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THREE 1,2,3,4-TETRABROMOCYCLOBUTANES

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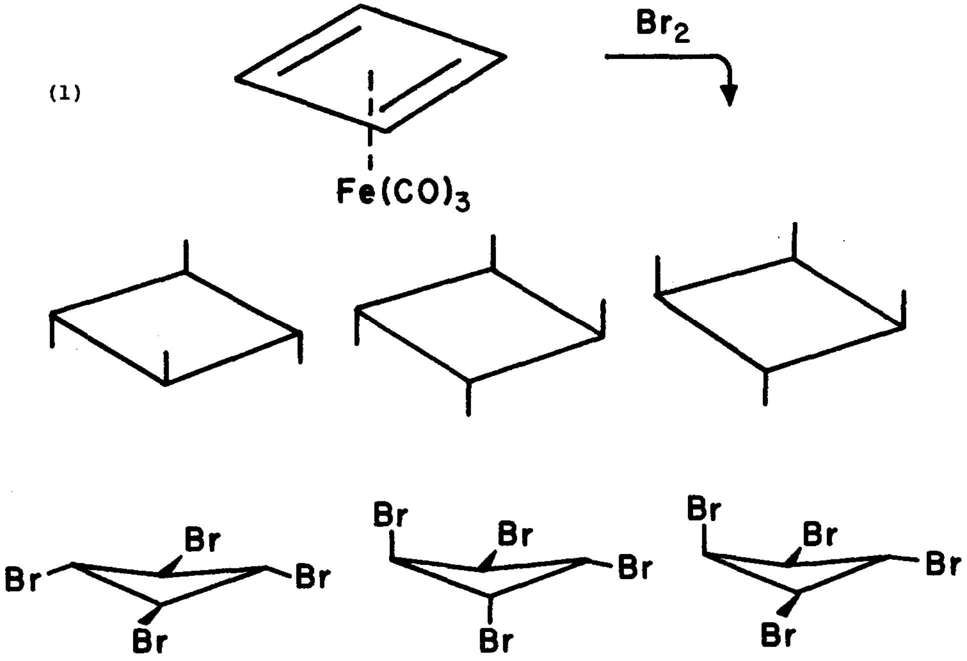
Pettit and his coworkers discovered many of the interesting reactions of the cyclobutadiene-iron tricarbonyl complex(1). We have now found that this complex reacts with bromine in carbon tetrachloride to produce a mixture of three of the four possible 1,2,3,4-tetrabromocyclobutanes. Separation of the pure isomers was accomplished with thick layer chromatography. The identity of each isomer was established by a combination of elemental analysis, n.m.r. and i.r. data. We have also established that the 1,2,3,4-tetrabromocyclobutane reported by Nenitzescu and collaborators(2) from the Hunsdiecker reaction (bromine and the silver salt of 3,4-dibromo-1,2-cyclobutanedicarboxylic acid) is a different mixture of the same three isomers (n.m.r., i.r. and chromatographic comparisons).

Cyclobutadiene-iron tricarbonyl (1) (Emerson, Watts and Pettit(3,4)) (0.77 g., 0.004 mole) in carbon tetrachloride (20 cc.) was added over 30 minutes to bromine (2.2 g., 0.014 mole) in the same solvent (40 cc.) maintained at 60°. After stirring overnight, filtration, and removal of the solvent, a residual brown oil was fractionated on 2 mm. silica gel thick layer plates, using carbon tetrachloride-hexane (6:4) as developing solvent. The only compounds which moved from the origin proved to be the three isomeric 1,2,3,4-tetrabromocyclobutanes (2A, 2B and 2C) in order of elution (R_F-values ca. 0.8, 0.7 and 0.4 respectively).

Eq. 1 describes the bromination reaction.

(1)



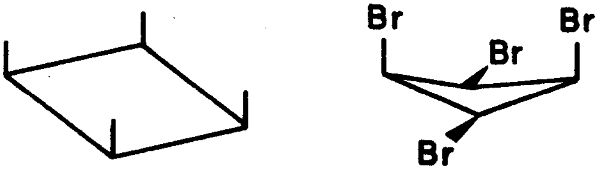
2A **2B** **2C**

(The dihedral angle in *cis*-1,3-dibromocyclobutane has been estimated by Wiberg and Lampman(5) as 146° [147° found by L. Walløe and O. Bastiansen (cf.5)].

Elemental analysis demonstrated that the empirical formulas for **2A**, **2B** and **2C** are $C_4H_4Br_4$:

	Calcd.	C, 12.92; H, 1.09; Br, 85.99
Found:	**2A**	C, 12.97; H, 1.06; Br, 85.63
	2B	C, 12.92; H, 0.94; Br, 86.25
	2C	C, 13.00; H, 1.05; Br, 86.26

Two of the isomers had *single* n.m.r. peaks, indicating four equivalent hydrogens. Isomer **2A**, m.p. 105-106°, had a peak at 5.73τ (CCl_4) and isomer **2B** (m.p. ∼ 40°) had a peak at 5.15τ (CCl_4). Isomer **2C** (m.p. 97-98°) had a complex n.m.r. spectrum consisting of two groups of multiplets at 4.8 and 5.5τ (CCl_4) with an intensity ratio of 1:3. The structure of **2C** could be assigned on the basis of its n.m.r. spectrum. The fourth possible isomer (2D) would probably be very difficult to form because of severe 1,3-bromine repulsions.



2D

The structure of 2A was chosen on the basis that axial hydrogens should appear at higher field in the n.m.r. spectrum than the average of the two axial and two equatorial hydrogens of isomer 2B. The analogous 1,2,3,4-tetracarbomethoxycyclobutanes follow this rule, with single n.m.r. peaks for the ring hydrogens at 6.52τ ($CDCl_3$) and 6.23τ ($CDCl_3$) (6.67τ ($CDCl_3$) and 6.15τ ($CDCl_3$), ref. 6) for the all-*trans* and *trans*-*cis*-*trans*-isomers, respectively. The infrared spectra of the three isomers are completely consistent with our assignments, the number of bands increasing markedly with decreasing symmetry.

2A: (CCl_4) 3000(m), 2985(m), 1260(vs), 1190(s), 1020(s), 835(s); (perfluorokerosene mull) 730(w), 535(w, broad) (in cm.$^{-1}$)

2B: (CCl_4) 2980(m), 2965(m), 1270(s), 1225(s), 1180(s), 1155(s), 915(s) (neat, KBr plates) 820(s), 780(w,broad) 535(w)(in cm.$^{-1}$)

2C: (CCl_4) 3005(m), 2975(m), 1280(m), 1250(vs), 1195(vs), 1155(s), 1095(s), 1015(s), 950(m) (perfluorokerosene mull) 825(s), 735(m), 540(w, broad) 490(w), 435(w) (in cm.$^{-1}$).

The yields of the three isomers obtained from the reaction of bromine with the iron tricarbonyl complex 1 and the silver salt of the dibromocyclobutane dicarboxylic acid were:

Isomer	Bromine and Complex 1 [a]	Silver salt [b]
2A	9%	9%
2B	3%	1%
2C	9%	2%

[a] average of a few runs

[b] reflects ratios but probably not optimum yield (two runs)

The primary difference between the two results is in the yield of **2C**. We may infer that complexation of the iron with the cyclobutadiene ring shields one side of the ring from reaction with bromine and thus favors *cis*-addition of bromine.

The tetrabromocyclobutanes represent an interesting and potentially useful set of reactive cyclobutane derivatives.

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