SHORT PAPER

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Reaction of 7-aza-norbornadiene and $[W(CO)_4(NCMe)_2]$[†]

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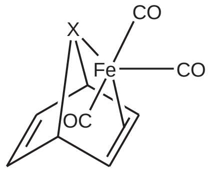
Three ring-opening products, 3-(*p*-toluenesulfonyl)-N-methoxy- carbonylpyrrole, 3-(*p*-toluenesulfonyl)pyrrole, and phenyl tolyl sulfone, were obtained from the reaction of 7-methoxycarbonyl-2-p-toluenesulfonyl-7-aza-norbornadiene and $[W(CO)_4(NCMe)_2]$.

Keywords: 7-aza-norbornadiene, $[W(CO)_4(NCMe)_2]$

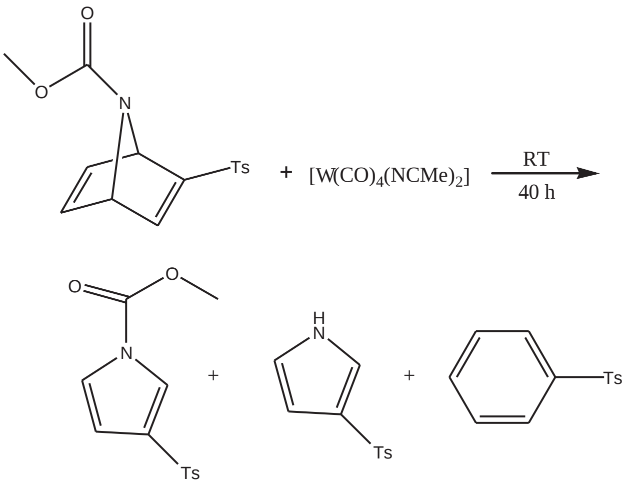
Treatment of 7-heteroatomnorbornadiene with iron carbonyl yielded complexes with the iron carbonyl situated at the *endo*-position.[1-10] When the 7-position of norbornadiene was substituted by either oxygen (7-oxa-NBD) or nitrogen (7-aza-NBD), the iron carbonyl was bound at their *exo*-position because of the additional interaction of the heteroatom. The oxa-complex $[Fe(7\text{-oxa-NBD})(CO)_4]$ was stable,[1,2] while the aza-complex was not and underwent ring opening reaction to yield nitrene extrusion products.[3,5,7,9] This reaction was ascribed to the coordination of nitrogen to iron, which weakened the C(1)–N(7) and C(4)–N(7) bonds. Tungsten carbonyl is also known to form a complex with norbornadiene.[11] Since tungsten is larger in size and possesses softer characteristics, it is interesting to examine the reaction of tungsten than Fe carbonyl and 7-aza-NBD. If the interaction between N(7) and tungsten exits in the reaction, as in the case of iron carbonyl, nitrene extrusion products should be observed.



X: NR, O

Result and discussion

$[W(CO)_4(NCMe)_2]$ was prepared from $[W(CO)_6]$ and two equivalents of Me_3NO in acetonitrile.[12] A mixture of $[W(CO)_4(NCMe)_2]$ and 7-methoxycarbonyl-2-*p*-toluene-sulfonyl-7-aza-norbornadiene in CH_2Cl_2 was stirred at room temperature for 40 h. After solvent was removed, products were separated by column chromatography. 3-(*p*-Toluenesulfonyl)-N-methoxycarbonylpyrrole (**A**) was obtained as a major product upon the extrusion of acetylene. 3-(*p*-Toluenesulfonyl)pyrrole (**B**) resulted from demethoxycarbonylation of compound **A**. A minor product, phenyl tolyl sulfone (**C**), came from nitrene extrusion. The structures of compounds **A** and **B** were determined based on two-dimensional NMR spectra (^{1}H COSY and ^{1}H-^{13}C COSY). To form compound **A**, the tungsten must form a coordination with double bond C(5)=C(6) first. Subsequent retro-cyclisation mediated by W yielded a pyrrole and an alkyne-W(CO) complex. The nitrene extrusion to yield sulfone **C** indicates the interaction between tungsten and N(7).



