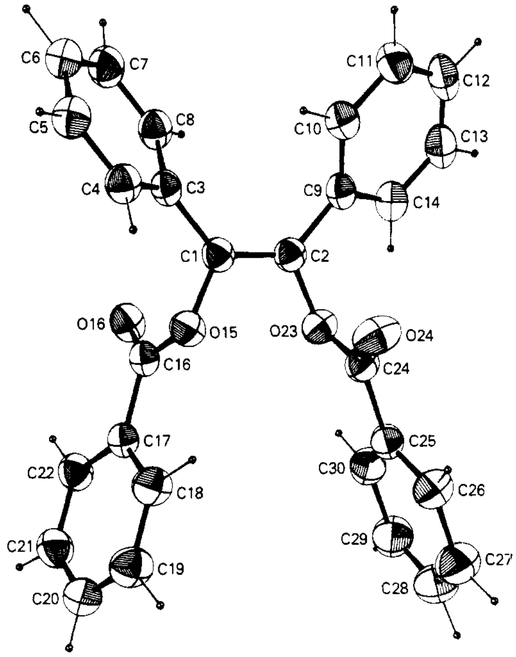


**Figure 1.** ORTEP drawing of **12** in its crystal conformation.

Reaction of **2** with benzoyl chloride (Scheme III) took a different course, furnishing the trans and cis isomers of 1,2-bis[(benzoyl)oxy]stilbene, **11** and **12**, in 31 and 20% yields, respectively, as well as recovered **1**. Here the dianion **2** has simply functioned as an electron-transfer agent and given the combination product of two benzoyl radicals, benzil, which is immediately further reduced, either by more **2** or, equally likely, by the excess potassium metal present. The mixture of enediolate dianions thus formed is finally benzoylated to **11** and **12**. Other organometallic species, e.g., lithium triphenylstannide, reduce benzoyl chloride in the same way to give **11** and **12**.[10]

Previous workers had assigned the geometries of **11** and **12** on the basis of the magnitude of the dipole moments for the two isomers, on the relative melting points (most *trans*-stilbenes have considerably higher melting points than the corresponding *cis* isomers), and on the ultraviolet spectra (the trans isomers usually exhibit an absorption maximum at longer wavelength and of greater intensity).[11] However, these parameters are not completely reliable for making assignments of geometry, especially for $\alpha,\alpha'$-disubstituted stilbenes. In the case of $\alpha,\alpha'$-dimethylstilbene and $\alpha,\alpha'$-dinitrostilbene, the absorption maximum of the cis isomer is at longer wavelength than that of the trans isomer.[12] It seemed desirable to put the assignments on

---

(9) (a) Anschutz, R. *Justus Liebigs Ann. Chem.* **1889**, *254*, 168–88. (b) Eliel, E. L. "Stereochemistry of Carbon Compounds"; McGraw-Hill: New York, 1962; p 196.

(10) Shirai, H.; Sato, Y.; Niwa, M. *Nippon Yakagawu Zasshi* **1970**, *90*, 59–75; *Chem. Abstr.* **1971**.

(11) (a) Bauld, N. L. *J. Am. Chem. Soc.* **1962**, *84*, 4345–7 and references therein. (b) *Ibid.* **1965**, *87*, 4788–91. (c) Fieser, L. F. *J. Chem. Educ.* **1954**, *31*, 291–303.

