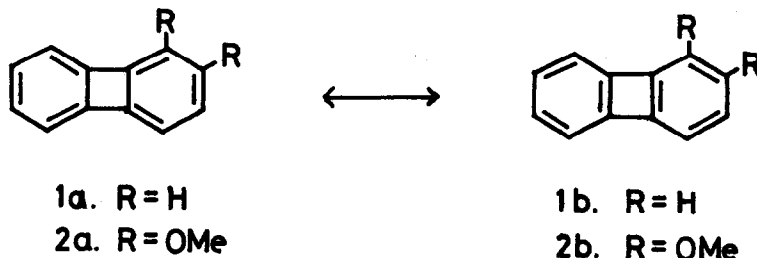


DICHLOROCARBENE ADDITION TO 1,2-DIMETHOXYBIPHENYLENE. A CHEMICAL EVIDENCE FOR BOND FIXATION IN BIPHENYLENE NUCLEUS

Masaru Sato, Akiko Uchida, Josuke Tsunetsugu, and Seiji Ebine*
Department of Chemistry, Faculty of Science, Saitama University
Urawa, Saitama 338, Japan

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It has been thought that biphenylene has a considerable extent of bond fixation to one of the Kekule's canonical structures, (1a), because of the strain effect caused by fusing the central four-membered ring and because of the avoidance of another canonical structure (1b) carrying an antiaromatic cyclobutadiene structure. Such a partial fixation of double bonds in the biphenylene nuclei was proved by electron diffraction¹ and X-ray analysis,² and was suggested from a theoretical study³ and insufficiently from the chemical facts that ethyl diazoacetate added to the C₂-C₃ bond of biphenylene⁴ and that dichlorocarbene added to the C_{8b}-C₁ and C₂-C₃ bonds of 1-methoxybiphenylene.⁵ We now wish to propose an additional and unequivocal evidence for bond fixation of biphenylenes in the addition reaction with dichlorocarbene.



1,2-Dimethoxybiphenylene (2a)⁶ reacted with dichlorocarbene, generated from chloroform (3 equiv.) and 33% aqueous sodium hydroxide in the presence of catalytic amount of cetyltrimethylammonium chloride,⁷ to give three chloromethoxybenzo[3,4]cyclobuta[1,2-c]tropone (6)-(8), two chloromethoxyfluorenones (9) and (10), and two dimethoxyfluorenones (11) and (12), along with the recovered starting material (70.0%). The m.p.'s, yields, IR, and NMR spectra of the compounds were summarized in Table 1. Benzo[3,4]cyclobuta[1,2-c]tropone derivatives (6), (7), and (8) had the molecular ion at m/e 244 in mass spectra,

