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THE SYNTHESES OF IRON CARBONYL COMPLEXES OF 2-SUBSTITUTED TROPONES

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2-Substituted tropones reacted with $Fe_2(CO)_9$ or with $Fe(CO)_5$ under irradiation to give iron tricarbonyl complexes coordinated at unsubstituted diene moiety. 2-Bromotropone afforded another iron tricarbonyl complex coordinated at substituted diene as a minor product. 2-Methyl-, 2-phenyl-, and 2-tosyloxytropones yielded di-π-allyl type diiron hexacarbonyl complexes. Furthermore, 2-dialkylaminotropones gave diiron hexacarbonyl complexes as a major product containing a new enamine type complex.

Tropone iron tricarbonyl was known to have characteristic chemical reactivities[1)] and physical properties, e.g. chiral property caused by distorted character of tropone moiety in the complex,[2)] compared with those of tropone itself. Since only few iron carbonyl complexes of substituted tropones have been reported.[1a,c,i 2c,3)] we have studied the syntheses of complexes from various 2-substituted tropones, the results of which will be reported in this paper.

According to the procedure of Eisenstadt,[1c)] reaction of 2-substituted tropones (1, X = Me, Ph, Br, OMe, OTs, CN) with about 2 molar equivalents of $Fe_2(CO)_9$ in refluxing ether or in benzene at 50 °C afforded the corresponding iron tricarbonyl complexes (2) coordinated at unsubstituted diene moiety as a major product. The reaction of 1 with $Fe(CO)_5$ in benzene under irradiation with 100 W high pressure mercury lamp was found to give 2 in the better yields. The yields were summarized in Table 1, and the physical and spectroscopic data of the products were shown in Table 2.

In the case of 2-bromotropone, two kinds of iron tricarbonyl complexes were isolated in total yield of 7.6%. These complexes could be separated by HPLC[4)] and the major complex (2c) was purified by recrystallization, but the minor one (3c) could not be obtained in pure state even by using of HPLC, because the minor one easily isomerized to the major one during purification. Heating of 2c or 3c at 50 °C attains equilibrium of 2c and 3c in the ratio of 90.6 : 9.4. The structures of 2c and 3c were determined as shown in the scheme in which $Fe(CO)_3$ group coordinated at unsubstituted and substituted diene moieties, respectively, by inspection of ^1H-NMR spectra.

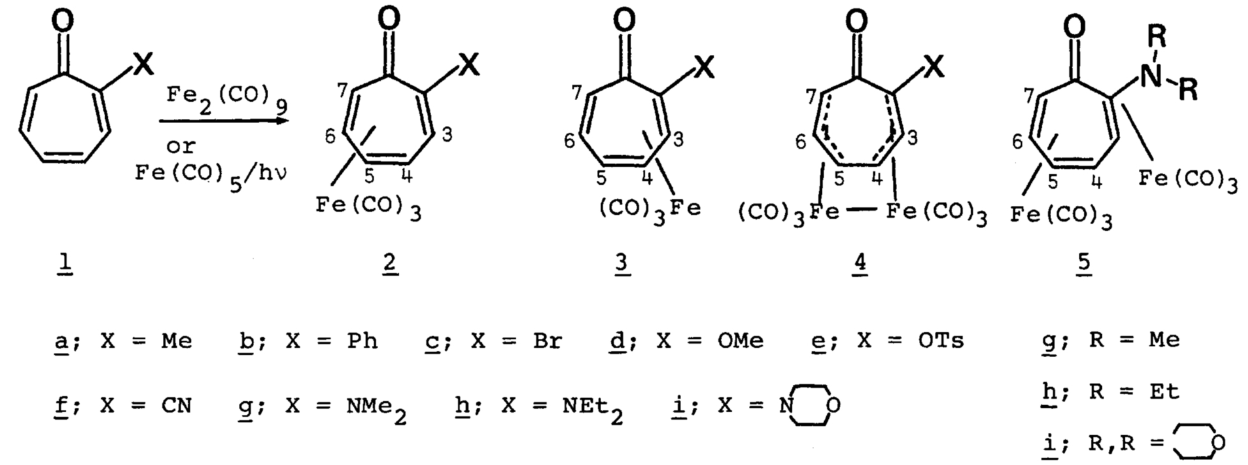

Table 1. Yields (%) of the complexes from 1a-i by the reaction with $Fe_2(CO)_9$ or with $Fe(CO)_5$/hν

1	2	3	4	5
a	55[1c)]	-	4.4	
b	74[1c)]	-	19	
c	7.6 (26.6)[a)]	b)	-	
d	27.6 (31.8)	-	-	
e	28.2 (44)	-	3.5	
f	9.1 (38)	-	-	
g	9.8	-	-	33.4
h	2.9 (6)	-	-	62.8 (3.9)
i	c)	-	-	55.9

a) Yields by $Fe(CO)_5$/hν are shown in parentheses. b) Yield of 3c is included in that of 2c. c) Extreme low yield.