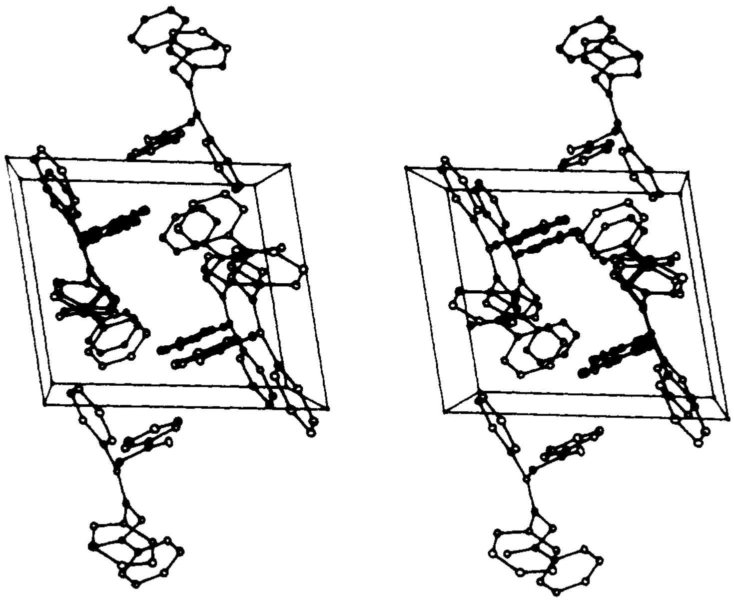


**Figure 2.** Packing diagram for **12**.

Table I. Bond Lengths (Å) for the Heavier Atoms

| | | | |
|---|---|---|---|
| C(1)-C(2) | 1.337 (3) | C(1)-C(3) | 1.474 (3) |
| C(1)-O(15) | 1.406 (3) | C(2)-C(9) | 1.469 (3) |
| C(2)-O(23) | 1.412 (3) | C(3)-C(4) | 1.389 (3) |
| C(4)-C(5) | 1.378 (4) | C(5)-C(6) | 1.376 (4) |
| C(6)-C(7) | 1.379 (4) | C(7)-C(8) | 1.381 (4) |
| C(8)-C(3) | 1.392 (3) | C(9)-C(10) | 1.388 (4) |
| C(9)-C(14) | 1.398 (4) | C(10)-C(11) | 1.384 (4) |
| C(11)-C(12) | 1.380 (4) | C(12)-C(13) | 1.384 (5) |
| C(13)-C(14) | 1.375 (4) | O(15)-C(16) | 1.361 (2) |
| C(16)-O(16) | 1.203 (2) | C(16)-C(17) | 1.478 (3) |
| C(17)-C(18) | 1.380 (3) | C(17)-C(22) | 1.385 (3) |
| C(18)-C(19) | 1.391 (4) | C(19)-C(20) | 1.361 (3) |
| C(20)-C(21) | 1.382 (4) | C(21)-C(22) | 1.382 (4) |
| O(23)-C(24) | 1.363 (2) | C(24)-O(24) | 1.194 (3) |
| C(24)-C(25) | 1.480 (3) | C(25)-C(26) | 1.382 (3) |
| C(25)-C(30) | 1.388 (4) | C(26)-C(27) | 1.390 (4) |
| C(27)-C(28) | 1.362 (5) | C(28)-C(29) | 1.369 (6) |
| C(29)-C(30) | 1.401 (4) | | |

Table II. Bond Angles (deg) for the Heavier Atoms[a]

| | | | |
|---|---|---|---|
| C(2)-C(1)-C(3) | 129.5 | C(2)-C(1)-O(15) | 115.7 |
| C(3)-C(1)-O(15) | 114.6 | C(1)-C(2)-C(9) | 130.8 |
| C(1)-C(2)-O(23) | 115.3 | C(9)-C(2)-O(23) | 113.9 |
| C(1)-C(3)-C(4) | 119.7 | C(1)-C(3)-C(8) | 122.1 |
| C(4)-C(3)-C(8) | 118.2 | C(3)-C(4)-C(5) | 121.3 |
| C(4)-C(5)-C(6) | 119.9 | C(5)-C(6)-C(7) | 119.6 |
| C(6)-C(7)-C(8) | 120.6 | C(3)-C(8)-C(7) | 120.3 |
| C(2)-C(9)-C(10) | 122.4 | C(2)-C(9)-C(14) | 119.1 |
| C(10)-C(9)-C(14) | 118.4 | C(9)-C(10)-C(11) | 120.6 |
| C(10)-C(11)-C(12) | 120.5 | C(13)-C(12)-C(11) | 119.4 |
| C(12)-C(13)-C(14) | 120.4 | C(9)-C(14)-C(13) | 120.7 |
| C(1)-O(15)-C(16) | 115.1 | O(15)-C(16)-O(16) | 122.2 |
| O(15)-C(16)-C(17) | 112.5 | O(16)-C(16)-C(17) | 125.3 |
| C(16)-C(17)-C(18) | 122.5 | C(16)-C(17)-C(22) | 118.1 |
| C(18)-C(17)-C(22) | 119.4 | C(17)-C(18)-C(19) | 119.8 |
| C(18)-C(19)-C(20) | 120.5 | C(19)-C(20)-C(21) | 120.1 |
| C(20)-C(21)-C(22) | 119.8 | C(17)-C(22)-C(21) | 120.4 |
| C(2)-O(23)-C(24) | 114.9 | O(23)-C(24)-O(24) | 122.1 |
| O(23)-C(24)-C(25) | 112.6 | O(24)-C(24)-C(25) | 125.3 |
| C(24)-C(25)-C(26) | 117.4 | C(24)-C(25)-C(30) | 122.2 |
| C(26)-C(25)-C(30) | 120.4 | C(25)-C(26)-C(27) | 120.2 |
| C(26)-C(27)-C(28) | 119.3 | C(27)-C(28)-C(29) | 121.4 |
| C(28)-C(29)-C(30) | 120.2 | C(25)-C(30)-C(29) | 118.5 |

