

## Identification of the Tricarbonyliron Complex of 7-Azabicyclo[2.2.1]heptadiene Derivatives as the Intermediate in Nitrene Extrusion Reactions

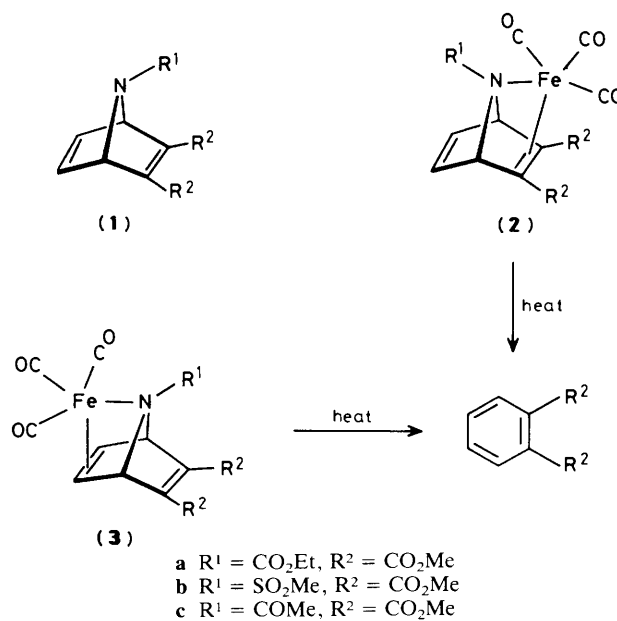
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Several tricarbonyliron complexes of *N*-substituted 7-aza-2,3-bismethoxycarbonylbicyclo[2.2.1]heptadiene have been isolated and identified as the intermediates of nitrene-extrusion reactions.

Heteroatom-extrusion reactions have been widely applied to 7-heteroatombicyclo[2.2.1]heptadiene derivatives for convenient preparations of aromatic compounds.<sup>1</sup> Among the best known examples are the 7-oxa-norbornadiene (norbornadiene = nbd) complexes due to their easy preparation *via* Diels-Alder cycloadditions.<sup>2-4</sup> Much less studied are the 7-aza-nbd complexes, not only because of the poor cycloaddition efficiency of the pyrroles, but also because of the lack of effective methods to extrude the nitrogen. In this report we describe a nitrene-extrusion reaction for the 7-aza-nbd complexes mediated by iron carbonyl complexes, through which several intermediates are isolated and identified.

Three 7-aza-nbd derivatives (**1a-c**) were prepared according to the published methods.<sup>5</sup> They were treated with  $\text{Fe}_2(\text{CO})_9$  in tetrahydrofuran (THF) at room temperature for 20 h, forming complexes (**2a**) (23%), (**2b**) (36%), (**2c**) (38%), and (**3a**) (18%), (**3b**) (27%), (**3c**) (trace). The structures were confirmed by spectroscopic analyses. Heating the purified samples of (**2a-c**) or (**3b**) in acetonitrile at 60 °C produced dimethyl phthalate in 100, 83, 95, and 93% yields respectively. These controlled thermolyses demonstrate that the nitrene-extrusion reactions proceed in a stepwise manner with the iron carbonyl complexes as key intermediates.



The molecular formulae of complexes (**2a—c**) and (**3a—c**) were determined by mass spectroscopy. † A consecutive loss of three CO groups from the parent peak confirmed the presence of three carbonyls bound to metal in each complex. All compounds showed strong i.r. absorptions at ca. 2000 cm<sup>-1</sup>, corresponding to the stretching frequencies of metallic CO. The stereochemical difference between complexes (**2a—c**) and (**3a—c**) arises in the relative position of the tricarbonyl-iron moiety, which may be chelated by either site of the 7-aza-nbd ligands. The geometry of each isomer pair can be resolved based on their <sup>1</sup>H and <sup>13</sup>C n.m.r. spectra. ‡ It is a common phenomenon for alkene-metal complexes that the n.m.r. chemical shifts of vinylic <sup>1</sup>H and <sup>13</sup>C nuclei move upfield upon co-ordination.<sup>6</sup> In the <sup>13</sup>C n.m.r. spectrum of (**2a**) the absorption of C(2,3) (δ 80.3) appears at a much higher field relative to C(5,6) (142.1), indicating the iron is bonded to C(2)=C(3). Conversely, the signal of C(2,3) (δ 146.4) in (**3b**) appears considerably downfield compared to that of C(5,6)

(69.8), indicating co-ordination between the iron and C(5)=C(6). A similar trend is also seen in the <sup>1</sup>H n.m.r. spectra. For instance, the H(5,6) signals of (**2a**) (δ 6.60) are located downfield of those of (**3a**) (3.55), and so are the H(5,6) signals of (**2b**) (6.70) compared to those of (**3b**) (3.50). Preliminary X-ray crystallography of (**2b**) shows that a co-ordination bond is formed between the nitrogen and the iron.

Complexes (**2a—c**) are more stable thermally than complexes (**3a—c**). The nitrene-extrusion reaction induced by heating (**3b**) at 60 °C proceeds about 100 times as fast as that of (**2b**). The enhanced stability seems to derive from the methoxy carbonyl groups conjugated by the co-ordinated double bonds.<sup>7</sup> Nevertheless, both isomers (**2b**) and (**3b**) produce the phthalate in comparably good yields. It may be concluded that the changing of geometry from (**2a—c**) to (**3a—c**) does not significantly affect the mechanism of the deamination.

