Tetrahedron Letters No.32, pp. 2195-2199, 1964, Pergamon Press Ltd.
Printed in Great Britain.

THE ABILITY OF CYCLOPENTADIENYLMANGANESETRICARBONYL TO STABILIZE A TRANSITION ALPHA-CARBONIUM ION

William E. McEwen, James A. Manning and Jacob Kleinberg
Departments of Chemistry
University of Massachusetts, Amherst, Massachusetts
University of Kansas, Lawrence, Kansas

(Received 27 May 1964; in revised form 23 June 1964)

There are several reactions of ferrocene, ruthenocene and osmocene compounds which indicate that the respective metallocenyl groups increase the stability, and thus the ease of formation, of transition alpha-carbonium ions. Reactions of these types have now been applied to suitable cyclopentadienylmanganesetricarbonyl compounds, and it has been established that this metallocene group is less effective than the other cited metallocene groups but more effective than a phenyl group in promoting the formation of a transition alpha-carbonium ion.

Benzoylcyclopentadienylmanganesetricarbonyl, $(CO)_3MnC_5H_4-COC_6H_5$, was prepared from cyclopentadienylmanganesetricarbonyl and benzoyl chloride by the method of Fischer and Pleszke (1). Reduction of this compound with sodium borohydride afforded α-hydroxybenzylcyclopentadienylmanganesetricarbonyl, m.p. 91.0-91.5°, in 80% yield. The action of acetic anhydride on the alcohol in pyridine solution gave α-acetoxybenzylcyclopentadienylmanganesetricarbonyl, m.p. 68.0-69.0°, in 85% yield.

Solvolysis of α-acetoxybenzylcyclopentadienylmanganesetricarbonyl in absolute ethanol gave α-ethoxybenzylcyclopentadienylmanganesetricarbonyl, a yellow liquid purified by chromatography on alumina, as the only isolable product. The rate of the solvolysis reaction was followed by infrared analysis, and the specific rate constant for the pseudo-first-order reaction at the reflux temperature (78.3°) was found to be $3.445X10^{-6} \pm 0.030X10^{-6}$ sec.$^{-1}$ (concentration of 5.696 mmole of the ester per 100.0 ml. of absolute ethanol). Although the exclusive formation of ether suggests that the $B_{Al}1$ mechanism of solvolysis is operative, the reaction is a very slow one compared to analogous reactions of other metallocenes. For example, whereas Richards and Hill (2) obtained a quantitative yield of α-ethoxyethylferrocene by heating α-acetoxyethylferrocene in absolute ethanol under reflux for 3.5 hours, we obtained but a 55% yield of α-ethoxybenzylcyclopentadienylmanganesetricarbonyl by heating α-acetoxybenzylcyclopentadienylmanganesetricarbonyl in absolute ethanol under reflux for 3 days, the remainder of the product being unchanged ester. Furthermore, α-acetoxyethylcyclopentadienylmanganesetricarbonyl, a yellow liquid, n_{D}^{26} 1.5537, was recovered quantitatively after having been heated under reflux in absolute ethanol for 3 days.

That the cyclopentadienylmanganesetricarbonyl group is more effective than a phenyl group in promoting formation of a transition carbonium ion was demonstrated by the fact that benzhydryl acetate, when heated under reflux for 3 days in absolute ethanol, gave no ethyl benzhydryl ether. A small amount of benzhydrol was obtained, but we believe that this arose by hydrolysis of recovered benzhydryl acetate on the alumina column used in the chromatographic separation of products. The infrared spectrum of the product, taken before the chromatographic separation, showed no decrease in the intensity of the carbonyl absorption peak of the starting ester.

Whereas vinylferrocene, vinylruthenocene and vinylosmocene readily add absolute acetic acid to give the respective α-acetoxyethylmetallocenes (3), vinylcyclopentadienylmanganesetricarbonyl, a yellow liquid purified by chromatography on alumina and prepared in three different ways by adaptations of procedures of Riemschneider and Kassahn (4), Taylor (5) and Buell, Kleinberg and McEwen (3), underwent no corresponding reaction. Also, vinylcyclopentadienylmanganesetricarbonyl showed no pronounced tendency to add hydrogen azide in benzene-acetic acid solution, although a very small amount of impure α-azidoethylcyclopentadienylmanganesetricarbonyl may have been isolated. Vinylferrocene, by way of contrast, readily adds hydrogen azide to give α-azidoethylferrocene (3).

