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HAPTOTROPIC REARRANGEMENT OF TRICARBONYL(2-ACYLOXYTROPONE)IRON

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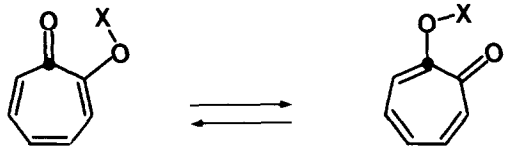
Summary: Respective two isomeric iron tricarbonyl complexes of 2-acetoxy- and 2-benzoyloxytropones were synthesized. These complexes rearranged to equilibrium mixtures of diastereomeric isomers, respectively, by 1,3-haptotropic rearrangement of iron tricarbonyl group but not by acyl migration and successive 1,2-haptotropic rearrangement, the mechanism having been clarified by the reaction of optically acitve complexes.

Previously, we reported that optically active tricarobnyl(tropone)iron racemized by 1,3-haptotropic rearrangemnet with relatively high activation free energy ($\Delta G^{\ddagger}$ = 25.5 kcal·mol^{-1}).[1] On the other hand, 2-acyloxy- and 2-trialkylsilyloxytropones were found to rearrange between 1 and 1' even at low temperature with relatively low activation free energy ($\Delta G^{\ddagger}$ = 8 ~ 11 kcal·mol^{-1}).[2] Here, we report the synthesis of 2-acyloxy- and 2-trimethylsilyloxytropone iron tricarbonyl complexes and their haptotropic rearrangement.

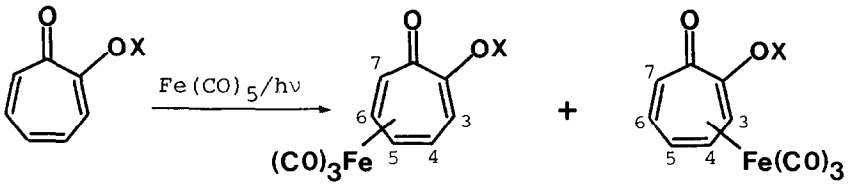


1 1'

a; X = Ac, b; X = COPh, c; X = $SiMe_2CHMeEt$

2-Acetoxytropone (1a) reacted with $Fe(CO)_5$ under irradiation with high pressure mercury lamp (100 w) to give a mixture of isomeric iron tricarbonyl complexes (2a and 3a) in 58% yield.[3] ^{1}H-NMR of the reaction mixture showed the ratio of 2a and 3a is 3 : 2. Similarly, 2-benzoyloxytropone (1b) afforded 3 : 2 mixture of 2b and 3b in 43.7% yield. However, 2-trimethylsilyloxytropone (1d) yielded only a complex (2d) in 7.8% yield accompanying unknown violet oil. The complexes (2 and 3) can be separated by medium pressure liquid chromatography using CIG prepacked column (cps-3), and their physical data are shown in Table 1.

The complexes (2a and 3a) slowly rearranged each other in solution ($CDCl_3$, benzene or hexane) at room temperature to their equilibrium mixture, respectively. The rearrangement of 2a was monitored in $CDCl_3$ by ^{1}H-NMR in the temperature range 40 ~ 55°C by way of the signal of methyl protons.