A **B** **C**

The different product distribution between the iron carbonyl complex and the tungsten carbonyl complex suggested a different binding fashion in the two cases. The iron carbonyl bound strongly with the double bond and the N(7). The interaction between iron and N(7) weakens the C(1)–N(7) and C(4)–N(7) bonds leading to a nitrene extrusion (major product) as well as retro-cyclisation. In contrast to the iron complex, the tungsten binds well with the double bond only leading to more pyrrole derivatives. The extrusion of acetylene process to form pyrrole derivatives is absent from the iron counterparts.[9] At temperatures above 140°C thermal decomposition of the 7-azanorboradiene through a retro [4+2] cycloaddition reaction pathway was found to be an irreversible process.[13] The extrusion of acetylene from ANB at room temperature in the presence of tungsten carbonyl indicates the relative strong bond between tungsten and the double bond. The weak tungsten-N(7) bonding is attributed to the mismatch of a large metal (soft) with a small ligand (hard).

Experimental

^{1}H and ^{13}C NMR spectra were obtained on Bruker AC-300 FT spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR spectra are recorded downfield from $SiMe_4$, IR spectra on a Perkin-Elmer 882 infrared spectrophotometer, elemental analyses on a Perkin-Elmer 2400EA instrument and mass spectra were carried out on a JEOL SX-102A spectrometer. Melting points were measured by a Yanato MICRO m.p. apparatus model MP-S3 and are uncorrected.

7-Methoxycarbonyl-tosyl-7-azanorbornadiene was prepared from reaction of N-methoxycarbonylpyrrole and ethynyl tolyl sulfone according to the literature.[9]

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Reaction of 7-methoxycarbonyl-2-p-toluenesulfonyl-7-azanorbornadiene and $W(CO)_4(NCMe)_2$: Under a nitrogen atmosphere and room temperature, to a $W(CO)_6$ (420mg, 1.2 mmol) in CH_3CN (40 ml), a CH_3CN (10 ml) solution of Me_3NO (188 mg, 2.5 mmol) was added by means of syringe. After additional stirring 1 h at same condition, the solvent was removed to dry under reduce pressure. This compound was allowed to react with 7-methoxycarbonyl-2-*p*-toluenesulfonyl-7-azanorbornadiene (305 mg, 1.0 mmol) in CH_2Cl_2 (40 ml) was added and then allow to stirring at room temperature for 40 h. After the solvent was removed under reduce pressure, the residue was suggested to separated by using silica gel column chromatograph eluted with ethyl acetate-hexane (1:2) to give 3-(*p*-toluenesulfonyl)-N-methoxycarbonylpyrrole **A** (135 mg, 48%), 3-(*p*-toluenesulfonyl)pyrrole **B** (18 mg, 8%), and phenyl tolyl sulfone **C** (15 mg, 6%). Physical data for compound **A**: white solid; m.p 116–117 ^{0}C; ^{1}HNMR 2.41(s, 3H), 4.01(s, 3H), 6.47(bs, 1H, H(4)), 7.30(d, 2H, *J* 8.0Hz), 7.26(bs. 1H, H(5)), 7.82(d, 2H, *J* 8.0Hz), 7.83 (s, 1H, H(2); ^{13}C NMR 21.52, 54.95, 110.71, 121.90, 123.34, 127.24, 129.80, 139.16, 144.03, 149.70; IR 1759, 1329, 1149cm^{-1}; MS(m/z, %) 279(M^+, 100), 172(69.8), 91(33.9); Anal. Calcd for $C_{13}H_{13}NO_4S$: C, 55.90%; H, 4.69%; N, 5.01% ; S, 11.48%. Found: C, 56.01%; H, 4.76%; N, 4.98; S, 11.46%. Physical data for compound **B**: white solid; m.p.145 ^{0}C ; ^{1}H NMR 2.39(s, 3H), 6.49(bs. 1H, H(4)), 6.77(br, 1H, H(5), 7.27 (d, 2H, *J* 8.0 Hz), 7.37(bs, 1H, H(2)), 7.81(d, 2H, *J* 8.0Hz), 8.79(bs. 1H, N-H); ^{13}C NMR 21.52, 108.51, 120.07, 122.15, 125.63, 126.89, 129.61, 140.56, 143.25; IR 3420, 1726,1326, 1152cm^{-1}; MS (%) 221(M^+, 100), 114(81.5), 91(20.8); HRMS m/z (M^+) for $C_{11}H_{11}NSO_2$: calcd 221.0511, obsd 221.0511. Compound **C**: white solid; m.p. 126–27°C. (lit.[14] 126-–127°C), the NMR and mass spectra are identical with authentic compound.

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