Formation of Two Benzocyclo-octatrienedione and 2,3-Benzohomotropone Derivatives by Dichlorocarbene Ring Expansion

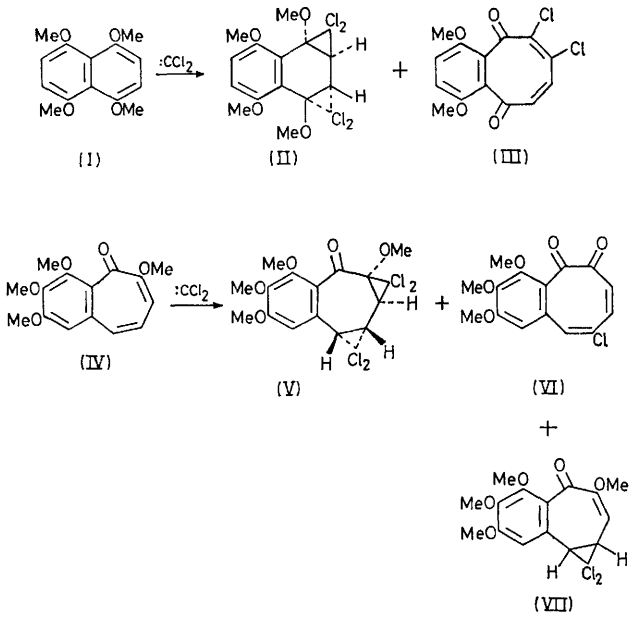
By JOSUKE TSUNETSUGU, MASARU SATO, and SEIJI EBINE*
(*Department of Chemistry, Saitama University, Urawa, 338, Japan*)

Summary Addition of dichlorocarbene to 1,4,5,8-tetramethoxynaphthalene (I) and the tetramethylpurpurogallin (IV) affords the benzocyclo-octatrienediones (III) and (VI) together with the bishomonaphthalene (II) and the benzobishomotropone (V), respectively.

CYCLO-OCTATRIENEDIONE and homotropone are of interest as potentially aromatic compounds. Dibenzocyclo-octatrienedione[1] and benzobishomotropone[2] have been synthesized, but attempts to obtain mono- and tri-benzocyclo-octatrienedione failed.[3] We report here the dichlorocarbene ring expansion[4] of compounds (I) and (IV) in attempts to obtain the hitherto unknown benzocyclo-octatrienedione, benzohomotropone, and/or heptalenoquinone.

Reaction of (I) with a large excess of dichlorocarbene[5] overnight afforded prisms (6%), m.p. 185° (from MeOH), identified as the bishomonaphthalene (II),† and orange-yellow needles (12·5%), m.p. 195—196° (from MeOH), identified as the dione (III). The *trans*-configuration of (II) was assigned unequivocally by use of molecular models. A symmetric structure for (III) was discarded because of the double doublets in the n.m.r. spectrum at δ 6·39 and 7·06. Compound (III) showed high CO i.r. absorption at 1702 cm^{-1}, which, together with the n.m.r. signal at δ 6·39, suggests a non-planar conformation of the cyclo-octatriene-

† All new compounds had satisfactory elemental analyses and spectral data in agreement with the proposed structures. Assignments were based on n.m.r. spectroscopy.



dione ring. Compound (III) is most probably formed *via* a 5- and/or 7-chlorotrimethoxy-2,3-benzotropone intermediate.

Under similar conditions, under nitrogen, compound (IV) afforded plates (34%), m.p. 150—151·5° (from MeOH), identified as the benzobishomotropone (V), a yellow oil (3%), m.p. 100° at 2 mmHg, identified as the dione (VI), and small amounts of pale yellow crystals, m.p. 139° (unstable in solution), identified as the benzohomotropone (VII). The coupling constant of 1·5 Hz between the cyclopropane hydrogen atoms in (V) leads to a dihedral angle of 115°. The *cis*-configuration for (V) is unlikely considering the interaction between the *gem*-dichloromethylene groups. The high CO i.r. absorption at 1723 cm^{-1}, and the n.m.r. signals at δ 6·35 and 6·72 from (VI) suggest a non-planar structure of the cyclo-octatrienedione ring. Compound (VII) is possibly an intermediate in the formation of compounds (V) and (VI).

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