a; X = Ac, b; X = COPh, d; X = $SiMe_3$, e; X = H

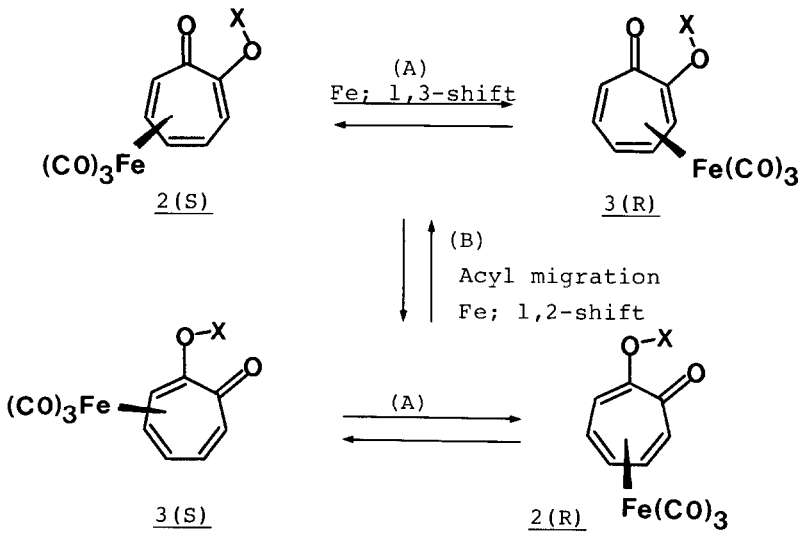
The activation energy for this rearrangement was found to be 26.7 kcal·mol^{-1}. Experimental parameters at 50°C were $\Delta G^{\ddagger}$ = 25.3 kcal·mol^{-1}, $\Delta H^{\ddagger}$ = 26.1 kcal·mol^{-1}, $\Delta S^{\ddagger}$ = 2.4 cal·mol^{-1}, and k = 2.4 x 10^{-5} s^{-1}. The similar rearrangement was observed for the complexes (2b and 3b), and the rearrangement of 2b was similarly monitored in $CDCl_3$ by ^{1}H-NMR in the temperature range 40 ~ 55°C by using H-7 protons. Thermodynamic parameters at 50°C were obtained as follows; Ea = 30.7 kcal·mol^{-1}, $\Delta G^{\ddagger}$ = 25.4 kcal·mol^{-1}, $\Delta H^{\ddagger}$ = 30.1 kcal·mol^{-1}, $\Delta S^{\ddagger}$ = 14.6 cal·mol^{-1}, and k = 2.4 x 10^{-5} s^{-1}. The complex (2d), however, did not isomerize under the similar condition, and instead the decomposition of the complex was observed.

There are two possible mechanisms for this rearrangement; mechanism (A) which proceeds by 1,3-iron shift and mechanism (B) which proceeds by acyl migration and successive 1,2-iron shift. If the reaction proceeds by mechanism (A), optically pure complexes 2(S) and 2(R) will give equilibrium mixtures of 2(S) and 3(R), and 2(R) and 3(S), respectively. If the reaction proceeds by mechanism (B), both of 2(S) and 2(R) will give racemic mixtures of 2 and 3, respectively. The reaction mechanism was clarified by using optically active complexes of 2.

The complexes (2a and 2b) were resolved into their optical isomers, respectively, on a column packed with DAICEL CHIRALPAK OT(+) using hexane and 2-propanol (97 : 3) as eluent. Both of the first fractions of the chromatography of 2a and 2b showed dextrorotatory and the second fractions showed levorotatory; UV and CD curves of the first fractions are shown in Fig. 1. Attempted resolution of 3a and 3b using the same column did not show two peaks, but the left (faster) and right (slower) parts of the peaks exhibit levo- and dextrorotatory, respectively, and opposite CD curves each other.

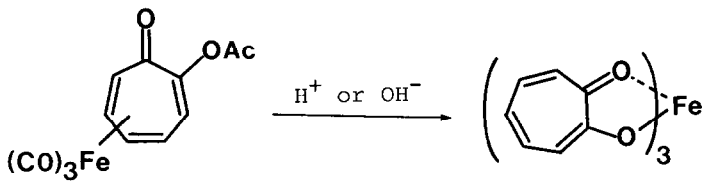
Heating of the solution of (+)-2a and (+)-2b in hexane at 60°C afforded equilibrium mixtures of (+)-2a and (-)-3a, and (+)-2b and (-)-3b, respectively. These results indicate that the rearrangement proceeds by 1,3-iron shift of mechanism (A).

The reason of inhibition of acyl migration in these complexes is supposed to be due to an instability of complexed tropylium ion[4] which must be formed as an intermediate of the migration.[2]



When 2a and 3a were dissolved in $CDCl_3$ in the presence of one drop of CF_3COOD, the complexes rapidly rearranged to give the same mixtures of 2a and 3a in the ratio of about 2 : 1, respectively. Furthermore, ^{1}H-NMR of 2a and 3a in CF_3COOD showed the similar pattern with that of tricarbonyl(tropone)iron itself[5] to form the same carbonium ion protonated at C-7 of 3a, respectively.

Tricarbonyl(tropolone)iron (2e) is a very interesting unknown complex. Hydrolysis of 2a by acidic or alkaline condition did not give the complex (2e), but only the known chelate complex (4) was obtained in good yield.