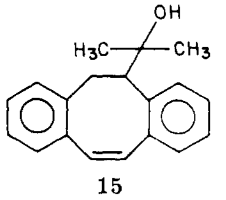
[a] Esd's are less than or equal to 0.3°.

a more secure basis, and accordingly, a single-crystal X-ray structure determination was undertaken. The higher melting trans isomer formed silky needles which were unsuitable for X-ray work. However, the cis isomer, **12**, formed chunky prisms (from acetone) of acceptable properties. The ORTEP projection is shown in Figure 1. From this result, the structure is indeed cis, as predicted on the basis of melting points, etc.

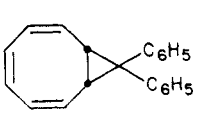
The molecular packing is shown in Figure 2. There are no unusually short intermolecular contacts and the packing, as betokened by the density, seems fairly efficient. The interatomic distances and angles (Tables I and II) are consistent with the chemical structure and no values appear worthy of comment. Since the molecule is not planar, there should be no extended conjugation and the bond lengths are as might be expected. The average bond lengths are essentially the same in all four benzene rings and individual variations can probably be accounted for by rigid-body vibration of the rings. The anisotropic thermal parameters are relatively large for some of the peripheral atoms but, since there can be no hydrogen bonds in this crystal, the values are not unreasonable.

The nonplanarity of the molecule explains the choice of space group since, were the molecule to possess the mirror plane of the chemical formula and thus crystallize in $P2_1/m$, there would be many close contacts of hydrogen atoms.

Condensation of **2** with acetone gave alcohol **15** in 38%



**15**



**16**

yield. The structure followed from the usual spectral data, in particular an ABX pattern in the 220-MHz NMR spectrum at $\delta$ 3.28–2.90.

In the case of **15**, intramolecular proton transfer in an intermediate monoanion seems unlikely to be responsible for the lack of formation of 2:1 products from acetone and **2**, as was observed with the parent COT dianion.[13] One possible explanation is that the reactivity of the monoan-

---

(12) (a) Suzuko, H. *Bull. Chem. Soc. Jpn.* **1952**, *25*, 145–50. (b) Stevens, T. E.; Freeman, J. P. *J. Org. Chem.* **1958**, *23*, 136–41.

(13) Cantrell, T. S.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 5877–84.

ions produced after reaction of **2** with one molecule of substrate is considerably greater than that of the corresponding anions formed in reactions of the parent nonannulated COT. This difference leads to rapid proton transfer, intramolecular in the case of reaction with acetyl chloride and intermolecular (from traces of weak acids present which are not reactive enough to protonate the dianion) in the case of condensation with acetone.

