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RE-EXAMINATION ON BROMINATION OF SUBSTITUTED BIPHENYLENES. FORMATION OF BENZOCYCLOOCTATETRAENE DERIVATIVES

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The bromination products of 2-methoxy- and 2-acetamido-3-bromobiphenylenes were not the biphenyl derivatives (3a) and (3b), which were previously assigned by McOmie et al., but the benzocyclooctatetraene derivatives (2a) and (2b), respectively.

Bromination of biphenylene and its derivatives is a fundamental reaction in biphenylene chemistry. Biphenylene itself was brominated to give benzocyclooctatetraene derivatives and some other addition products.[1-3] On the other hand, it was reported that 2-methoxy- (1a)[4] and 2-acetamido-3-bromobiphenylenes (1b)[5] were brominated to give biphenyl derivatives. To accomodate these inconsistencies, we re-examined bromination of 1a and 1b.

3-Bromo-2-methoxybiphenylene (1a) was brominated in dichloromethane to give tribromo compound 2a,[6] mp 118-119 °C, in 70% yield. The same compound was previously prepared on bromination of 1a in acetic acid and assigned by McOmie and co-workers as 4,6,2'-tribromo-3-methoxybiphenyl (3a) by its IR and UV spectra.[4] However, its NMR spectrum showed two olefinic doublets (J=1.2 Hz) at δ 6.53 and 6.66, which were very similar to that of 3,8-dibromobenzocyclooctatetraene (5) (δ 6.51, $J_{4,7}$=1.6 Hz).[2] The UV spectrum of 2a resembles that of 5 rather than 2,2'-dibromobiphenyl. In addition, 2a was converted with trifluoroacetic acid to 3,6,8-tribromo-4,5-benzocycloocta-2,4,6-trien-1-one (4)[6] in high yield, whose structure was assigned by its spectral data. IR(KBr): 1680 cm^{-1}. PMR($CDCl_3$): δ 4.81 (d, 1H, J=9.6 Hz, H-8), 6.73 (d, 1H, J=9.6 Hz, H-7), 7.18 (s, 1H, H-2), and 7.2-8.0 (m, 4H, Ar-H). CMR($CDCl_3$): δ 53.5 (C-8) and 185.2 (C-1). The X-ray crystallographic analysis confirmed that 4 had a benzocyclooctatrienone framework.[7] On the basis of these data the tribromo compound 2a should be assigned not to 4,6,2'-tribromo-3-methoxybiphenyl (3a) but 3,6,8-tribromo-5-methoxybenzocyclooctatetraene. Such type of preferentialring-opening was also confirmed by bromination of 3,6-dibromo-2,7-dimethoxybiphenylene[1] and 3-bromo-1,2-dimethoxybiphenylene[6] to give the corresponding benzocyclooctatetraene derivatives 6[6] and 7[6] in 89 and 36% yields, respectively. The structures of 6 and 7 were assigned by UV and NMR spectral analogy to 2.

The bromination of 3-bromo-2-acetamidobiphenylene (1b) in dichloromethane at room temperature gave colorless needles 2b, mp 156-157 °C, in nearly quantitative yield. 2b showed the same mp and UV spectra as those previously obtained by bromination of 1b in acetic acid at 80 °C and assigned to 4,6,2'-tribromo-3-acetamidobiphenyl (3b) by Baker et al.[2] PMR($CDCl_3$): δ 2.03 (s, 3H, CH_3), 6.72 (d, 1H, J=

1.3 Hz), 6.94 (d, 1H, J=1.3 Hz), 7.3 (broad s, 1H), 7.44 (s, 4H, Ar-H). These PMR data are similar to those of 2a and 5. Similarly to 2a, 2b was hydrolyzed in boiling ethanol with 48% hydrobromic acid to tribromo ketone 4 in 80% yield. These facts proved that 2b should be assigned to 3,6,8-tribromo-5-acetamidobenzocyclooctatetraene. The compound 3b, proposed by Baker et al.[5] to the bromination product of 1b, was actually prepared in the following manner. The reaction of m-nitrobenzenediazonium tetrafluoroborate with bromobenzene in the presence of 18-crown-6[8] gave 2'-bromo- and 4'-bromo-3-nitrobiphenyl in good yield. The former (separated in 13% yield) was converted to 3b, colorless needles, mp 117-118 °C, according to Baker et al.[5] PMR($CDCl_3$): δ 2.26 (s, 3H, $COCH_3$), 7.15-7.55 (m, 4H, H-3'-H-6'), 7.70 (broad s, 1H, NH), 7.97 (s, 1H, H-2), and 8.45 (s, 1H, H-5). MS (75 eV): m/e 445 (M^+, 18%), 447 (M^++2, 40%), 449 (M^++4, 44%), 451 (M^++6, 14%). 3b gave IR spectrum different from 2b. Thus, 2b was unequivocally proved not to be 3b. The bromination of 1 to 2 may be illustrated as in the Scheme.

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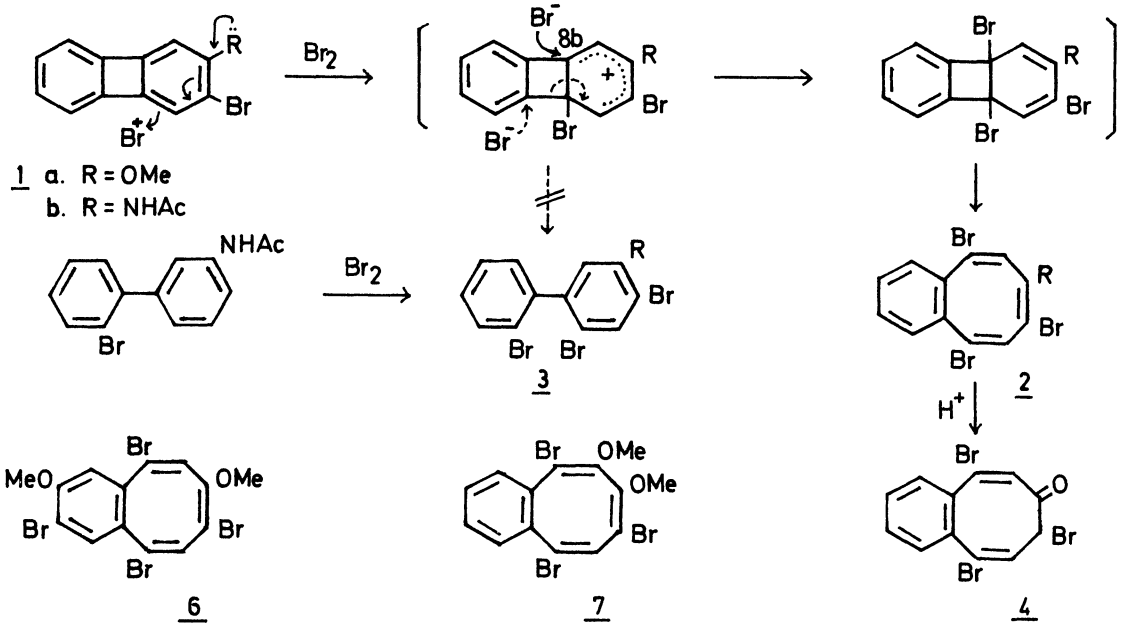

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