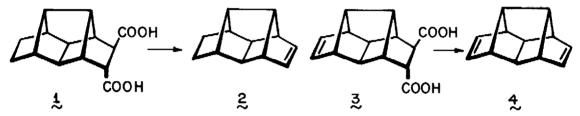
## OXIDATIVE DECARBOXYLATION OF VICINAL DICARBOXYLIC ACIDS AS PROMOTED BY CUPROUS OXIDE IN QUINOLINE

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In connection with another study, we required access to hydrocarbons  $\underline{2}$  and  $\underline{4}$  from  $\underline{1}$  and  $\underline{3}$ , respectively, which diacids are readily available from a product of the Domino Diels-Alder reaction involving 9,10-dihydrofulvalene and dimethyl acetylenedicarboxylate.<sup>1</sup> Of the methods

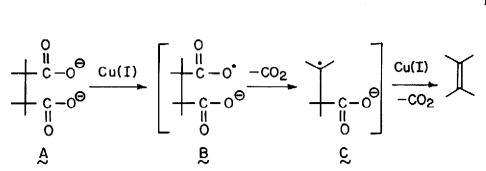


available to accomplish this objective (e.g.,  $Pb(OAc)_4$ ,  $^2 PbO_2$ ,  $^3$  perester decomposition,  $^4$  anodic oxidation,  $^5$  and transition metal catalysis  $^6$ ), only the electrochemical procedure has proven successful. However, because the yields were invariably low and the procedure limited to small quantities, this approach proved tedious and inconvenient. Consequently, a new method to achieve this synthetic transformation which was simple, rapid, and efficient, while also amenable to large scale manipulation, was sought.

Conceptually, our procedure was designed to bypass the possible intervention of transient carbocations such as those postulated <sup>2</sup> in Fb(OAc)<sub>4</sub>-promoted bisdecarboxylations, because of the well established tendency of 2-norbornyl systems (and particularly that derived from 2)<sup>7</sup> for structural rearrangement. The decarboxylation of aromatic acids with copper and copper salts has now been examined sufficiently to implicate one-electron transfer reactions of the carboxylate anions and generation of free radical intermediates (or their covalently bonded copper equivalents).<sup>8</sup> The comparable degradation of aliphatic <u>monocarboxylic</u> acids has made its appearance in only a few studies,<sup>9</sup> and mechanistic details are therefore lacking. However, it was anticipated that interaction of Cu(I) with dianion A might lead via B to alkyl radical C, the further redox reaction of which with Cu(I) would deliver olefin. In this manner, the known reluctance<sup>10</sup> of 2-norbornyl radicals to undergo isomerization would be utilized effectively.

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Dissolution of a vicinal diacid in quinoline containing 2 equiv each of  $Cu_2O$  and 2,2'dipyridyl and subsequent heating to  $180-185^O$  for several hours served to generate the corresponding olefin in yields which were at least comparable to, and often much higher than those

Diacid	Olefin	Yield, %	Comparative Results
1	2~	42.2	Electrolysis (20-27%); Pb(OAc) <sub>4</sub> (0%).
3	4~	57.0	Electrolysis (20-45%). <sup>1a</sup>
Соон	B	72.1	Pb(OAc) <sub>4</sub> (16.4%). <sup>11</sup>
соон	R	61.7	Electrolysis (30-40%); Fb(OAc) <sub>4</sub> (30-40%). <sup>12</sup>
A	A	52.0	Pb <sub>2</sub> 0/decalin, 150 <sup>0</sup> (~ 25%); <sup>3a</sup> Ni(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (53%). <sup>8a</sup>
		43.4	Pb(OAc) <sub>4</sub> (10-30%); <sup>13</sup> Electrolysis (51%). <sup>14</sup>

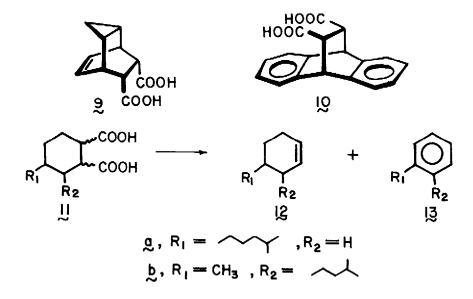
Table I.	Cu(I)-Promoted	Oxidative	Bisdecarboxylations
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realized by alternative methods (Table I). Two typical procedures follow. Although the given examples are small scale experiments and are therefore illustrative of reaction efficiency at this level, we emphasize that the method is readily amenable to scale-up.

A. (Continuous distillation from reaction mixture). A mixture of 5 (1.911 g, 10.4 mmol), red cuprous oxide (3.126 g, 21.8 mmol), 2,2'-dipyridyl (3.254 g, 20.8 mmol), and powdered glass (200 mg) in quinoline (15 ml) contained in a 25 ml flask fitted with a short-path distillation head was heated under N<sub>2</sub> with magnetic stirring for 2 hr at 140° and 36 hr at 185°.<sup>15</sup> Water was removed by syringe from the collected distillate, molecular sieves were added, and the dried liquid was vacuum transferred (45°/0.1 mm). There was obtained 0.508 g (52.0%) of 6.

B. (Product extraction from quinoline). A mixture of  $\underline{7}$  (1.52 g, 5.84 mmol), red cuprous oxide (1.67 g, 11.7 mmol), 2,2'-dipyridyl (1.82 g, 11.7 mmol), and powdered glass (200 mg) in 5 ml of quinoline was stirred under N<sub>2</sub> at 180° for 21 hr.<sup>15</sup> The cooled mixture was poured onto 2 <u>N</u> HCl (40 ml), filtered, and extracted with pentane (3x). The combined organic layers were washed further with 2 <u>N</u> HCl (<sup>4</sup>x) and water (2x) before drying and solvent evaporation. Filtration through silica gel (20 g, elution with 10% ether in pentane) afforded 430 mg (43.4%) of <u>8</u>.

Although the present technique is exceptionally serviceable in many instances, the high temperatures required can prove to be disadvantageous in certain situations. This is particularly so when the dicarboxylic acid can experience facile retrograde Diels-Alder fragmentation or when the development of benzenoid character is possible. Thus, treatment of 9 and 10



as above afforded cycloheptatriene and anthracene, respectively, in high yields. With  $\underline{11a}$  and  $\underline{11b}$ , the aromatics  $\underline{13a}$  (29.4%) and  $\underline{13b}$  (34.9%) proved to be the dominant products. Suitable control experiments demonstrated that  $\underline{12a}$  (14.7%) and  $\underline{12b}$  (5%) were stable to the reaction conditions.

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