2-Methyl-, 2-phenyl-,and 2-tosyloxytropones afforded di-π-allyl type diiron hexacarbonyl complexes (4) as minor products. The structure of 4 were determined by the studies of ^{1}H-NMR spectra; thus ^{1}H-NMR of the complexes (4) showed the similar pattern with that of tropone diiron hexacarbonyl complex (4; X = H).[1i)]

2-Dimethylaminotropone reacted with excess of $Fe_2(CO)_9$ in dry ether at 40 °C to give diiron hexacarbonyl complex (5g) as a major product besides iron tricarbonyl complex (2g). The similar reaction can be generally seen in other 2-dialkylaminotropones; 2-diethylamino- and 2-morpholinotropones gave the same two type complexes (2h and 5h) and (2i and 5i), respectively, but 2i was not obtained in pure state because of its very small quantity. The structures of the complexes (5) were established on the basis of spectroscopic data, especially by FD mass, ^{1}H-NMR and IR spectra as follows. Molecular ion peak of 5g appeared at m/e 429 corresponding to diiron hexacarbonyl complex. In the NMR of 5g, two methyl signals appeared nonequivalently at δ 2.33 and 2.79 ppm, and the ring protons, H-5 and H-6, appeared at δ 5.78 and 6.20 ppm, respectively, and the pattern is different from those of di-π-allyl type complexes 4, but similar to those of 2.

Table 2. Physical and spectroscopic data of the complexes [a)]

Compd	Mp θm/°C	^{1}H-NMR ($CDCl_3$, 90 MHz) δ ppm (multiplicities; J in Hz)	λ_{max}^{EtOH}/ nm (log ε)
2c	118-119 (d)	2.63(t,m;8.8;H-4), 3.36(br d;9.0;H-7), 6.41(m;H-5,6), 7.15(d;8.8;H-3)	230(4.25),282(3.90), 320sh(3.46),461(2.70)
2d	88-89	2.82(d,t;7.3,1.5;H-4), 3.19(d,d;7.3,1.6; H-7), 3.40(s;OMe), 5.55(d;8.8;H-3), 6.32 (m;H-5,6)	234(4.26),279(3.91) 326(3.64),461(2.43)
2e	166-168 (d)	2.43(s;Me), 2.61(t,m;8.9;H-4), 3.11(br d; 8.8;H-7), 6.49(m;H-5,6), 6.61(d;9.1;H-3) 7.30(d;8.3;2H), 7.78(d;8.3;2H)	227(4.44),270sh(3.96), 310sh(3.62),454(2.62)
2f	174-175 (d)	2.68(d,d,d;8.8,7.0,1.6;H-4), 3.31(d,d; 7.3,1.6;H-7), 6.49(m;H-5,6),7.39(d;8.8; H-3)	225(4.33),285(4.00), 320sh(3.79),472(2.97)
2g	oil	2.38(s;2Me), 2.85(d,t;7.0,1.7;H-4, 3.17 (d,d;7.0,1.3;H-7), 5.45(d;8.8;H-3), 6.27 (m;H-5,6)	238(4.24),344(3.72), 490(2.73)
2h	56-60	0.91(t;7.0;2Me), 2.78(q;7.0;2-CH$_2$-), 2.86(m;H-4), 3.19(d,d;7.0,1.6;H-7), 5.45 (d;8.8;H-3), 6.27(m;H-5,6)	230sh(4.23),348(3.66), 495(2.83)
3c		2.64(br t;H-5), 5.26(d,11.0;H-7), 6.28 (d,d;7.3,5.5;H-4), 6.60(d,d;11.0,7.9; H-6), 6.95(d,d;5.5,1.3;H-3)	
4a	96-99 (d)	1.63(s;Me), 3.38(d,d;7.1,1.6;H-7), 4.4~ 4.8(m;H-3~6)	250sh(4.32),344(3.99), 435(3.50)
4b	137-139 (d)	3.39(d;7.9;H-7), 4.6~5.0(m;H-3~6), 7.28 (m;Ph)	240sh(4.44), 343(3.99), 438(3.55)
4e	174-175 (d)	2.43(s;Me), 3.27(d,d;7.5,1.7;H-7), 4.5~ 4.8(m;H-4~6), 5.27(d;7.5;H-3), 7.31(d; 8.4;2H), 7.85(d;8.4;2H)	222(4.61),343(3.93), 431(3.50)
5g	127-130 (d)	2.33(s;Me), 2.79(s;Me), 3.33(d,d;7.7,1.3; H-7), 3.49(m;H-3,4), 5.76(d,d,m;7.7,5.0; H-5), 6.20(d,d,d;7.7,5.0,1.2;H-6)	327(4.04),470sh(3.30)
5h	145 (d)	1.0(t;7.0;Me), 1.04(t;7.0;Me), 2.13(d,q; 14.0,7.0;1H), 2.40(d,q;14.0,7.0;1H), 2.77(d,q;14.0,7.0;1H), 3.33(d,d;7.7,1.1; H-7), 3.4~3.6(m;H-3,4), 3.70(d,q;14.0, 7.0;1H), 5.77(d,d,d,d;5.3,5.3,2.0,1.0; H-5), 6.19(d,d,d;7.7,5.3,1.0;H-6)	327(4.05),490sh(3.27)
5i	164-165 (d)	2.2(m;1H), 2.7(m;2H), 3.1~3.6(m;2H,H-3,4, 7), 3.8(m;3H), 5.8(m;H-5), 6.2(d,d;7.7, 4.6;H-6)	230sh(4.41),329(3.97), 450sh(3.11)

