A Simple Synthesis of Bitropones and Conversion of 2,2′-Bitropone into Dicyclohepta[*b,d*]furan Dication, a Novel Dication Species

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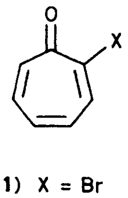
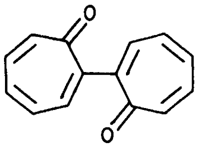
The nickel-catalysed coupling of 2-, 3-, and 4-bromotropone gave the corresponding bitropones in moderate yields; 2,2′-bitropone was converted by trifluoromethanesulphonic anhydride into dicyclohepta[*b,d*]furan dication, a novel tricyclic dication system.

Although bitropones have attracted considerable interest because of the nature of their bitropylium derivatives and their potential use for the synthesis of novel π-electron systems, no bitropone derivative has been reported to date. Recently, we have reported the reductive coupling of vinyl, aryl, benzyl, and phenacyl halides using an active nickel complex.[1] We now report the first synthesis of bitropones (**2**), (**6**), and (**7**), using this active nickel complex, and the formation of dicyclohepta[*b,d*]furan dication (**8**) and the dihydroxy-bitropylium salts (**10**) and (**11**) under acidic conditions.

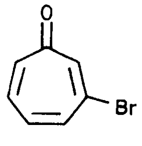
A typical procedure involves treatment of 2-bromotropone (**1**)[2] (1 equiv.) at 50 °C for 3 h with the active nickel complex which is generated *in situ* by reduction of $NiBr_2(PPh_3)_2$ (0.1 equiv.) with active zinc (2 equiv.) in the presence of Et_4NI (1 equiv.) in benzene. 2,2′-Bitropone (**2**) was obtained in 67% yield [based on the recovered starting material (63%); colourless crystals, m.p. 161—162.5 °C, *m/z* 210 (M^+); i.r. (KBr) 1620 and 1565 cm^{-1}; ^1H n.m.r. (CD_2Cl_2) δ 7.4—6.9 (m); ^{13}C n.m.r. ($CDCl_3$) δ 185.5, 153.8, 141.4, 135.4, 135.2, 134.0, and 133.4]. Since (**2**) decomposed slowly in the reaction medium, its yield decreased after the complete reaction of (**1**) with the active nickel complex. Compounds (**1**) and (**2**) were easily separable by chromatography on silica gel. Similarly, treatment of 2-chlorotropone (**3**)[2] with the active nickel complex in benzene at 50 °C for 3 h gave (**2**) in 52% yield with 58% recovered starting material.



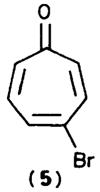
(1) X = Br
(3) X = Cl



(2)



(4)



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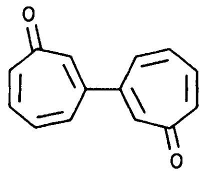
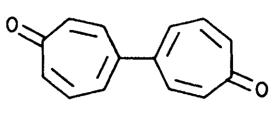
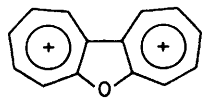


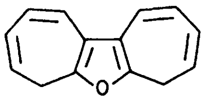
(6)



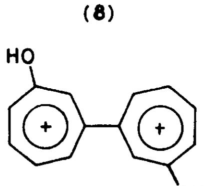
(7)



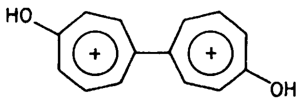
2 $CF_3SO_3^-$
(8)



(9)



2 $CF_3SO_3^-$
(10)



2 $CF_3SO_3^-$
(11)

Similar coupling of 3- and 4-bromotropones (**4**)[3] and (**5**)[3] with the active nickel complex (0.3 equiv.) in tetrahydrofuran (THF) at 50 °C for 3 h also afforded the 3,3′- and 4,4′-bitropones (**6**) and (**7**), respectively [(**6**), colourless crystals, m.p. 163—164.5 °C, 50% yield, with 65% of recovered (**4**), *m/z* 210 (M^+), i.r. (KBr) 1640 and 1575 cm^{-1}; ^1H n.m.r. (CD_2Cl_2) δ 7.2—6.9 (m), ^{13}C n.m.r. ($CDCl_3$) δ 186.6, 150.1, 143.0, 141.0, 135.8, 135.4, and 134.5; (**7**), pale yellow crystals, m.p. 177.5—179 °C, 47% yield, with 60% of recovered (**5**), *m/z* 210 (M^+), i.r. (KBr) 1633 and 1575 cm^{-1}; ^1H n.m.r. (CD_2Cl_2) δ 7.4—6.9 (m); ^{13}C n.m.r. ($CDCl_3$) δ 187.0, 148.6, 142.2, 142.1, 136.3, 135.5, and 133.5]. Bitropones (**2**), (**6**), and (**7**) are reasonably stable and can be stored at 0 °C for weeks without decomposition.

Although (**2**) decomposed in CH_2Cl_2 in the presence of trifluoroacetic acid or triflic (trifluoromethanesulphonic) acid, treatment of (**2**) with triflic anhydride in CH_2Cl_2, which has been found to be very useful for the preparation of dication ethers,[4] gave the tricyclic dication (**8**) in high yield on the basis of its ^1H n.m.r. spectrum [extremely hygroscopic yellow solid, ^1H n.m.r. (CD_2Cl_2–CD_3CN, 1:1; −20 °C) δ 10.8—10.4 (2H, m) and 10.1—9.5 (8H, m)]. The structure of (**8**) was confirmed by reduction with $NaBH_4$.[5] Treatment of (**8**) with $NaBH_4$ in MeCN–diglyme at −50 to 20 °C afforded a mixture of dihydro-dicyclohepta[*b,d*]furans [in 75% yield based on (**2**), containing (**9**) as the major isomer (*ca.* 40% of the mixture)]. In contrast to (**2**), the bitropones (**6**) and (**7**) formed the corresponding dihydroxy-bitropylium ditriflates (**10**) and (**11**), on treatment with triflic acid in CH_2Cl_2 [^1H n.m.r. (CD_2Cl_2–CD_3CN, 1:1; −20 °C) δ 9.0—8.4 (m) for (**10**) and (**11**)].

Received, 3rd July 1985; Com. 945

References

1 M. Iyoda, M. Sakaitani, T. Miyazaki, and M. Oda, *Chem. Lett.*, 1984, 2005; M. Iyoda, M. Sakaitani, H. Otsuka, and M. Oda, *ibid.*, 1985, 127; M. Iyoda, K. Sato, and M. Oda, *Tetrahedron Lett.*, in the press; M. Iyoda, M. Sakaitani, A. Kojima, and M. Oda, *ibid.*, in the press.

2 W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, 1952, **74**, 5683; B. J. Abadir, J. W. Cook, J. D. Loudon, and D. K. V. Steel, *J. Chem. Soc.*, 1952, 2350; T. Nozoe, S. Seto, and S. Matsumura, *Proc. Jpn. Acad.*, 1952, **28**, 483; T. Nozoe, S. Seto, S. Ito, T. Sato, and K. Katono, *ibid.*, 1952, **28**, 488.

3 M. G. Banwell, *J. Chem. Soc., Chem. Commun.*, 1982, 847, and references cited therein.

4 P. J. Stang, G. Maas, D. L. Smith, and J. A. McCloskey, *J. Am. Chem. Soc.*, 1981, **103**, 4837.

5 H. Volz and M. Volz-de Lecea, *Liebigs Ann. Chem.*, 1971, **750**, 136.