Estimations of the aromatic character of **2** by calculation of so-called *Q* values from NMR spectral parameters indicate that **2** is definitely a delocalized aromatic system with a diatropic ring current.[6b] However, benzannelation is known to reduce the "aromaticity" and stability of nonbenzenoid aromatic systems, particularly in cases where the fused benzene ring(s) results in a lowering of symmetry of the resuling species.[14] It is possible that decreased aromatic character of **2** (as compared to that of the parent cyclooctatetraene dianion) and consequent increased basicity lie behind the differences in behavior presently observed.

The lower stability and increased electron-donating power of **2** are shown in its behavior with other substrates. Reaction with diphenyldichloromethane gave only recovered **1** and tetraphenylethylene, the result of electron transfer from **2** to the dihalide. In a separate experiment it was found that the parent cyclooctatetraene dianion and the same dihalide gave 21% of tetraphenylethylene, but as well, 57% of condensation product 9,9-diphenylbicyclo[6.1.0]nonatriene (**16**). Cyclooctatetraene dianion itself undergoes analogous condensations with dichloromethane and carbon tetrachloride;[15] however, **2** and these dihalides gave only recovered **1**.

## Experimental Section

NMR spectra were obtained on Varian A-60A and HR-220 instruments. IR spectra were obtained on a Perkin-Elmer 397 spectrometer and mass spectra on a Hitachi Perkin-Elmer RMU-6E instrument. Chromatography was performed with 200–350-mesh silica gel. Melting points were determined on a Fisher-Johns block and are uncorrected.

**Carbonation of 2.** To a solution of **1** (1.0 g, 0.50 mmol) in THF (100 mL) was added freshly cut potassium metal (0.8 g), and the resulting suspension was stirred under argon at 0–5 °C for 36 h. The resulting dark red solution was filtered under argon pressure through a plug of glass wool to remove excess potassium and was poured onto powdered dry ice. After the reaction mixture had come to room temperature, water and ether were added and the layers then separated. From the ether layer there was recovered 0.32 g of unchanged **1**. The aqueous layer was slowly poured into cold 10% hydrochloric acid, resulting in the appearance of a white gum. After standing in the cold overnight, the gum crystallized. Filtration of the resulting white solid and recrystallization by concentration of dilute solutions in acetone gave pure anhydride **7** as chunky white prisms: mp 246–247.5 °C dec (0.46 g, 51% based on unrecovered **1**); IR (KBr) $\nu_{max}$ 1858 (w), 1786 (s) cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 7.20 (8 H, m), 6.98 (2 H, s), 4.64 (2 H, s); *m/e* 276 (chemiionization, parent), 232. Anal. ($C_{18}H_{12}O_3$): C, H.

The mother liquor from filtration of anhydride **7** was concentrated under reduced pressure to ca. one-fourth its original volume and cooled. The resulting white solid was recrystallized by stirring it in boiling benzene and adding hot THF until the solid just dissolved. Cooling the resulting solution overnight at −20 °C and filtration gave dicarboxylic acid **4** (0.28 g, 22%) as fluffy white needles: mp 217–218 °C; IR 3400–2600 (br), 1700 (s) cm$^{-1}$; mass spectrum *m/e* 294 (46), 276 (25), 250 (20), 248 (54), 204 (82), 203 (100). Anal. ($C_{18}H_{14}O_4$): C, H.

An ether solution of diacid **4** was treated with a slight excess of ethereal diazomethane. Evaporation of the ether and recrystallization of the residue from benzene–hexane gave the corresponding dimethyl ester **6** as colorless chunky prisms: mp 172–173 °C; IR (KBr) 1730 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 7.18 (8 H, m), 7.02 (2 H, s), 4.95 (2 H, s), 3.72 (6 H, s); UV $\lambda_{max}$ 250 nm ($\epsilon$ 6000); *m/e* 322 (P, 20), 261 (100), 203 (79). Anal. ($C_{20}H_{18}O_4$): C, H.

