Notes

Solvolysis Studies with 2-(*p*-Ferrocenylphenyl)ethyl-*1,1*-d_2 Tosylate

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Solvolytic studies on 2-(*p*-ferrocenylphenyl)ethyl-*1,1*-d_2 tosylate (1-OTs-*1*-d_2) were undertaken in the present work because the ferrocenyl group is a relatively uncommon substituent in solvolysis reactions and its effects on isotopic scramblings have never been investigated. Arylation of ferrocene[1] was effected with diazotized *p*-aminophenylacetic acid to give *p*-ferrocenylphenylacetic acid, which was in turn converted to the methyl ester, reduced with $LiAlD_4$ to 2-(*p*-ferrocenylphenyl)ethanol-*1,1*-d_2 (1-OH-*1*-d_2), and then treated with tosyl chloride in pyridine to give 1-OTs-*1*-d_2. The solvolyses were carried out in 80% acetone–20% H_2O, glacial HOAc, 97% HCOOH, and F_3CCOOH. Because of decomposition, no product could be isolated from the trifluoroacetolysis. The esters derived from the acetolysis and formolysis were hydrolyzed to 1-OH-d_2, and D scramblings in all the solvolysis products were measured by the nmr absorptions of the C-1 and C-2 protons of 1-OH-d_2 at δ 3.8 and 2.8. The pertinent data are summarized in Table I. For comparison, isotopic scrambling results from analogous solvolysis of labeled 2-phenylethyl tosylate are also included in Table I.

The data in Table I show enhancements in the extent of label scrambling in solvolyses of 1-OTs-*1*-d_2 relative to similar reactions with the unsubstituted 2-phenylethyl tosylate. These results support the conclusion that the ferrocenyl group as a substituent is electron donating.[2] The complete scrambling of the label in the recovered tosylate in one of the acetolysis runs also shows the occurrence of extensive internal returns, as has been observed in the acetolysis of the unsubstituted 2-phenylethyl tosylate.[3]

For the 1-OTs system, detailed kinetic studies would present difficulties, since the highly colored reactant would preclude rate determinations using indicators. Moreover, the nonvolatility of both 1-OTs and its solvolysis products as well as the overlapping of their nmr spectra prevented the use of vpc or nmr for kinetic investigations. However, from the reaction conditions and the yeilds of products and recovered tosylate given in Table I, it is apparent that, of the reactions investigated, solvolysis in aqueous acetone is the slowest, and probably formolysis is faster than acetolysis. The least amount of isotopic scrambling is also found for the reaction in acetone–H_2O, and this may reflect a smaller extent of *p*-ferrocenylphenyl participation with its consequent slower reaction rate. The complete scrambling of the label over C-1 and C-2 in the products from acetolysis and formolysis is similar to results observed in analogous reactions with 2-(*p*-methoxyphenyl)ethyl tosylate,[4] both the *p*-methoxy and *p*-ferrocenyl substituents being electron donating.

Experimental Section

Methyl *p*-Ferrocenylphenylacetate. Arylation of 70.0 g (0.38 mol) of ferrocene was carried out with diazotized *p*-aminophenylacetic acid using the general method described by Little, *et al.*[1] The reaction mixture was stirred overnight, poured into H_2O, and then repeatedly extracted with $CHCl_3$ until the extract became colorless. After drying over $MgSO_4$ and removal of the $CHCl_3$, the residue was esterified by refluxing for 2 days in 500 ml of MeOH containing 20 ml of concentrated HCl. The reaction mixture was poured into H_2O and extracted with benzene, the extract was dried over $MgSO_4$, the solvent was removed, and the residue was chromatographed through an alumina column (2 ft × 1.5 in.) with elution by a 7:2 (by volume) mixture of toluene–Skelly F, giving 25.7 g (yellow band) of recovered ferrocene and 25.9 g (orange band, 32% based on the consumed ferrocene) of methyl *p*-ferrocenylphenylacetate: nmr ($CDCl_3$) δ 7.1 (m, Ar H's, 4), 4.28, 4.13 (t's, C_5H_4, 4), 4.00 (s, C_5H_5, 5), 3.34 (s, CH_3, 3), 3.28 (s, CH_2, 2). The material was utilized directly for the next step in the synthesis.

2-(*p*-Ferrocenylphenyl)ethyl-*1,1*-d_2 Tosylate (1-OTs-*1*-d_2). The above methyl ester (25.9 g) was reduced with 2.0 g of $LiAlD_4$ in anhydrous ether in the usual manner. The product was chromatographed through the alumina column, giving 2.4 g of recovered ester (orange band, eluted with benzene) and 17.4 g (80%) of 1-OH-*1*-d_2 (golden band, eluted with ether), recrystallized from ether–pentane as golden granules: mp 91–92°; nmr ($CDCl_3$) δ 7.0–7.5 (m, Ar H's, 8), 4.58, 4.26 (t's, C_5H_4, 4), 4.00 (s, C_5H_5, 5), 2.80 (s, C-2 H's, 2), 1.55 (s, OH, 1). The corresponding nondeuterated 1-OH showed triplets at δ 3.80 and 2.80 for the C-1 and C-2 protons.

