

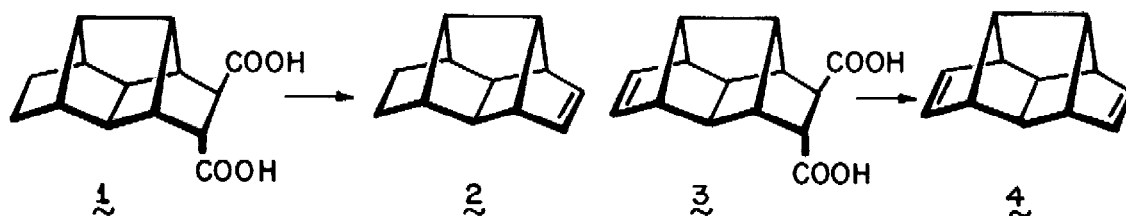
OXIDATIVE DECARBOXYLATION OF VICINAL DICARBOXYLIC ACIDS
AS PROMOTED BY CUPROUS OXIDE IN QUINOLINE

Robert A. Snow, Charles R. Degenhardt, and Leo A. Paquette*

Evans Chemical Laboratories, The Ohio State University, Columbus, Ohio 43210

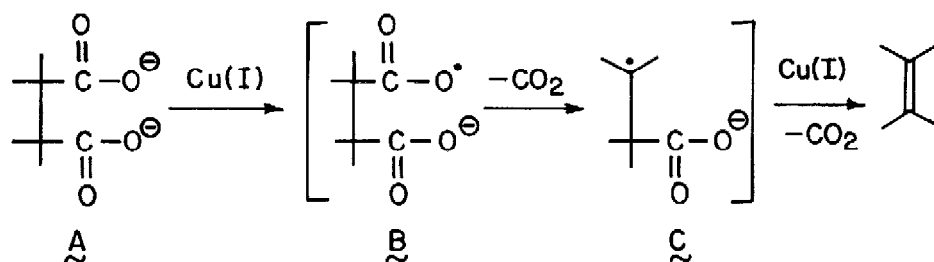
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In connection with another study, we required access to hydrocarbons 2 and 4 from 1 and 3, respectively, which diacids are readily available from a product of the Domino Diels-Alder reaction involving 9,10-dihydrofulvalene and dimethyl acetylenedicarboxylate.¹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



available to accomplish this objective (e.g., $\text{Pb}(\text{OAc})_4$,² PbO_2 ,³ perester decomposition,⁴ anodic oxidation,⁵ and transition metal catalysis⁶), 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 postulated² in $\text{Pb}(\text{OAc})_4$ -promoted bisdecarboxylations, because of the well established tendency of 2-norbornyl systems (and particularly that derived from 2)⁷ 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).⁸ The comparable degradation of aliphatic monocarboxylic acids has made its appearance in only a few studies,⁹ and mechanistic details are therefore lacking. However, it was anticipated that interaction of $\text{Cu}(\text{I})$ with dianion A might lead via B to alkyl radical C, the further redox reaction of which with $\text{Cu}(\text{I})$ would deliver olefin. In this manner, the known reluctance¹⁰ of 2-norbornyl radicals to undergo isomerization would be utilized effectively.



Dissolution of a vicinal diacid in quinoline containing 2 equiv each of Cu₂O and 2,2'-dipyridyl and subsequent heating to 180-185° for several hours served to generate the corresponding olefin in yields which were at least comparable to, and often much higher than those

Table I. Cu(I)-Promoted Oxidative Bisdecarboxylations

Diacid	Olefin	Yield, %	Comparative Results
 1	 2	42.2	Electrolysis (20-27%); Pb(OAc) ₄ (0%). ⁷
 3	 4	57.0	Electrolysis (20-45%). ^{1a}
 5	 6	72.1	Pb(OAc) ₄ (16.4%). ¹¹
 7	 8	61.7	Electrolysis (30-40%); Pb(OAc) ₄ (30-40%). ¹²
 9	 10	52.0	Pb ₂ O/decalin, 150° (~25%); ^{3a} Ni(CO) ₂ (PPh ₃) ₂ (53%). ^{6a}
 11	 12	43.4	Pb(OAc) ₄ (10-30%); ¹³ Electrolysis (51%). ¹⁴

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

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References

- (1) (a) L. A. Paquette and M. J. Wyvratt, J. Am. Chem. Soc., 96, 4671 (1974); (b) D. McNeil, B. R. Vogt, J. J. Sudol, S. Theodoropoulos, and E. Hedaya, ibid., 96, 4673 (1974).
- (2) R. A. Sheldon and J. K. Kochi, Org. React., 19, 279 (1972) and references contained therein.
- (3) (a) W. von E. Doering, M. Farber, and A. A. Sayigh, J. Am. Chem. Soc., 74, 4370 (1952); (b) W. von E. Doering and M. Finkelstein, J. Org. Chem., 23, 141 (1958).
- (4) E. N. Cain, R. Vukov, and S. Masamune, Chem. Commun., 98 (1969).
- (5) P. Radlick, R. Klem, S. Spurlock, J. J. Sims, E. E. van Tamelen, and T. Whitesides, Tetrahedron Lett., 5117 (1968); H. H. Westberg and H. J. Dauben, Jr., ibid., 5123 (1968).
- (6) (a) B. M. Trost and F. Chen, Tetrahedron Lett., 2603 (1971); (b) W. G. Dauben, G. T. Rivers, R. J. Twieg, and W. T. Zimmerman, J. Org. Chem., 41, 887 (1976).
- (7) C. R. Degenhardt, unpublished results.
- (8) T. Cohen and R. A. Schambach, J. Am. Chem. Soc., 92, 3189 (1970); J. Chodowska-Palika, and M. Nilsson, Acta Chem. Scand., 27, 1029 (1973).
- (9) W. G. Dauben and R. J. Twieg, Tetrahedron Lett., 531 (1974).
- (10) P. D. Bartlett, G. N. Fickes, F. C. Haupt, and R. Helgeson, Accounts Chem. Res., 3, 177 (1970) and references cited therein.
- (11) G. A. Russell, G. W. Holland, K.-Y. Chang, R. G. Keske, J. Mattox, C. S. C. Chung, K. Stanley, K. Schmitt, R. Blankespoor, and Y. Kosugi, J. Am. Chem. Soc., 96, 7237 (1974).
- (12) Y. E. Rhodes, P. E. Schueler, and V. G. DiFate, Tetrahedron Lett., 2073 (1970).
- (13) K. Kitahonoki and Y. Takano, Tetrahedron Lett., 1597 (1963); C. M. Christopher and J. Wolinsky, J. Am. Chem. Soc., 90, 113 (1968).
- (14) H. Plieninger and W. Lehnert, Chem. Ber., 100, 2427 (1967).
- (15) The formation of a metallic copper mirror was noted in a number of the cases described in this study. When the mirror was not observed, a dark-colored sludge was formed instead.