2a 4

Table 1. Physical Data for the Complexes (2 and 3).

2a: mp 102-103°C; ^{1}H-NMR ($CDCl_3$): δ 2.10(s,Me), 2.65(t,m, J=8.8 Hz, H-4), 3.20 (d,m, J=8.8, H-7), 6.31(d, J=8.8, H-3), 6.45(m, H-5,6); UV (EtOH): λ_{max} (log ε), 230nm(4.28), 270sh(3.96), 320sh(3.59), 450(2.53); IR (KBr): 2060, 2010, 1985, 1750, 1640, 1635 cm^{-1}

3a: mp 77-80°C; ^{1}H-NMR ($CDCl_3$): δ 2.15(s, Me), 2.73(t, J=7.6, H-5), 5.15(d, J= 11, H-7), 6.27(d,d, J=7.3, 5.3, H-4), 6.43(d,d, J=5.1, 1.5, H-3), 6.64(d,d, J=11, 8.2, H-6); UV (EtOH): λ_{max}(log ε), 235nm(4.21), 280sh(3.89), 320sh (3.51), 444(2.55); IR (KBr): 2075, 2070, 2000, 1990, 1750, 1640 cm^{-1}

2b: mp 157-158°C; ^{1}H-NMR ($CDCl_3$): δ 2.70(t,m, J=8.8, H-4), 3.27(d,m, J=8.8, H-7), 6.4(m, H-3,5,6), 7.5(m, 3H, Ph), 8.0(m, 2H, Ph); UV (EtOH): λ_{max} (log ε), 232nm(4.47), 270sh(4.06), 320sh(3.62), 450(2.56); IR (KBr): 2075,

2010, 1990, 1985, 1725, 1635 cm^{-1}

3b: mp 150-151°C; ^{1}H-NMR ($CDCl_3$): δ 2.78(t, J=7.5, H-5), 5.22(d, J=11, H-7), 6.30(d,d, J=7.4, 5.3, H-4), 6.55(d, J=5.3, H-3), 6.66(d,d, J=11, 8.0, H-6), 7.46(m, 3H, Ph), 8.07(m, 2H, Ph); UV (EtOH): λ_{max}(log ε), 232nm(4.48), 280sh (4.01), 320sh(3.55), 440(2.60); IR (KBr): 2070, 2010, 1995, 1730, 1640 cm^{-1}

2d: mp 62-65°C; ^{1}H-NMR ($CDCl_3$): δ 0.13(s, 3Me), 2.72(t,d, J=8.7, 0.9, H-4), 3.16(d, J=7.3,H-7), 5.88(d, J=8.7, H-3), 6.44(m, H-5,6); UV (isooctane): λ_{max}(log ε), 229nm(4.29), 270sh(3.94), 320sh(3.70), 460(2.66); IR (KBr): 2070, 2010, 1990, 1980, 1960, 1635 cm^{-1}

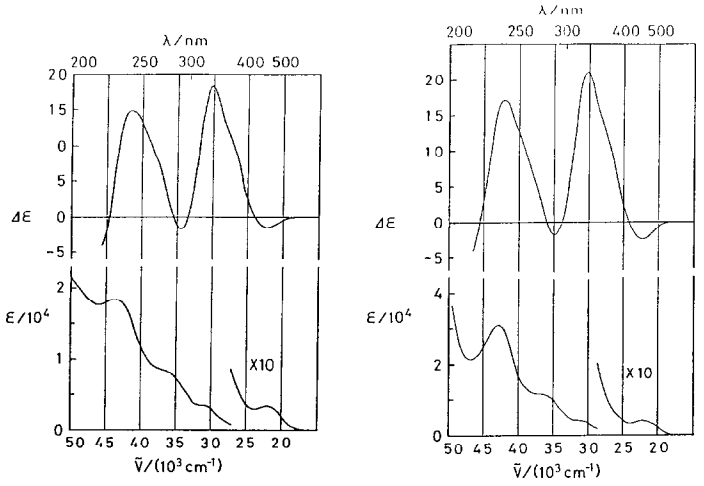


Fig. 1. Absorption (bottom) and CD (top) curves of the first fractions of 2a (left) and 2b (right) in CH_3CN at room temperature.

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