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† Mass spectrum of (**2a**): *m/z* 421 (*M*<sup>+</sup>, 0.8%), 393 (1.1, *M*<sup>+</sup> - CO), 390 (1.5, *M*<sup>+</sup> - OMe), 365 (6.7, *M*<sup>+</sup> - 2CO), 337 (11, *M*<sup>+</sup> - 3CO), 292 (46), 222 (21), 192 (14), 163 (100); (**2b**): *m/z* 427 (*M*<sup>+</sup>, 0.4%), 396 (0.4, *M*<sup>+</sup> - OMe), 371 (1.9, *M*<sup>+</sup> - 2CO), 343 (7.1, *M*<sup>+</sup> - 3CO), 285 (2.1), 264 (8.7), 194 (5.4), 163 (100); (**2c**): *m/z* 391 (*M*<sup>+</sup>, 0.7%), 363 (0.9, *M*<sup>+</sup> - CO), 360 (0.6, *M*<sup>+</sup> - OMe), 335 (4.2, *M*<sup>+</sup> - 2CO), 307 (0.7, *M*<sup>+</sup> - 3CO), 266 (23), 208 (44), 163 (100). I.r. (KBr, *v*<sub>max</sub>, cm<sup>-1</sup>) (**2a**): 2065, 2000, 1980, 1760, 1725, 1698; (**2b**): 2060, 2000, 1980, 1680; (**2c**): 2060, 1990, 1747, 1723, 1691; (**3a**): 2095, 2000, 1985, 1722; (**3b**): 2095, 2015, 1985, 1730.

‡ <sup>1</sup>H N.m.r. (200 MHz, solvent CDCl<sub>3</sub>, standard SiMe<sub>4</sub>) spectrum of (**2a**): δ 1.10 (3 H, t, *J* 7 Hz), 3.76 (6 H, s), 4.06 (2 H, q, *J* 7 Hz), 5.35 (2 H, br), 6.60 (2 H, br); (**2b**): δ 2.60 (3 H, s), 3.75 (6 H, s), 5.40 (2 H, s), 6.70 (2 H, s); (**2c**): δ 1.90 (3 H, s), 3.80 (6 H, s), 5.44 (2 H, m), 6.69 (2 H, m); (**3a**): δ 1.10 (3 H, t, *J* 7 Hz), 3.55 (2 H, s), 3.80 (6 H, s), 4.08 (2 H, q, *J* 7 Hz), 5.10 (2 H, s); (**3b**): δ 2.70 (3 H, s), 3.50 (2 H, s), 3.84 (6 H, s), 4.95 (2 H, s). <sup>13</sup>C N.m.r. (standard using the centre peak of CDCl<sub>3</sub> at δ 76.90) spectrum of (**2a**): δ 13.7, 51.8, 57.3 (C-1, 4), 64.7, 80.3 (C-2,3), 142.1 (C-5,6), 155.4, 172.6, 208.1; (**2c**): δ 21.3, 51.9, 57.4 (C-1,4), 79.1 (C-2,3), 142.8 (C-5,6), 172.5, 176.9, 207.4, 208.1; (**3b**): δ 40.4, 52.6, 57.6 (C-1,4), 69.8 (C-5,6), 146.4 (C-2,3), 163.2, 207.8.

## References

- 1 H. N. C. Wong, T.-K. Ng, and T.-Y. Wong, *Heterocycles*, 1983, **20**, 1815.
- 2 H. N. C. Wong, Y. D. Xing, Y. F. Zhou, Q. Q. Gong, and C. Zhang, *Synthesis*, 1984, 787; N. Z. Huang, Y. D. Xing, and D. Y. Ye, *ibid.*, 1982, 1041.
- 3 P.-s. Lei and P. Vogel, *Organometallics*, 1986, **5**, 2500; P. Vioget, M. Bonivento, R. Roulet, and P. Vogel, *Helv. Chim. Acta*, 1984, **67**, 1630.
- 4 C.-H. Sun and T. J. Chow, *Heterocycles*, 1988, **27**, 217; C.-H. Sun and T. J. Chow, *J. Organomet. Chem.*, 1987, **333**, C21.
- 5 R. Kitzing, F. Fuchs, M. Joyeux, and H. Prinzbach, *Helv. Chim. Acta*, 1968, **51**, 888; H. Prinzbach, R. Fuchs, and R. Kinzing, *Angew. Chem.*, 1968, **80**, 78.
- 6 T. J. Chow, Y.-S. Chao, and L.-K. Liu, *J. Am. Chem. Soc.*, 1987, **109**, 797; T. J. Chow and Y.-S. Chao, *J. Organomet. Chem.*, 1985, **296**, C23; T. J. Chow, M.-Y. Wu, and L.-K. Liu, *ibid.*, 1985, **281**, C33.
- 7 T. J. Chow, T.-H. Lin, S.-M. Peng, and M.-C. Cheng, *J. Organomet. Chem.*, 1986, **316**, C29.