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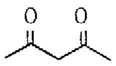
A TRIPOD HEXAKETONE AS A LIGAND FOR MANGANESE

J. E. Hallgren* and G. M. Lucas
General Electric Company
Corporate Research & Development Center
Schenectady, New York 12301

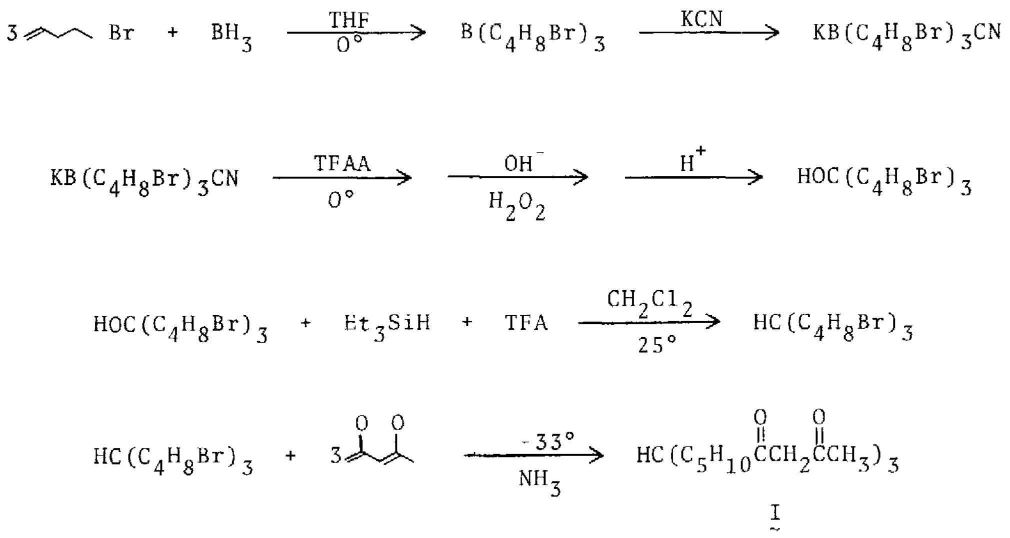
The synthesis of 10-(nona-6,8-dionyl)-2,4,16,18-nonadecatetraone and 11-(deca-7,9-dionyl)-2,4,18,20-uncosatetraone is described. The former hexaketone was found to form a very stable manganese (III) chelate, which upon reduction was found to be kinetically inert toward ligand substitution unlike virtually all manganese II complexes.

Manganese tris(acetylacetonate) has been shown to be a catalyst for the oxidation of a variety of organic substrates.[1] A serious limitation is the lability of the manganese (II) tris(acetylacetonate)anion formed upon reduction of manganese (III) tris-(acetylacetonate), Equation 1. Often the acetylacetone generated from this solvolysis reaction leads to interfering side reactions and a decrease in catalyst activity.

$Mn(acac)_3^- + \text{solvent} \longrightarrow Mn(acac)_2(\text{solvent})_2 +$ 

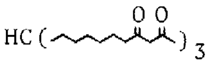
In the course of study of manganese catalyzed oxidations, it was desirable to obtain a strongly chelated manganese compound with redox properties similar to manganese (III) tris(acetylacetonate) but with greatly reduced ligand lability. Although manganese ß-diketonate complexes are well-documented in the literature, both manganese-(II) and -(III) tris(acetylacetonate) have been prepared and characterized,[2,3,4] similar complexes containing a single poly-(ß-diketonate) ligand appear to be unknown. We wish to describe our efforts to prepare such a polyketone and its manganese complex.

Examination of the X-ray crystal structure[5] of manganese (III) tris(acetyl acetonate) led us to select a tripod ligand containing three acetylacetonate moieties. Inspection of a Dreiding molecular model suggested that with three β-diketonate moieties separated by five or six methylene units undue strain would not be introduced into the molecule. The ligands were prepared by Scheme 1 shown below.