a) Complexes of a-f show orange to reddish orange, and complexes of g-i show violet.

Methylene protons of diethylamino group of 5h appeared as four nonequivalent signals (see Fig. 1). Furthermore, 5g, 5h, and 5i showed carbonyl bands at 1605, 1600, and 1610 cm^{-1}, respectively in the IR spectra (KBr). From these data we assigned the structures 5 shown in the scheme, containing one Fe(CO)$_3$ group coordinates to unsubstituted diene and the other one coordinates to enemine moiety, although the stereochemistry of two Fe(CO)$_3$ groups is not clear.

Heating of the complex 5g in benzene at 80 °C afforded 2-dimethylaminotropone and iron tricarbonyl complex (2g) in 74.7 and 23.7% yield, respectively.

Electronic absorption spectra of these complexes consist of three or four bands and the longest bands arise from charge transfer (CT) transition, which shifted to longer wavelength from 448 nm for tropone iron tricarbonyl to 495 nm for 2-diethylaminotropone iron tricarbonyl complex.

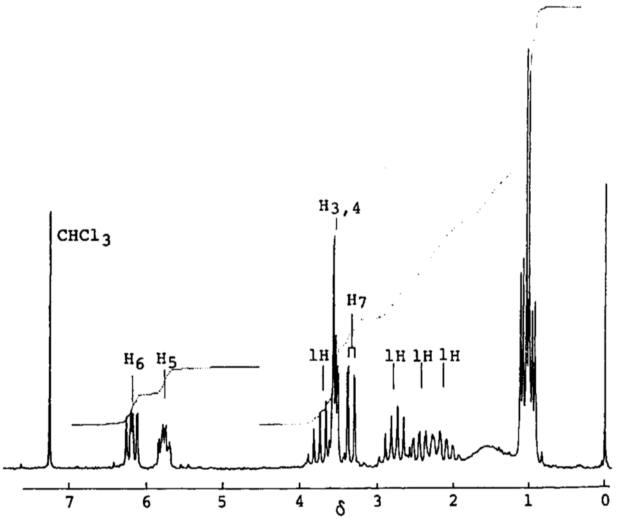

Fig. 1. ^{1}H-NMR spectrum of 5h in $CDCl_3$ at 90 MHz.

References

1) a) D. F. Hunt, G. C. Farrant, and G.T. Rodeheaver, J Organomet. Chem., 38, 349 (1972); b) B. F. G. Johnson, J. Lewis, P. McArdle, and G. L. P. Randall, J.Chem. Soc., Dalton, 1972, 2076; c) A. Eisenstadt, J. Organomet. Chem., 80, 245 (1974); 97, 443 (1975); 113, 147 (1976); d) R. Gompper and W. Reiser, Tetrahedron Lett., 1976, 1263; e) Z. Goldschmidt and Y. Bakal, ibid., 1976, 1279; Z. Goldschmidt and S. Antebi, ibid., 1978, 1225; f) M. Frank-Neumann and D. Martina, ibid., 1975, 1759; M. Frank-Neumann, F. Brion, and D. Martina, ibid., 1978, 5133; g) M. Cavazza, G. Marganti, and F. Pietra, J. Org. Chem., 45, 2001 (1980); h) M. Yasuda and K. Kanematsu, ibid., 47, 110 (1982); i) N. Morita and T. Asao, Chem. Lett., 1982, 1575.

2) a) S. Litman, A. Gedanken, Z. Goldschmidt, and Y. Bakal, Chem. Commun., 1978, 983; b) K. J. Karel, T. A. Albright, and M. Brookhart, Organometallics, 1, 419 (1982); c) A. Tajiri, N. Morita, T. Asao, and M. Hatano, Angew. Chem., Int. Ed. Engl., 24, 329 (1985).

3) E. H. Braye and W. Hübel, J. Organomet. Chem., 3, 25 (1965); A. J. Birch, D. E. Cross, J. Lewis, D. A. White, and S. B. Wild, J. Chem. Soc., A, 1968, 332.

4) The complexes were separated by HPLC on a column packed with DAICEL CHIRALPAK OT(+) using a mixture of hexane and 2-propanol (97 : 3) as solvent.

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