

A New Synthetic Route to Squaric Acid as a Chelating Agent

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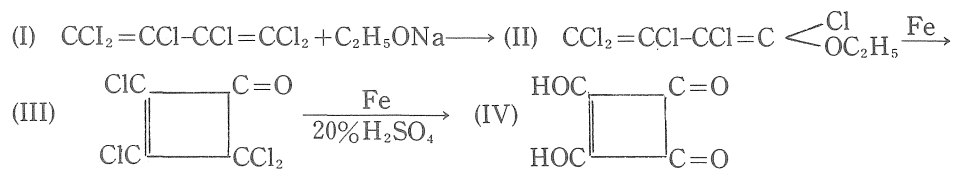
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Abstract A convenient method was established for the preparation of squaric acid as a chelating agent. The method is characterized by (i) the choice of easily available hexachloro-1,3-butadiene (HCB) as the starting material, (ii) the use of catalytic amounts of iron for cyclization and hydrolysis, (iii) no use of any special apparatus such as autoclave and corrosion-resisting vessel, and (iv) no inclusion of any complicated procedure. An interesting bilateral chelating character of the acid was also described.

Squaric acid¹⁾ is an interesting chelating agent for both inorganic and coordination chemists because of its bilateral bridge-formation character as well as the presence of aromaticity.²⁾ However, the acid is still puzzling in the field of coordination chemistry. The main reason is that no suitable method has been known for preparing the compound without any trouble on a large scale. For workers desiring to prepare small amounts of the compound, the prior³⁾ and its slightly modified methods⁴⁾ may still be used; however these are inadequate to obtain enough amounts of the compound to be utilized as a chelating agent. We recently succeeded in finding a new convenient method for obtaining the acid on a "ligand-scale". The paper is thus concerned with the synthetic route to squaric acid and the bilateral character thereof as a chelating agent.

Preparation of Squaric Acid

Our procedure is outlined as follows :



(I) 1,1,2,3,4,4-Hexachloro-1,3-butadiene (HCB). Reagent grade of HCB was

purchased from Wako Pure Chemical Ind., Ltd.

(II) *1-Ethoxy-1,2,3,4,4-pentachloro-1,3-butadiene*. Two hundred and ten grams (0.81mol) of HCB and a solution of 28 g (1.2mol) of metallic sodium in 500 ml of absolute ethanol were charged into a litre-flask equipped with a reflux condenser. The mixture was heated for 2 h. In this stage, care should be taken to avoid abrupt bumping due to the rapid ethoxylation. After sodium chloride precipitated was filtered off, excess ethanol was distilled out from the filtrate. The remainder was then distilled at 130°C under 20 mmHg to yield 95 g of colorless, sweet-smelling 1-ethoxy-1, 2, 3, 4, 4-pentachloro-1, 3-butadiene.

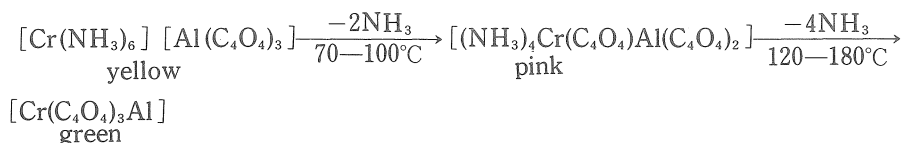
(III) *Perchlorobutenone*. Ninety five grams (0.35mol) of II and catalytic amounts (about 3 mg) of iron powder were placed in a 300 ml flask equipped with a reflux condenser. The mixture was heated at 160–180°C for 30 min with occasional stirring. Black oil of a sharply irritating odor was thus obtained, which was distilled at 180°C under 20 mmHg to give 69 g of faintly yellow, oily perchlorobutenone.

(IV) *Squaric Acid*. Sixty nine grams (0.33mol) of III, 300 ml of 20% sulfuric acid and catalytic amounts (about 3 mg) of iron powder were put in a 500 ml flask provided with a reflux condenser. The content was heated at 160°C for 2–3 h with continuous stirring. The addition of iron in catalytic amounts was extremely effective to promote the hydrolysis. When the iron was absent, the yield of the desired compound was significantly reduced. The resulting mixture was then allowed to stand in a refrigerator. White crystals were soon obtained and were recrystallized from hot water. Yield 15 g.

Found: C, 42.18; H, 1.84%. Calcd for $H_2C_4O_4$: C, 42.12; H, 1.79%.

Bilateral Character of Squaric Acid

Squaric acid generally resembles oxalic acid in coordination behavior toward metal ions, but the former is superior to the latter in both dissociating and reducing abilities.⁵⁾ The most attractive point of the squarate ion is its bilateral character; *viz.*, the ion has a potency of functioning bilaterally toward two metal ions concurrently. This makes it possible to find a new reaction pattern of metal complexes in the solid-phase. In fact, the model complex $[Cr(NH_3)_6][Al(C_4O_4)_3]$ which we synthesized underwent a very interesting reaction upon heating as shown below:



In the reaction, squarate ion initially coordinated to Al (III) ion migrates to Cr (III) ion via the formation of an intermediate in which the squarate ion functions bilaterally toward both metal ions.

References

- 1) The names "squaric acid" and "squarate" for 3,4-dihydroxy-3-cyclobutene-1,2-dione and its dianion have come from square planar structure. For convenience, both the names are used in this paper.
- 2) a) J. Aihara, *Bull. Chem. Soc. Jpn.*, **47**, 2899 (1974); b) W. M. MacIntyre and M. S. Werkema, *J. Chem. Phys.*, **40**, 3563 (1964).
- 3) J. D. Park, J. R. Lacher, and S. Cohen, *J. Am. Chem. Soc.*, **81**, 3480 (1959); **84**, 2919 (1962).
- 4) M. Ito and R. West, *J. Am. Chem. Soc.*, **85**, 2580 (1963).
- 5) R. Tsuchiya, A. Uehara, M. Sakui, and E. Kyuno, *Chem. Lett.*, **1974**, 1511.