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REACTIONS OF 1,1,4,4-TETRAPHENYL-3-BROMOBUTA-1,2-DIENE-4-OL WITH MERCURIC ACETATE

A POSTULATION OF n,π-COMPLEXED MERCURINIUM ION

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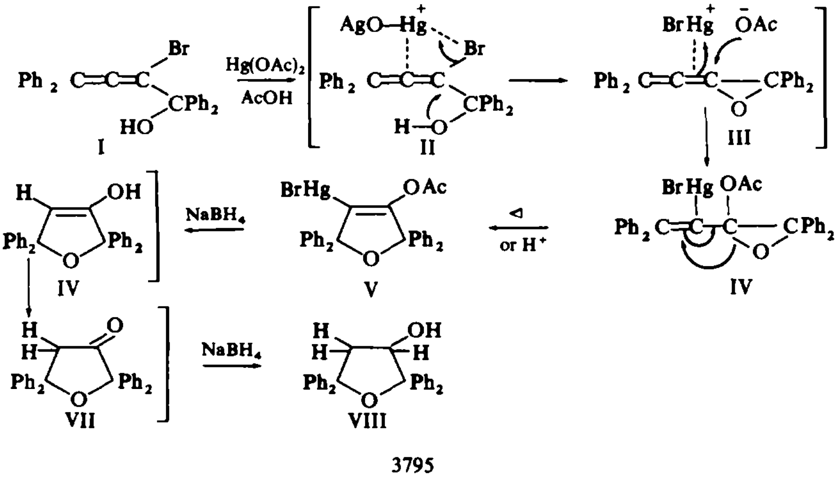
Abstract—The title compound reacts with mercuric acetate and affords various cyclization products depending on the conditions employed. These reactions are interpreted via a n,π-complexed mercurinium ion mechanism.

IN THE oxymercuration of allenes, the σ-bridged mercurinium ion has been postulated as the initial allene-mercuric salt adduct,[1—3] but in the reactions of the bromoallene alcohol (I)[4] with mercuric acetate, the n,π-complexed mercurinium ion was considered the initial allene-mercuric salt adduct. We now record these reactions and postulate a n,π-complexed mercurinium ion mechanism.

Heating a mixture of I, with an equimolar amount of mercuric acetate in acetic acid, yielded V in a 67% yield. The structure of V was identified by reduction[5] to VIII, which may proceed through the ketone (VII), keto-form of the vinyl alcohol VI derived from V by deoxymercuration.[5] When the reaction of I with mercuric acetate in acetic acid was carried out at room temperature, the intermediate IV was isolated in a 92% yield. The intermediate IV has no definite m.p. (ca. 80°), since it gradually converts into V on heating. On heating in acetic acid, IV is easily converted into V. Treatment of an alcoholic solution of IV with a catalytic amount of hydrochloric acid also afforded V, quantitatively.

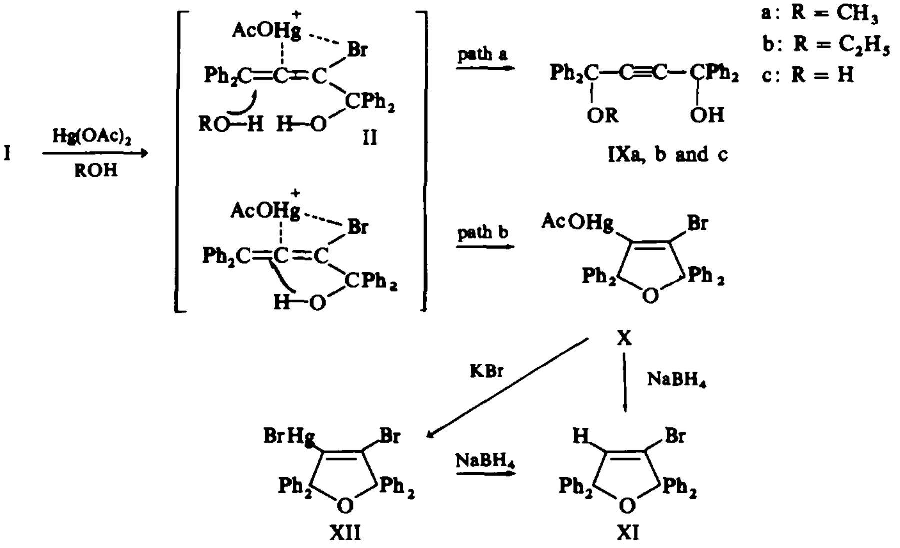
SCHEME I



The above reaction can be interpreted as shown in Scheme I, in which π.... Hg.... Br complexed mercurinium ion (II) is assumed on the basis of the proved mercury-π[6] and mercury–halogen[7] coordinations. In the mercurinium ion (II), it is not clear which π-orbital of the allene is coordinated to mercury although the one lying in the same plane as the Br atom is more reasonable. In II, the formation of a σ-bond between mercury and bromine is accompanied with epoxidation yielding a π-complexed epoxide–mercury salt (III). Acetoxymercuration of III affords IV. The preference for the π-complexed intermediate (III) over the reported σ-bridged mercurinium ion[1–3] will be discussed later.

