

Protonated 3-methyl-2-butenal and protonated 4-methyl-3-penten-2-one can be regarded as hydroxyallyl cations. Their nmr spectra in  $\text{HO}_3\text{SF}$  were unchanged from 25 to 112° and 25 to 88°, respectively.

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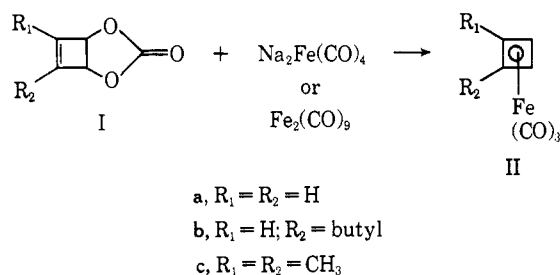
\* Address correspondence to this author.

N. C. Deno,\* Robert C. Haddon, Edward N. Nowak  
Department of Chemistry, The Pennsylvania State University  
University Park, Pennsylvania 16802  
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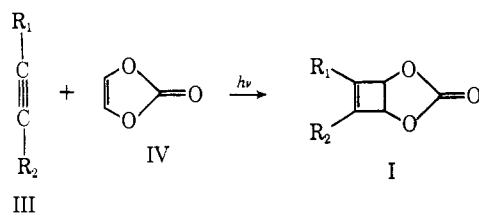
### Cyclobutadieneiron Tricarbonyl Complexes

Sir:

Treatment of *cis*-3,4-carbonyldioxycyclobutenes (I) with reducing iron carbonyl complexes gives cyclobutadieneiron tricarbonyl complexes (II) in good yields.



The hitherto unknown *cis*-3,4-carbonyldioxycyclobutenes (I) can be prepared in reasonable yields by the photolysis of vinylene carbonate (IV) with the appropriate acetylene (III). This procedure represents a simple



and convenient route to a wide variety of previously unavailable cyclobutadiene complexes. In particular, monosubstituted complexes not available by alkylation of the parent system and 1,2-disubstituted complexes which cannot be made by alkylation of the monosubstituted complexes can be prepared by this method. Also this procedure provides the unsubstituted complex in reasonable yields from readily available starting materials.

The cyclobutadiene complexes that have been previously prepared have proved very useful as synthetic intermediates and as convenient precursors for the study of the chemistry and electronic structure of cyclobutadiene.<sup>1</sup> However, published procedures require the use of materials that are not readily available,<sup>2,3</sup> or are not suited for the preparation of complexes with a variety of substituents.<sup>2-4</sup>

(1) R. Reeves, T. Devon, and R. Pettit, *J. Amer. Chem. Soc.*, **91**, 5890 (1969), and references therein.

(2) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965); this procedure requires cyclooctatetraene as a starting material.

(3) M. Rosenblum and G. Gatsonis, *ibid.*, **89**, 5074 (1967).

In the most useful reported preparations, 3,4-dihalo-cyclobutenes<sup>2,4,5</sup> are reduced with iron carbonyl complexes. It was thought that the *cis*-3,4-carbonyldioxycyclobutenes (I) would yield cyclobutadiene complexes and iron carbonates under reducing conditions and should be easy to prepare with a variety of substituents. A key feature of these bicyclic compounds should be their resistance to the well-known cyclobutene ring-opening reactions. Consequently, photolysis<sup>6</sup> of vinylene carbonate<sup>7</sup> (IV) in acetone with an excess of the appropriate acetylene was attempted, and gave the *cis*-3,4-carbonyldioxycyclobutene in 20–40% yields along with vinylene carbonate dimer. All the derivatives were thermally stable and were easily isolated by fractional distillation at reduced pressure.<sup>8</sup>

Treatment of the *cis*-3,4-carbonyldioxycyclobutenes (Ia–c) with either the disodium salt of iron tetracarbonyl dianion<sup>5</sup> (1.3 equiv) in tetrahydrofuran for 2 hr, or with excess diiron enneacarbonyl in cyclohexane at 55° gave the corresponding cyclobutadiene complexes (IIa–c) in good yields.<sup>9</sup> All of the complexes showed the characteristic carbonyl stretching frequencies in the infrared near 1980 and 2050  $\text{cm}^{-1}$ ,<sup>2,4</sup> and their mass spectra were characterized by a large parent peak followed by peaks for the successive loss of the three CO groups.<sup>2,4</sup> The unsubstituted complex (IIa), obtained in 37% yield, showed a single nmr signal at  $\tau$  6.05 (lit.<sup>2</sup> 6.09) and gave infrared spectra and retention times on the gas chromatograph identical with an authentic sample.<sup>10</sup> The butyl derivative (IIb) (bp 70–72° (1 mm)), obtained in 50% yield, gave nmr signals at  $\tau$  6.08 (singlet), 6.12 (singlet), 8.02 (quartet), 8.65 (multiplet), and 9.12 (triplet). The ratio of the peak areas was 2:1:4:8:6. There was no detectable coupling between the two different types of cyclobutadiene ring protons.<sup>4,11</sup> The dimethyl derivative (IIc), obtained in 30% yield, showed two singlets at  $\tau$  8.22 and 6.12, in the ratio of 3:1 (lit.<sup>11</sup> 8.24 and 6.10).

Studies are presently under way to extend this procedure to the preparation of other synthetically useful and theoretically interesting cyclobutadiene complexes.

**Acknowledgments.** We gratefully acknowledge the support of a National Science Foundation Institutional grant administered by Michigan State University for partial support of this project.

(4) B. W. Roberts, A. Wissner, and R. A. Rimerman, *ibid.*, **91**, 6208 (1969); also, this reaction gives low yields (7–9%) of the desired compounds.

(5) R. G. Amiel, P. C. Reeves, and R. Pettit, *Chem. Commun.*, 1208 (1967).

(6) W. Hartman, *Chem. Ber.*, **101**, 1643 (1968).

(7) Available from Aldrich Chemical Co. or easily prepared from ethylene carbonate by the procedure of M. S. Newman and R. W. Addor (*J. Amer. Chem. Soc.*, **75**, 1264 (1953)) or from chloroethylene which is commercially available.

(8) A report of the preparation and chemistry of these compounds will be presented at a later date.

(9) The anion procedure is the preferred route since 4–5 equiv of diiron enneacarbonyl added over a 24-hr period was required to complete the reaction.

(10) Samples prepared by the method given in ref 2 were obtained from Professors H. Hart and E. LeGoff.

(11) H. A. Brune, W. Eberius, and H. P. Wolff, *J. Organometal. Chem.*, **17**, 485 (1968); H. Huther, *Chem. Ber.*, **101**, 1485 (1968).

Robert H. Grubbs

Department of Chemistry, Michigan State University  
East Lansing, Michigan 48823

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