**Reaction of 2 with Acetyl Chloride.** A solution of **2** prepared from 1.5 g of **1** in 150 mL of THF was added dropwise under argon to acetyl chloride (3 g) in THF at −10 to 0 °C and then stirred for an additional hour. The reaction mixture was poured into water, the mixture was extracted three times with ether, and the combined organic layers were washed with 5% bicarbonate and water and dried (MgSO$_4$). Evaporation of the ether gave a syrupy residue which was chromatographed on a 2.5 × 35 cm column of silica gel and eluted with 200 mL each of 5:1 hexane–benzene, 3:1, 2:1, and 1:1 hexane–benzene, 5:1 benzene–chloroform, and 3:1 benzene–chloroform. Fractions of 125 mL were collected. Fractions 7–9 (out of 12) solidified on standing overnight and were combined and recrystallized from ca. 3:1 pentane–dichloromethane at −20 °C. There was thus obtained ketone **10** as colorless prisms: mp 90–91.5 °C (0.36 g, 28%); IR (KBr) 1709 cm$^{-1}$; NMR (CDCl$_3$) $\delta$ 7.3–7.1 (8 H, m), 2.92 (2 H, s), 4.38, 3.69, and 3.12 (AMX, $J_{AM}$ = 6.8, $J_{AX}$ = 11.4, $J_{MX}$ = 14 Hz), 7.95 (3 H, s); *m/e* 246 (28), 205 (100), 204 (32). Anal. ($C_{18}H_{16}O$): C, H.

**Condensation of 2 with Acetone.** A solution of **2**, prepared in the usual way from 1.0 g of **1** and 0.6 g of freshly cut potassium, was added under argon to 3.0 g of reagent grade acetone in THF at −10 °C. The reaction mixture was stirred for 3 h, warmed to 20 °C, and poured onto ice. Workup by chromatography on a 20 × 350 mm column of silica gel gave the following: (1) 0.4 g of recovered **1**, eluted with 2:1 and 1:1 hexane–benzene; (2) alcohol **13** (from the fractions eluted with benzene and 10:1 benzene–chloroform) as an oil which crystallized on standing overnight. Recrystallization from 3:1 pentane–dichloromethane gave tiny white prisms: mp 119–120.5 °C (0.28 g, 38% based on unrecovered **1**); IR (KBr) 3590 (m), 3530 (m), 1125, 1100, 1068 cm$^{-1}$; NMR (CDCl$_3$, 220 MHz) $\delta$ 7.1 (8 H, m), 6.87 (2 H, AB, $J$ = 11.8 Hz), 3.44–2.98 (AMX, $J$ = 11.0, 10.8, 7.1 Hz), 1.41 (1 H, s, br), 1.30 and 1.22 (3 H each, s); mass spectrum *m/e* (chemiionization) 264 (P, 70), 206 (100). Anal. ($C_{18}H_{20}O$): C, H.

**Reaction of 2 with Diphenyldichloromethane.** A solution of **2**, prepared in the usual way from 1.0 g of **1**, was added under argon to 3.0 g of diphenyldichloromethane in 30 mL of THF at −10 °C. The red color of the solution of **2** was quenched on contact with the alkyl halide. The reaction mixture was poured into water and the resulting suspension extracted twice with ether. The ether extracts were combined, washed with water, dried, and evaporated to give a pale yellow semicrystalline mass which was triturated with 1:1 benzene–hexane. Cooling in ice and filtration gave a white solid which was recrystallized from benzene–hexane to afford tetraphenylethylene (1.6 g), whose melting point and mixture melting point (227–228 °C) were identical with that of an authentic sample. Chromatography of the mother liquors on silica gel and elution with hexane and mixtures of benzene and hexane gave an additional 0.5 g of tetraphenylethylene and, in earlier fractions, 0.62 g of recovered **1**.

**Reaction of 2 with Benzoyl Chloride.** A solution of **2** prepared from 1.0 g of **1** in the usual way was added to 3.0 g of benzoyl chloride in THF at 0 °C; chromatography of the product mixture on silica gel gave, first, silky white needles of **11**, mp 181–182 °C (31%), followed in later fractions by flat white prisms of **12**, mp 157–158 °C (20%).