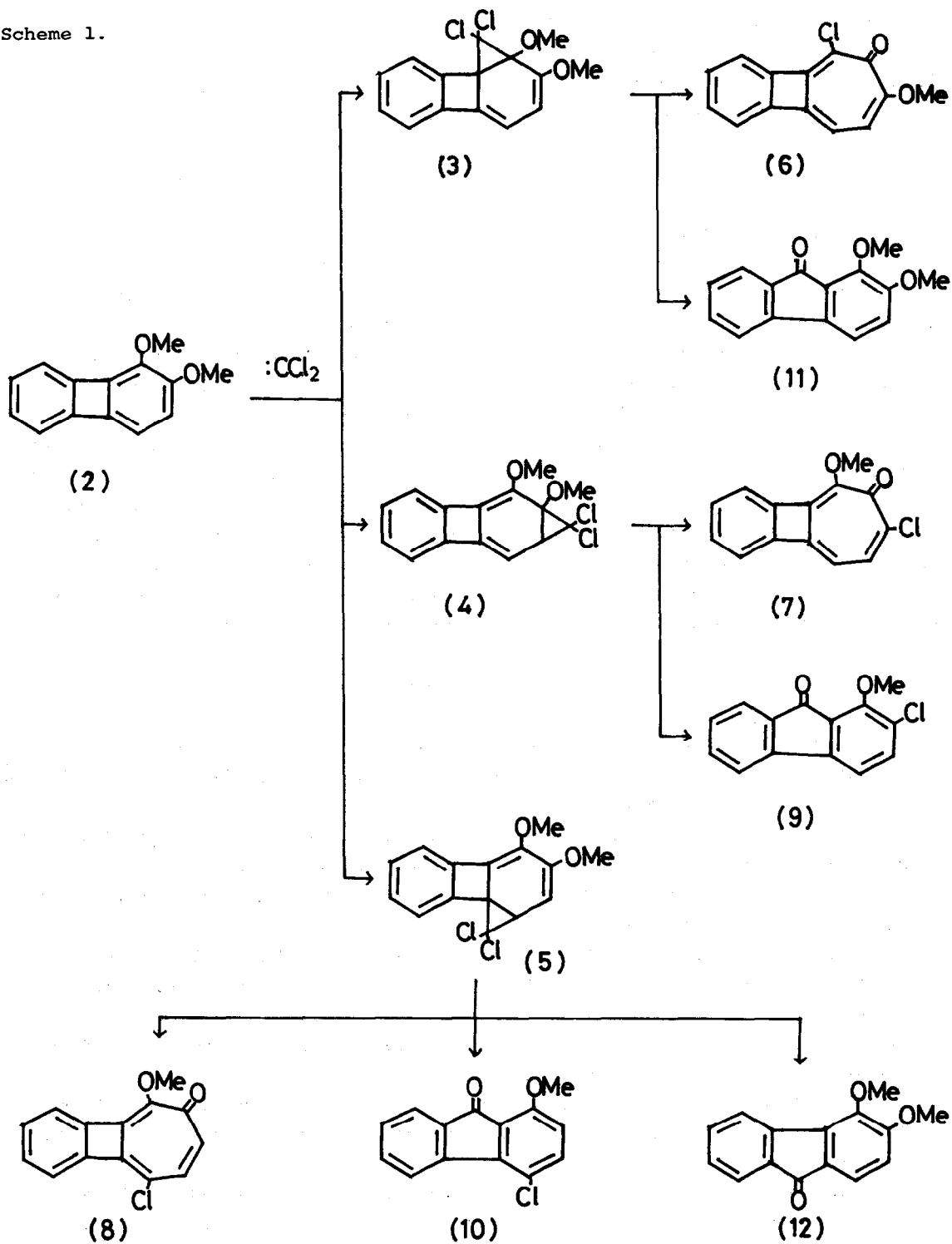
Table 1. Products^a from the reaction of (2) with dichlorocarbene

Compound	Melting point(°C)	Yield (%)	IR (cm ⁻¹)	NMR (δ, ppm; J, Hz)
(6)	150-151	1.3	1613	3.80(s, 3H), 6.29(s, 2H), 7.0-7.5(m, 4H)
(7)	142-143	0.6	1608	4.07(s, 3H), 6.20(d, 1H, J=9.0) 7.05-7.45(m, 4H), 7.42(d, 1H, J=9.0)
(8) ^b	135-136	5.6	1602	4.08(s, 3H), 6.37(d, 1H, J=13.2) 6.71(d, 1H, J=13.2), 7.12-7.4 (m, 4H)
(9)	122-122.5	4.7	1705	4.30(s, 3H), 7.18(d, 1H, J=7.8) 7.25-7.75(m, 5H)
(10)	152-152.5	0.8	1706	3.95(s, 3H), 6.83(d, 1H, J=9.5) 7.56(d, 1H, J=9.5), 7.25-7.8 (m, 3H), 8.2(m, 1H)
(11) ^c	113-114	0.9	1710	3.89(s, 3H), 4.12(s, 3H), 6.94 (d, 1H, J=8.2), 7.19(d, 1H, J= 8.2), 7.2-7.75(m, 4H)
(12) ^c	142.5	1.9	1702	3.92(s, 3H), 3.96(s, 3H), 6.75 (d, 1H, J=8.3), 7.05-8.0(m, 4H) 7.44(d, 1H, J=8.3)

a. All new compounds have a satisfactory elemental analysis. b. Reference 6.
c. Reference 8.