The formation of the n,π-complexed salt (II) was considered in the reaction of I and mercuric acetate in alcohol to afford IX and X. When the reaction was carried out in the following media, products were: in methanol, IXa (54%) and X (14%); in ethanol, IXb (41%) and X (18%); in aqueous acetone, IXc (71% as the form of 1 :1 acetone complex)[8] only. The mercuric compound (X) was identified by reduction to XI.[9] Similar reduction of the dibromo derivative (XII), obtained by shaking an acetone solution of X with aqueous potassium bromide, also afforded XI.

Scheme II

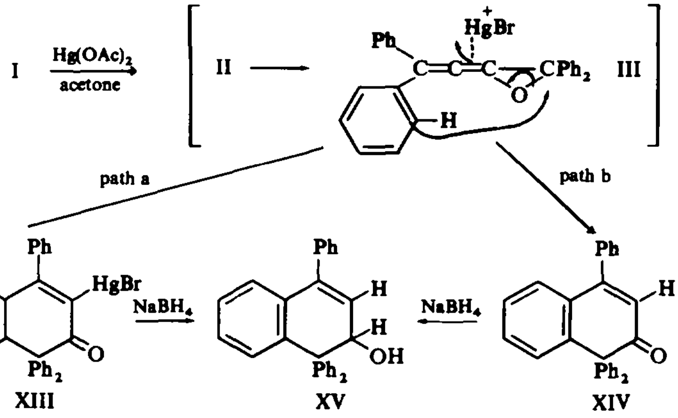


In the reaction, two competing paths may be involved as shown in Scheme II. One involves the formation of a σ-bond between mercury and bromine followed by migration of an π-electron pair and oxylation at the terminal carbon, i.e. Retro-propargyl rearrangement (path a). Another, is the formation of a σ-bond between mercury and the central carbon of the allene accompanied by intramolecular cyclization (path b). As the bulkiness of the alkyl group of the hydroxy compound was increased the yield of IX was decreased and that of X was increased.

The different reactions in acetic acid and in alcohol may be due to the nucleophilicity of the reagents. This interpretation is reasonable since it has been known[10] that an alkoxy group reacts more readily with the terminal carbon of 3,4-dibromo-1,1,6,6-tetraphenylhexa-1,2,4,5-tetraene than does an acetoxy group.

The n,π-complexed salt (II) is again applicable to the interpretation of the reaction of I with mercuric acetate in acetone to afford XIII (8%) and XIV (27%). The reduction of XIII and XIV gave the same product XV.

SCHEME III



The reaction probably proceeds through III, which was derived from II in the manner shown in Scheme I. Since no nucleophilic species is present in the medium, when the σ-bond between allene carbon and mercury (path a) or hydrogen of Ph ring (path b) is formed, π-electrons of the Ph ring react with the terminal carbon to yield dihydronaphthenones. If the mercury salt (III) is σ-bonded rather than π-complexed, XIII should be produced predominantly. Our present experimental results support the π-complexed mercurinium ion (III) as the more likely intermediate, even though it is not clear why the central-carbon of the allene of III forms the σ-bond more readily with hydrogen than with mercury.

EXPERIMENTAL

All m.p.s were uncorrected. IR spectra were recorded on a grating spectrophotometer IR-G of the Japan Spectroscopic Co., in Nujol mull. NMR spectra were recorded on a Japan Electron Optics Laboratory 4H-100 Spectrometer, in $CDCl_3$, using TMS as an internal standard. Mol wts were determined in benzene by a Hitachi Perkin–Elmer apparatus model 115.

Reaction of I *with mercuric acetate in acetic acid.* A soln of I (1·81 g, 4 mmoles) and mercuric acetate (1.28 g, 4 mmoles) in AcOH (30 ml) was heated under reflux for 30 min. Crystals were collected by filtration and were recrystallized from acetone to afford V as colourless prisms, (1·90 g, 67%), m.p. 249–250°; ν_{max} cm^{-1}, 1735 (CO), 1630 (C=C), 1220 (CO—O) and 1050 (C—O—C). (Found: C, 51·06; H, 3·02. Calc. for $C_{30}H_{23}O_3$ HgBr: C, 50·63; H, 3·23%).