**Reaction of Cyclooctatetraene Dianion with Diphenyldichloromethane.** A solution of dilithium cyclooctatetraenide in 90:10 ether–THF was prepared in the manner previously described[4] from 5.2 g of COT and 1.0 g of lithium shavings. This solution was added under argon dropwise to 2.8 g of diphenyldichloromethane in 30 mL of dry THF at 0 °C and stirred for 2 h while warming to room temperature. The reaction mixture was poured into ice water and extracted with three 50-mL portions of ether. The combined organic layers were washed twice with water, dried, and evaporated. Trituration of the resulting yellow

---

[14] (a) Iyoda, M.; Morigari, M.; Nakagawa, M. *Tetrahedron Lett.* **1974**, 3627–30. (b) Yasuhara, A.; Satake, T.; Iyoda, M.; Nakagawa, M. *Ibid.* **1975**, 895–8. (c) Yasuhara, A.; Iyoda, M.; Satake, T.; Nakagawa, M. *Ibid.* **1975**, 3931–4. (d) Mitchell, R. H.; Carruthers, R. J.; Mazuch, M. *J. Am. Chem. Soc.* **1978**, *100*, 1007–8. (e) Otsubo, T.; Gray, R.; Boekelheide, V. *Ibid.* **1978**, *100*, 2449–56.

[15] (a) Katz, T. J.; Garratt, P. J. *J. Am. Chem. Soc.* **1963**, *85*, 2852–53. (b) *Ibid.* **1964**, *86*, 5194–5203.

Table III. Crystal and Experimental Data

molecular formula: $C_{28}H_{20}O_4$
molecular weight: 420.5
habit: monoclinic prisms
radiation: Cu K$\alpha$ (graphite monochromator)
wavelength: 1.5418 Å
space group: $P2_1$ (No. 4)
cell dimensions (from least-squares refinement of plus/minus data)
  $a$ = 9.4212 (9) Å
  $b$ = 11.1806 (10) Å
  $c$ = 10.8498 (14) Å
  $\beta$ = 100.309 (11)°
$V$ = 1124.4 Å$^3$
$Z$ = 2
$D_m$ = 1.22 (2) g cm$^{-3}$
$D_x$ = 1.243 g cm$^{-3}$
crystal size: 0.3 × 0.2 × 0.2 mm$^3$
reflections: 2318 (304 unobserved: 1$\sigma$)
maximum $(\sin\theta)/\lambda$: 0.62 Å$^{-1}$
diffractometer: Enraf-Nonius CAD-4
least-squares weighting: after Peterson and Levy[20]
function minimized: $\Sigma w(F_o - F_c)^2$
Anisotropic temperature factor:
  $\exp[-2\pi^2\Sigma_i\Sigma_j U_{ij}h_ih_ja_i{}^*a_j{}^*]$
Final $R$ factor (observed reflections only): 3.3%

oil with benzene, cooling in ice, and filtration gave 0.33 g of tetraphenylethylene, identical with an authentic sample. Addition of hexane to the resulting mother liquor and cooling at −5 °C gave two crops of pale yellow solid (total 7.0 g, 51%). Recrystallization of this material from benzene–hexane gave pure 9,9-diphenylbicyclo[6.1.0]nonatriene as colorless prisms: mp 107–108 °C (5.9 g); NMR ($CDCl_3$) $\delta$ 7.19 (10 H, m), 6.06 (4 H, d, $J$ = 3.1 Hz), 5.82 (2 H, s br), 3.35 (2 H, s, br); mass spectrum $m/e$ 270 (P, 12), 181 (100).

**X-ray Analysis of 12.** Details of the experimental results are given in Table III. The X-ray intensity data were collected by standard techniques and Lorentz and polarization corrections were applied by local programs. No absorption corrections were made or deemed necessary. The space group, given the molecular formula, could not be assigned unambiguously to either $P2_1$ or $P2_1/m$ but the intensity statistics suggested the lower symmetry. Assuming space group $P2_1$, the phase problem was attacked by using MULTAN[16,17] and a unique solution was obtained which showed most of the heavier atoms. Further refinement was routine and the final $R$ factor of 3.3% confirmed the choice of space group. The nonhydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms with isotropic parameters. The scattering factors used were those provided in XRAY 72[18] which was used for all calculations not mentioned explicitly. The atomic and thermal parameters are available on request from the authors. Figure 1 shows the molecule in its crystal conformation and Figure 2 the molecular packing.