SCHEME 1

Hydroboration of the substituted olefin proceeded smoothly in THF at 0°C. Attempted replacement of the boron atom with a COH fragment by the procedure of Brown[6] using carbon monoxide led to extensive dehydrobromination due to the high temperatures employed for the alkyl migration step (150°C, 3 hours). The method of Pelter[7] (KCN, $(CF_3CO)_2$, 0°) was more satisfactory. Accordingly, the borate solution was allowed to react with one equivalent of KCN for 4 hours at room temperature, then treated with three equivalents of trifluoroacetic anhydride at 0-5°C for 8 hours. Excess trifluoroacetic anhydride was removed under reduced pressure and the residue treated with alkaline 30% hydrogen peroxide at 0°C. The residue was acidified then extracted with CH_2Cl_2 to obtain the tertiary alcohol in 35% overall yield. Reduction of the alcohol to the hydrocarbon was effected in 80% yield by treatment with 1 equivalent of Et_3SiH and an excess of trifluoroacetic acid in CH_2Cl_2 at room temperature overnight.[8] The tribromide was purified by distillation [180-185° (0.2 mm)] and then converted to the hexaketone by a modification of the method of Hauser.[9] Reaction of the tribromide with three equivalents of the disodium salt of acetylacetonate in liquid ammonia afforded I. After recrystallization from hexane, the hexaketone was isolated in 9% overall yield as white plates, mp 27°C. Anal. Found: C, 70.0; H, 9.95. Calcd: C, 70.3; H, 9.6. ir (film): 1600 (s). Hnmr ($CDCl_3$): δ1.2-1.8 (25H, m, methylene and methinyl), 2.05 (9H, s, methyl), 2.26 (6H, t, J = 7Hz, α-methylene) and 5.50 ppm (3H, s, methinyl). FD-MS m/e: 478(P^+) and 159.3 (P^{+3}). Similarly II was prepared from 5-bromo-1-pentane in 12% overall yield. Anal. mp 24°C Found: C, 72.5; H, 9.0. Calcd: C, 72.4; H, 9.0. ir (film) 1600 (s). Hnmr ($CDCl_3$): 1.2-1.8 (28H, *m, met-ylene and methinyl), 2.05 (9H, s, methyl), 2.26 (6H, t, J=7Hz, α-* methylene) and 5.50 ppm (3H, s, methinyl). FD-MS m/e: 514 (P^+) and 171.3 (P^{+3}).



II

The manganese (III) complex of I was obtained by a procedure analogous to that of Hammond.[10]

$$\mathrm{I} + \mathrm{Mn(OAc)_2} \cdot 4\mathrm{H_2O} \xrightarrow[\mathrm{O_2}]{\mathrm{CH_2Cl_2/H_2O}} \underset{\mathrm{III}}{\mathrm{Mn(I)}}$$

To an emulsion of 1.0 g of I (2.0 mmol) in CH_2Cl_2 and 0.5 g (2.0 mmol) of $Mn(OAc)_2 \cdot 4H_2O$ in water was added excess NH_4OH and the resulting mixture stirred in air at room temperature for 3 hours. The prodcut was isolated from the organic phase and recrystallized from CH_2Cl_2/hexane to obtain 0.4 g (38%)

of I as a shiny black crystalline solid, mp 158-160°C. Anal. Found: C, 63.5; H, 8.0; Mn, 10.7. Calcd: C, 63.4; H, 8.1; Mn, 10.4. FD-MS m/e 530 (P^+). Molecular weight was determined by the method of Rast in Naphthalene. Found. 580 Calcd. 530.

The manganese (III) complex of II could not be prepared by an analogous procedure. A manganese oxide and the starting hexaketone were the only isolated products. It is assumed that considerable steric strain would be contained in the complex resulting in a low affinity of II for the Mn(III). Dreiding molecular models, however, suggest that such a complex should be essentially strain free.

Complex III could be cleanly reduced in THF by sodium/naphthalene to prepare the air sensitive manganese (II) anion. HPLC analysis of reaction mixture failed to detect the uncomplexed ligand in solution. By contrast after reduction of $Mn(acac)_3$, copious quantities of acetylacetone could be detected.

REFERENCES

1. See, for example: A. R. Doumaux, U.S. Patent 3,634,406 (Union Carbide, 1972) Chem. Abst. 76 P85, 427 m (1973); A. Fusi, R. Ugo, G. M. Zanderighi, J. Catal. 34 175 (1974); T. Matsuzaki, J. Imamura, Nippon Kagaku Kaishi 1377 (1975).
2. J. P. Fackler, Prog. Inorg. Chem. 7 361 (1966).
3. G. H. Cartledge, J. Amer. Chem. Soc., 73 4416 (1951).

4a. R. G. Charles, Inorg. Syn. 6, 164 (1960).

4b. F. P. Dwyer and A. M. Sargeson, Proc. Roy. Soc. N S Wales, 90 29 (1956).

5. B. R. Stults, R. S. Marianelli, and V. W. Day, Inorg. Chem. 18 1853 (1979).
6. H. C. Brown, Accts. Chem. Res. 2 65 (1969).
7. A. Pelter, M. G. Hutchings, K. Row, and K. Smith, J. Chem. Soc. Perkin I 138 (1975).
8. F. A. Carey and H. S. Tremper, J. Org. Chem., 36, 758 (1971).
9. K. G. Hampton, R. J. Light, and C. R. Hauser, J. Org. Chem. 30 1413 (1965).
10. G. S. Hammond, D. C. Nonhebel, and C. S. Wu, Inorg. Chem. 2 73 (1963).

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