and the strong absorption near 1600 cm⁻¹ in IR spectra. Their electronic spectra were closely similar to those of other benzocyclobutatropones reported previously.⁵ In the NMR spectra, (8) showed two olefinic doublets at δ 6.37 and 6.71 ppm (J=13.2 Hz), and similarly (7) at δ 6.20 and 7.42 ppm (J=9.0 Hz). The large coupling constant in the former and the small one in the latter mean the intervention of a double and single bond, respectively, between the vicinal protons and hence (8) and (7) are assigned to be 9- and 7-chloro-5-methoxybenzo-[3,4]cyclobuta[1,2-c]tropones, respectively. The two olefinic protons in (6) appeared accidentally as a singlet at δ 6.29 ppm but on addition of the shift reagent (Eu-fod) the singlet separated into two doublets (J=9.0 Hz), whereby (6) is assigned to be 5-chloro-7-methoxybenzo[3,4]cyclobuta[1,2-c]tropone. Two dimethoxyfluorenones, (11) and (12), were identified as 1,2- and 3,4-dimethoxyfluorenones,⁸ respectively, by the mixed m.p. and coinciding IR spectra with the authentic samples.⁹ Two chlorofluorenones, (9) and (10), were also identified as 2- and 4-chloro-1-methoxyfluorenones, respectively, by the mixed m.p. and IR spectral coincidence with the authentic samples prepared by another route:

Scheme 1.



1-methoxyfluorenone¹⁰ was chlorinated with sulphenyl chloride in the presence of azobisisobutyronitrile to give 2- and 4-chloro-1-methoxyfluorenes in 23 and 57% yields, respectively. 9-Chloro-5-methoxybenzo[3,4]cyclobuta[1,2-c]tropone (8) was readily rearranged with acid to 4-chloro-1-hydroxyfluorenone (yellow needles, m.p. 158-159°C),^{6, 11} which was identical with a sample prepared by treatment of (10) with boron tribromide, followed by hydrolysis. These conversions would support additionally the structural assignment described here.

The formation of these products seems to be elucidated best as proceeding through the reaction path shown in Scheme 1. Dichlorocarbene added to (2) giving the intermediate adducts (3), (4), and (5). (5) converted spontaneously to (8) and, on the other hand, was attacked by a hydroxide ion at C_{4a} and C_{8b} to give (10) and (12), respectively. The path to fluorenone derivatives is similar to that in the reaction between 1-methoxybiphenylene and dichlorocarbene.⁵ Similarly, the adduct (3) afforded (6) and (11), and the adduct (4) did (7) and (9). Thus, the addition of dichlorocarbene must have taken place at the fixed C_{8b}-C₁, C₂-C₃, and C₄-C_{4a} double bonds of the canonical structure (2a) of 1,2-dimethoxybiphenylene. No adduct from another canonical structure (2b) was obtained. This is the first example in the reaction of biphenylene series where all the possible products resulting from one of the Kekule's canonical structures are obtained, and this observation serves as an unequivocal evidence for the bond fixation of 1,2-dimethoxybiphenylene in some chemical reactions.

References and footnotes

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10. We thank Prof. K. Suzuki (Utsunomiya Univ.) for kindhearted offer of the 1-methoxyfluorenone and also Dr. K. Takahashi (Tohoku Univ.) for the NMR measurements.
11. The m.p. of 4-chloro-1-hydroxyfluorenone was mistyped as 108-110°C in the preceding paper,⁶ and should be corrected to the right value described here.