After the final refinement, a reading of French and Wilson's paper[19] on the estimation of "unobserved" intensities suggested that the data might be useful as a test for the techniques described therein. Accordingly all $F$ values were recalculated by using the equations given by French and Wilson and refined treating all reflections as observed. The $R$ factor was somewhat higher, 3.9%, and the standard deviations of bond lengths marginally better. With the standard technique, which uses "unobserved" reflections only if they calculate higher than the cutoff level (here 1$\sigma$), the standard deviations ranged from 0.0025 to 0.0057 Å, and with values estimated by the French and Wilson technique, the range was 0.0024–0.0055 Å. It may be concluded that, for a crystal which has reasonably low thermal parameters and X-ray intensity data collected by modern diffractometric techniques, the standard method of treating "unobserved" intensities is entirely adequate.

**Acknowledgment.** The authors thank William Landis of NIH for the mass spectra on the compounds described and Dr. Herman Ziffer for providing access to the 220-MHz NMR spectrometer.

**Registry No.** **1**, 262-89-5; **2**, 71837-32-6; **4**, 71837-33-7; **6**, 71837-34-8; **7**, 71837-35-9; **10**, 71837-36-0; **11**, 1924-29-4; **12**, 1924-28-3; **13**, 42788-51-2; **15**, 71837-37-1; **16**, 71837-38-2; dipotassium 1,2:5,6-dibenzocyclooctatetraenide, 71837-83-7; acetyl chloride, 75-36-5; acetone, 67-64-1; diphenyldichloromethane, 2051-90-3; tetraphenylethylene, 632-51-9; dilithium cyclooctatetraenide, 59391-85-4.

---

(16) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect A* **1971**, *27*, 368.

(17) Main, P.; Woolfson, M. M.; Germain, G. "MULTAN-72, A Computer Program for the Automatic Solution of Crystal Structure"; Universities of York and Lourain, 1972.

(18) Stewart, J. M.; Kruger, G. J.; Ammon, H. L.; Dickinson, C.; Hall, S. R. "XRAY 72", Technical Report TR-192; Computer Center: University of Maryland, 1972.

(19) French, S.; Wilson, K. *Acta Crystallogr., Sect. B* **1978**, *34*, 517–25.

---

# Stereochemistry of Cuprate Addition to 4-, 5-, and 6-Alkylcycloheptenones

Clayton H. Heathcock,* Ted C. Germroth, and Samuel Lindsay Graham

*Department of Chemistry, University of California, Berkeley, California 94720*

*Received June 26, 1979*

The reactions of cycloheptenones **1**–**7** with $Me_2CuLi$ and $(t\text{-}Bu)_2CuLi$ have been studied. Stereostructures of the resulting diastereomeric products have been determined by comparison with known compounds, by unambiguous synthesis, or by the use of $^{13}C$ NMR spectroscopy. Good stereoselectivity is observed in the reaction of $Me_2CuLi$ with enones **2**, **4**, and **7** and in the reaction of $(t\text{-}Bu)_2CuLi$ with enones **1**, **5**, and **6**.

During the course of our research to develop stereoselective syntheses of pseudoguaianolides, we became interested in the stereoselectivity of cuprate addition to substituted cycloheptenones. In principle, such a route might be used to establish the required relative stereostructure about the cycloheptane ring in guaianolides and pseudoguaianolides, provided suitably high stereoselectivity is realized. Although a large literature has accumulated describing the stereochemical outcome of 1,4-additions of organometallic reagents to a variety of substituted cyclohexenones,[1] no systematic study dealing with cycloheptenones has appeared. The facts that until recently substituted cycloheptenones have been difficult to prepare and that little is known regarding conformational preferences for cycloheptane rings may account for this lack of experimental investigation. In this paper, we describe the preparation of a number of monosubstituted

---

(1) See G. H. Posner, *Org. React.*, **19**, 1 (1972); see pp 18–22 and 31–43 for a review.

0022-3263/79/1944-4481$01.00/0