Stabilization of Enols as Transition-metal Complexes

By C. H. DEPUY,* R. N. GREENE, and T. E. SCHROER
(*Department of Chemistry, University of Colorado, Boulder, Colarado* 80302)

UNSTABLE compounds such as cyclobutadiene can be stabilized in the form of a transition-metal complex[1,2] as suggested by Longuet-Higgins and Orgel in 1956.[3] An interesting similarity is the possibility of complexing the less stable of a pair of tautomers. Lewis[4] has recently prepared the complex of the dienone tautomer of phenol (I). We report the preparation of transition-metal complexes of butadiene-1- and -2-ol and some of their derivatives, and the observation of an *anti–syn* re-arrangement in basic solution.

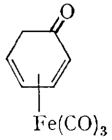
2-Acetoxybutadiene tricarbonyliron (IIa) was prepared by the reaction of 2-acetoxybutadiene[5] with di-iron nonacarbonyl in benzene. The yellow, crystalline complex (m.p. 51—52°) is air stable and has an n.m.r. spectrum typical of the tricarbonyliron compounds of 2-substituted butadienes.[6] Reaction of (IIa) with methyl-lithium in ether followed by acidification gives an ether solution of tricarbonyl 2-hydroxybutadieneiron (IIb) which is air sensitive but stable in solution. Reaction of (IIb) with benzoyl bromide in base gives the benzoate (IIc) (m.p. 57—58°). Analytical, i.r., n.m.r., and mass spectral data were all in accord with assigned structures.

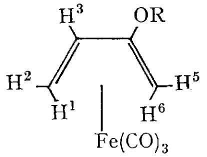
An n.m.r. spectrum of tricarbonyl-2-hydroxybutadieneiron (IIb) was obtained in deuteriobenzene: δ 5·88 (s, OH), 4·94 (t, 3-H), 1·88 (d, 5-H), 1·28 (dd, 2-H), 0·11 (d, 6-H), −0·57 (dd, 1-H). Its pK_a value, as determined by potentiometric titration in 48% aqueous ethanol, is 9·24. This corresponds to a pK_a of about 8·5 in water, approximately that of acetylacetone.

syn- and *anti*-1-Acetoxybutadienetricarbonyl iron [(IIIa) and (IVa)] were prepared by the reaction of *trans*- and *cis*-1-acetoxybutadiene,[7] respectively, with nonacarbonyl di-iron in hexane at 25°. These compounds are both liquids, and their structural assignments are supported by their n.m.r. spectra. *syn*-Tricarbonyl-1-hydroxybutadiene iron (IIIb) is formed when (IIIa) is treated with methyl-lithium in ether. This alcohol is more air sensitive than the 2-isomer, and decomposition to paramagnetic products has so far prevented the recording of its n.m.r. spectrum. It is approximately as acidic as the 2-isomer. Reaction of an ether solution of (IIIb) with benzoyl bromide in base gives the benzoate (IIIc) (m.p. 59—60°), fully characterized by analysis, i.r., n.m.r., and mass spectral data.

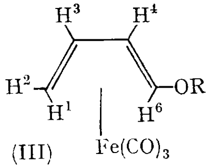
The *anti*-acetate (IVa), when treated with methyl-lithium, acidified, and then benzoylated, gives the *syn*-benzoate (IIIc) (36%), indicating that an *anti–syn* rearrangement had taken place. This rearrangement is rapid at low temperatures; treatment of (IVa) with methyl-lithium followed by benzoyl bromide at −60° gives a 30:70 mixture of *anti*-benzoate (IVc) and *syn*-benzoate (IIIc).

(I)

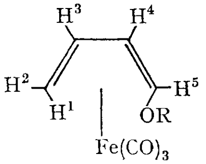




(II)



(III)



(IV)

(II)—IV : a, R=Ac; b, R=H; c, R=COPh

These functionally substituted diene complexes may make possible a more detailed study of the chemical reactivity and electronic structure of organic ligands.

This work was supported by fellowships from the N.S.F. (to R.N.G.) and N.D.E.A. (to T.E.S.).

(*Received, June 6th,* 1968; *Com.* 819.)

---

[1] R. Criegee and G. Schroeder, *Annalen*, 1959, **623**, 1.
[2] G. F. Emerson, L. Watts, and R. Pettit, *J. Amer. Chem. Soc.*, 1965, **87**, 131.
[3] H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1956, 1969.
[4] A. J. Birch, P. E. Cross, J. Lewis, D. A. White, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 332.
[5] H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, 1949, **41**, 2920.
[6] E. O. Fischer and H. Werner, "Metal π-Complexes", Elsevier, Amsterdam, 1966, vol. **1**, p. 159.
[7] K. K. Georgieff and A. Dupre, *Canad. J. Chem.*, 1960, **38**, 1070.