Sodium borohydride reduction of V. A mixture of V (300 mg), NaBH4 (100 mg) and EtOH (10 ml) was heated under reflux for 1 hr. After removal of Hg metal, water was added to the filtrate. The crystals formed were washed with water and recrystallized from benzene–pet. ether (b.p. 70–80°) to give VIII as colourless prisms (150 mg, 91%), m.p. 146°; ν_{max} cm^{-1}, 3560 (OH) and 1020 (C—O—C); NMR τ, 2·57 (m, C_6H_5, 20H), 4·95 (t, CH, 1H), 7·10 (o, CH_2, 2H) and 8·53 (b, OH, 1H, disappeared upon shaking with D_2O). (Found: C, 85·48; H, 6·15; mol wt, 388. Calc. for $C_{28}H_{24}O_2$: C, 85·68; H, 6·16%; mol wt, 392).

Isolation and reaction of the intermediate (IV). A soln of I (9·0 g, 20 mmoles) and mercuric acetate (6·4 g, 20 mmoles) in AcOH (80 ml) was allowed to stand at room temp for 1·5 hr. The soln was poured into ice-water, and the crystalline solid washed with water successively and dried to afford IV, as a colourless crystalline powder (13·0 g, 92%), m.p. ca. 80° ν_{max} cm^{-1}, 1755 (CO), 1635 (C=C), 1220 (CO—O), and 1170, 1005 and 920 (epoxide); NMR τ, 2·70 (m, C_6H_5, 20H) and 7·95 (t, CH_3, 3H). (Found: C, 51·03; H, 3·45, Calc. for $C_{30}H_{23}O_2$ HgBr: C, 50·63; H, 3·23%).

Heating a soln of IV in AcOH for 30 min afforded V in a quantitative yield. When a soln of IV in EtOH was treated with a catalytic amount of HCl at room temp for 10 min, V was also obtained, quantitatively.

Reaction of I *and mercuric acetate in alcohol.* A soln of I (453 mg, 1 mmole) in MeOH (10 ml) was treated with mercuric acetate (320 mg, 1 mmole) at room temp for 30 min. Crystals separated and were washed with MeOH to leave X (100 mg, 14%), m.p. > 300°; ν_{max} cm^{-1}, 1615 (C=C), 1590 (CO), 1320 (CO—O) and 1010 (C—O—C). (Found: C, 50·43; H, 3·12. Calc. for $C_{30}H_{23}O_3HgBr$: C, 50·63; H, 3·23%).

The two MeOH layers were combined, decomposed with water and extracted with ether. The ether soln was washed with water and dried over Na_2SO_4. Crude crystals remained after evaporation of the ether and were recrystallized from pet. ether (b.p. 70–80°) to afford IXa as colourless needles (220 mg, 54%), m.p. 112–113°; ν_{max} cm^{-1}; 3350 (OH) and 1060 (C—O—C); NMR τ, 2·60 (m, C_6H_5, 20H), 6·65 (s, CH_3, 3H) and 7·13 (s, OH, 1H, disappeared upon shaking with D_2O). (Found: C, 85·86; H, 6·27. Calc. for $C_{29}H_{24}O_2$: C, 86·11; H, 5·98%).

When a soln of I (453 mg, 1 mmole) in EtOH (10 ml) was treated with mercuric acetate (320 mg, 1 mmole) under the conditions used for the reaction in MeOH, X (130 mg, 18%) and IXb were obtained as colourless prisms (210 mg, 41%), m.p. 107–108°. For IXb: ν_{max} cm^{-1}, 3400 (OH) and 1070 (C—O—C); NMR τ, 2·60 (m, C_6H_5, 20H), 6·45 (q, CH_2SH), 7·08 (b, OH, 1H, disappeared upon shaking with D_2O) and 8·75 (t, CH_3, 3H). (Found: C, 85·81; H, 6·07. Calc. for $C_{30}H_{26}O_2$: C, 86·02; H, 6·26%).

An acetone soln of X was shaken with KBr aq, and the resultant mercuric bromide (XII) was separated by filtration and recrystallized from acetone, m.p. 191° (dec); ν_{max} cm^{-1}, 1620 (C=C) and 1015 (C—O—C). (Found: C, 46·25; H, 2·78. Calc. for $C_{28}H_{20}OHgBr_2$: C, 46·54; H, 2·77%).