The 1-OH-*1*-d_2 (13.8 g) was converted to 1-OTs-*1*-d_2 by treatment with TsCl in pyridine at 0°. The product, taken up in ether,

Table I
Data from Solvolyses of 2-(*p*-Ferrocenylphenyl)ethyl-1,1-d_2 Tosylate

Solvent	Reaction conditions, Run 1	Reaction conditions, Run 2	Yield, %: Reaction product, Run 1	Yield, %: Reaction product, Run 2	Yield, %: Recovered tosylate, Run 1	Yield, %: Recovered tosylate, Run 2	Rearrangement of label from C-1 to C-2, %: Reaction product, Run 1	Rearrangement of label from C-1 to C-2, %: Reaction product, Run 2	Rearrangement of label from C-1 to C-2, %: Recovered tosylate, Run 1	Rearrangement of label from C-1 to C-2, %: Recovered tosylate, Run 2	Product from PhEtOTs
80% acetone–20% H_2O	Reflux, 60 hr	Reflux, 116 hr	27	47	70	48	15	16	0	0	6[a]
Glacial HOAc	100°, 17 hr	100° 48 hr	59	74	10	0	50	50	50		32.6[b]
97% HCOOH	60°, 17 hr	60°, 18 hr	52	58	0	0	50	50			41, 45[c]
F_3CCOOH	Reflux, 2 hr	25°, 17 hr	Decomposition								50[d]

[a] Work of Miss M. Vetter in this laboratory, using D labels. [b] From acetolysis of 2-phenylethyl-*1*-^{14}C tosylate at 115° for 74 hr: J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *J. Amer. Chem. Soc.*, **91,** 1154 (1969). [c] From formolysis of 2-phenylethyl-*1*-^{14}C tosylate in 90 and 100% HCOOH in the presence of sodium formate at reflux for 20 hr: C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Can. J. Chem.*, **35,** 1417 (1957). [d] From J. E. Nordlander and W. G. Deadman, *J. Amer. Chem. Soc.*, **90,** 1590 (1968), using D labels.

was decolorized with activated charcoal and recrystallized several times from ether–pentane, yielding 10.5 g (51%) of fine orange needles: mp 92–93°; nmr (CCl_4) δ 6.8–7.7 (m, Ar H's, 8), 4.46, 4.16 (t's C_5H_4, 4), 3.90 (s, C_5H_5, 5), 2.86 (s, C-2 H's, 2), 2.37 (s, CH_3, 3).

Anal. Calcd for $C_{25}H_{22}D_2O_3SFe$: C, 64.94; H and D, 5.63. Found: C, 64.22; H and D, 5.50.

Solvolysis Reactions. All solvents were deoxygenated by several hours of refluxing while a stream of N_2 was bubbled through the liquid. The reactions were carried out under N_2 using 0.50 g of 1-OTs-*1*-d_2 and 50 ml of solvent under the conditions given in Table I. Each reaction mixture was worked up by pouring into ice–H_2O, extraction with ether, washing with $NaHCO_3$ solution and then with H_2O, and chromatographing the residue from the extract through alumina which separated any unreacted tosylate from the product. In preliminary trials, it was noted that, while 1-OH and 1-OAc from solvolyses in acetone–H_2O and in HOAc were stable over alumina, passage of the formolysis product through the alumina column resulted largely in cleavage of the formate to the alcohol. Consequently, after separation of any unreacted tosylate, the acetolysis and formolysis products were hydrolyzed by refluxing for 8 hr in 50 ml of dioxane–20 ml of 10% NaOH and all D scramblings were measured using the resulting 1-OH-d_2.

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Registry No. Methyl *p*-ferrocenylphenylacetate, 12290-33-4; 2-(*p*-ferrocenylphenyl)ethyl-*1,1*-d_2 tosylate, 43225-00-9; 2-(*p*-ferrocenylphenyl)ethanol-*1,1*-d_2, 43189-89-5; *p*-aminophenylacetic acid, 1197-55-3.

References and Notes

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(2) D. W. Slocum and C. R. Ernst, *Advan. Organometal. Chem.*, **10**, 79 (1972).
(3) J. L. Coke, F. E. McFarlane, M. C. Mourning, and M. G. Jones, *J. Amer. Chem. Soc.*, **91**, 1154 (1969).
(4) E. J. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); M. G. Jones and J. L. Coke, *J. Amer. Chem. Soc.*, **91**, 4284 (1969).