When benzene is caused to react with 1,2-dichloroethane in the presence of anhydrous aluminum chloride, only 1,2-diphenylethane is produced (6). This shows that, in this reaction, the possible transition carbonium ion $C_6H_5CH_2CH_2^{\oplus}$ has no particular tendency to rearrange to $C_6H_5\text{-}\overset{\oplus}{C}H\text{-}CH_3$, even though the latter carbonium ion is more stable than the former. In the reaction of ferrocene with 1,2-dichloroethane, however, the important driving force leading to the formation of an α-metallocenylcarbonium ion is again manifested, and the sole product is 1,1-diferrocenylethane (7). In the present study, reaction of 1,2-dichloroethane with cyclopentadienylmanganesetricarbonyl in the presence of anhydrous aluminum chloride gave only the symmetrical disubstituted ethane, ethylene-bis-cyclopentadienylmanganesetricarbonyl, m.p. 119-120°. The symmetrical structure was indicated by the nuclear magnetic resonance spectrum, which exhibited two peaks at δ values of 4.6 and 2.4 p.p.m.

Whereas the sulfuric acid-catalyzed decomposition of ferrocenylphenylcarbinyl azide is known (8,9,10) to give a complex mixture of products, including nitrogen, ferrocenecarboxaldehyde, aniline, the two diastereoisomeric forms of 1,2-diferrocenyl-1,2-diphenylethane, benzoylferrocene and ferrocenylphenylcarbinol, α-azidobenzylcyclopentadienylmanganesetricarbonyl, an orange liquid, n_D^{25} 1.6201, behaved in an entirely different manner when treated with sulfuric acid. First of all, it underwent reaction at a far slower rate than the ferrocene analog. Secondly, both nitrogen and carbon monoxide were evolved, and the organic products were intractable. Control experiments carried out on cyclopentadienylmanganesetricarbonyl itself indicated that it too lost carbon monoxide when treated in solution with mineral acids or generalized Lewis acids. For example, when a solution of cyclopentadienylmanganesetricarbonyl in chloroform was treated with antimony pentachloride, a bright red precipitate formed immediately. After a minute or two this solid evolved carbon monoxide and turned brown, then black.

Unlike the α-hydroxyethyl and α-hydroxybenzyl derivatives of ferrocene, the corresponding derivatives of cyclopentadienylmanganesetricarbonyl did not undergo displacement of the hydroxyl group by the azido group of hydrogen azide in acetic acid solution. However, α-azidoethylcyclopentadienylmanganesetricarbonyl, a red liquid, n_D^{25} 1.6141, and α-azidobenzylcyclopentadienylmanganesetricarbonyl, respectively, were obtained in good yields by reaction of the alcohols with hydrogen azide in the presence of trichloroacetic acid (11). Satisfactory analyses were obtained for these and all other new compounds reported in this communication.

Acknowledgment. This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is made to the donors of the fund.

REFERENCES

1. E. O. Fischer and K. Pleszke, Chem. Ber., 91, 2719 (1958).
2. J. H. Richards and E. A. Hill, J. Amer. Chem. Soc., 83, 3840 (1961).
3. G. R. Buell, J. Kleinberg and W. E. McEwen, Tetrahedron Letters, 16 (1959); J. Amer. Chem. Soc., 84, 40 (1962).
4. R. Riemschneider and H. G. Kassahm, Chem. Ber., 92, 3208 (1959).
5. R. Taylor, Chemistry and Industry, 1684 (1962).
6. G. S. Kolesnikov, V. V. Korshak and T. V. Smirnova, Isvest. Akad. Nauk. S.S.S.R., 126, 307 (1959).
7. K. L. Rinehart, Jr., P. A. Kittle and A. F. Ellis, J. Amer. Chem. Soc., 82, 2082 (1960).

8. A. Berger, J. Kleinberg and W. E. McEwen, Chemistry and Industry, 204 (1960).

9. A. Berger, W. E. McEwen and J. Kleinberg, J. Amer. Chem. Soc., 83, 2274 (1961).

10. D. E. Bublitz, J. Kleinberg and W. E. McEwen, J. Amer. Chem. Soc., 84, 1845 (1962).

11. S. N. Ege and K. W. Sherk, J. Amer. Chem. Soc., 75, 355 (1953).