Reaction of I *and mercuric acetate in aqueous acetone.* A soln of I (227 mg, 0·5 mmole) and mercuric acetate (160 mg, 0·5 mmole) in 30% aqueous acetone (10 ml) was allowed to stand at room temp for 30 min. After concentration of the soln to ca. 5 ml, crystals were separated and recrystallized from acetone to give IXc as 1 : 1 acetone complex,[8] colourless prisms (160 mg, 71%). The IR spectrum of the acetone complex of IXc was identical with that of an authentic sample prepared according to the literature.[8]

Sodium borohydride reduction of X *and* XII. A mixture of X (355 mg, 0·5 mmole)·NaBH4 (100 mg) and EtOH (20 ml) was heated under reflux for 1 hr. After removal of Hg metal, water was added to the filtrate. Crude crystalls separated and were recrystallized from EtOAc to afford XI as colourless prisms (266 mg, 80%), m.p. 175° (lit.[9] 175°). A mixed m.p. of XI and an authentic sample[9] showed no depression.

The treatment of XII under conditions employed for X afforded XI in a 85% yield.

Reaction of I *and mercuric acetate in acetone.* A soln of I (1·81 g, 4 mmoles) and mercuric acetate (1·28 g, 4 mmoles) in acetone (20 ml) was allowed to stand at room temp for 30 min. An exothermic reaction occurred and crystals formed. These were recrystallized from acetone to yield XIII as pale yellow needles (200 mg, 8%), m.p. 295° (dec); ν_{max} cm^{-1}, 1655 (CO) and 1590 (C=C). (Found: C, 51·95; H, 3·09. Calc. for $C_{28}H_{19}O$ HgBr: C, 51·61; H, 2·92%).

The acetone layer was evaporated to dryness and extracted with ether (100 ml). The ether soln was washed with water and dried over Na_2SO_4. Crystals obtained by the concentration of the ether soln to ca. 10 ml, were recrystallized from EtOH–acetone to afford XIV as yellow prisms (400 mg, 27%), m.p. 166–167; ν_{max} cm^{-1}, 1665 (CO) and 1610 (C=C); NMR τ, 2·90 (m, phenyl, 19H) and 3·90 (s, =CH, 1H); λ_{max} (EtOH) mμ(ε), 240 (sh) (8100), 265 (7500) and 316 (8900). (Found: C, 90·23; H, 5·26; mol wt, 362. Calc. for $C_{28}H_{20}O$: C, 90·29; H, 5·41%; mol wt, 372).

Sodium borohydride reduction of XIII *and* XIV. A mixture of XIV (930 mg, 2·5 mmoles), $NaBH_4$ (200 mg) and EtOH (70 ml) was heated under reflux for 30 min. After removal of Hg metal, water was added to the filtrate. The crude crystals were washed with water, dried and recrystallized from EtOH to afford XV as colourless needles (910 mg, 98%), m.p. 184–185°; ν_{max} cm^{-1}, 3560 (OH), 1625 (C=C) and 1080 (C—O); NMR τ, 2·65 (m, phenyl, 19H), 3·93 (d, J = 3 c/s, =CH, 1H), 4·57 (d, J = 3 c/s, CH, 1H) and 2·38 (s, OH, 1H, disappeared upon shaking with D_2O). (Found: C, 89·88; H, 5·78; mol wt, 371. Calc. for $C_{28}H_{22}O$: C, 89·80; H, 5·92%; mol wt, 374).

The treatment of XIII (300 mg, 0·45 mmole) with $NaBH_4$ (100 mg) in EtOH (10 ml) under the same condition employed for XIV, gave XV (150 mg, 90%), m.p. 184–185°. IR spectral data and mixed m.p. determination showed that XV was identical with that derived from XIV.

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REFERENCES

[1] R. K. Sharma, B. A. Shoulders and P. D. Gardner, *J. Org. Chem.* **32**, 241 (1967).
[2] W. L. Waters and E. F. Kiefer, *J. Am. Chem. Soc.* **89**, 6261 (1967).
[3] W. L. Waters, W. S. Linn and M. C. Caserio, *Ibid.* **90**, 6741 (1968).
[4] F. Toda, T. Komoda and K. Akagi, *Bull. Chem. Soc. Japan* **41**, 1493 (1968).
[5] H. C. Brown and P. Geoghegan, Jr., *J. Am. Chem. Soc.* **89**, 1522 (1967).
[6] E. F. Kiefer, W. L. Waters and D. A. Carlson, *Ibid.* **90**, 5127 (1968).
[7] E. F. Kiefer and W. Gericke, *Ibid.* **90**, 5131 (1968).
[8] F. Toda and K. Akagi, *Tetrahedron Letters* 3695 (1968).
[9] H. Tani and F. Toda, *Bull. Chem. Soc. Japan* **37**, 470 (1964).
[10] M. Higashi, F. Toda and K. Akagi, *Chem. & Ind.* 491 (1969).