Metal Ion Catalysis of Oxygen-Transfer Reactions. IV. The Molybdenum-Catalyzed Oxidation of Substituted Azobenzenes[1a]

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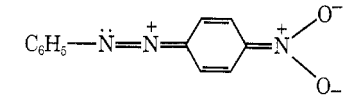
The scope of hydroperoxide oxidations, as catalyzed by molybdenum compounds, has widened perceptibly in recent years. Such oxidations have been used to convert alkenes to epoxides,[2] imines to imine oxides,[3] tertiary amines to amine oxides,[4] and substituted anilines to nitrobenzenes.[5] We here report extension of the use of the molybdenum–hydroperoxide combination to the oxidation of substituted azobenzenes to azoxybenzenes, a conversion which is generally carried out with peroxycarboxylic acids. In comparing the two methods, we find that the yields of azoxy compounds from the metal-catalyzed reactions compare favorably with those from the peroxy acids, but reactions with the RO_2H–Mo systems are considerably slower. In favorable cases, the catalyzed oxidations exhibit significant regiospecificity; moreover, we would anticipate them to be useful for azo oxidations in cases where a peracid-sensitive group (such as keto) lies elsewhere in the molecule. The catalyzed oxidations have not been effective in the oxidation of azobenzonitriles.

In conjunction with *tert*-butyl hydroperoxide, we have used, as catalysts, molybdenum hexacarbonyl [$Mo(CO)_6$] and the dipivaloylmethane chelate of molybdenum(VI) [$MoO_2(dpm)_2$],[6] both of which are soluble in hydrocarbon solvents. Reaction conditions, yields, and conversions are summarized in Table I.

The marked similarity between the $MoO_2(dpm)_2$-catalyzed oxidations here described and the $MoO_2(acac)_2$-catalyzed epoxidation of olefins (for which kinetic evidence points to a nonradical path[2b]) suggests a polar mechanism featuring the transfer of electron-deficient oxygen to one of the azo nitrogens, and the observed catalytic ineffectiveness of those metal centers which promote homolysis of hydroperoxides[6] may be taken as further evidence for the heterolytic character of the catalyzed azo oxidations. Moreover, with each of the unsymmetrically substituted azobenzenes, the distribution of isomeric azoxy products from the $MoO_2(dpm)_2$-catalyzed reaction corresponds closely to that from the oxidation with peroxyacetic acid.[7] Note that, in the one case where we find a difference, the $MoO_2(dpm)_2$-catalyzed oxidation of the monomethoxy derivative is significantly more regiospecific than the oxidation with CH_3CO_3H.

The *p*-Cl substituent appears to have little directive effect in reactions of this kind, for oxidations of the 4-chloro compound yield mixtures of azoxy products with the α isomer only slightly predominant.[8] In the oxidation of the nitro and monomethoxy compounds, the sites at which attack preferentially occurs, both with *t*-BuO_2H–$MoO_2(dpm)_2$ and with CH_3CO_3H, are consistent with significant contributions of structures 1 (N_β deactivated)[8] and 2 (N_α activated). The reaction of the methoxy derivative in acetic acid is, however, complicated by the partial conversion of this azo compound to its conjugate acid,[9] with protonation principally at N_α, which is the more nucleophilic nitrogen. In the latter oxidation the ratio of the two possible azoxy products will depend not only on the mode of partition of the azo compound between two acidic and one basic forms, but also on the rate of oxidation of each form. The oxidation with *t*-BuO_2H–$MoO_2(dpm)_2$, which is carried out in a nonacidic medium, is free from this complexity and yields only the α product.



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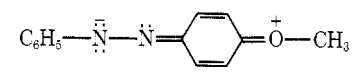

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With $Mo(CO)_6$ as catalyst, the hydroperoxide oxidation of the monomethoxy compound yields a mixture of nearly equal quantities of α and β azoxy products. This striking change in selectivity argues strongly that substantial alteration in mechanism has resulted from variation in the oxidation state and the ligand environment of molybdenum. The $MoO_2(dmp)_2$-catalyzed reaction may be reasonably assumed to proceed through the same type of Mo(VI)–hydoperoxide complex which has been shown[2b] to intervene in the $MoO_2(acac)_2$-catalyzed epoxidation of cyclohexene. For the $Mo(CO)_6$-catalyzed reaction, in which the active catalytic species[10] features molybdenum in one of its lower oxidation states, reaction through a ternary complex of metal, substrate, and oxidant, such as those characterized in oxidation catalyzed by the lower oxidation states of rhodium and iridium,[11] remains a clear possibility. Suggested transition states for the two types of catalyzed oxidation are shown schematically as **3** and **4**.