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IONIC 3,4-BIS(BROMODIPHENYL)CYCLOBUT-3-ENE-1,2-DIONE AND 3,4-BIS(DIPHENYLMETHYLENE)CYCLOBUTANE-1,2-DIONE. A NOVEL PHOTOOXYGENATION OF 1,2-DIBROMO-3,4-BIS(DIPHENYLMETHYLENE)CYCLOBUT-1-ENE

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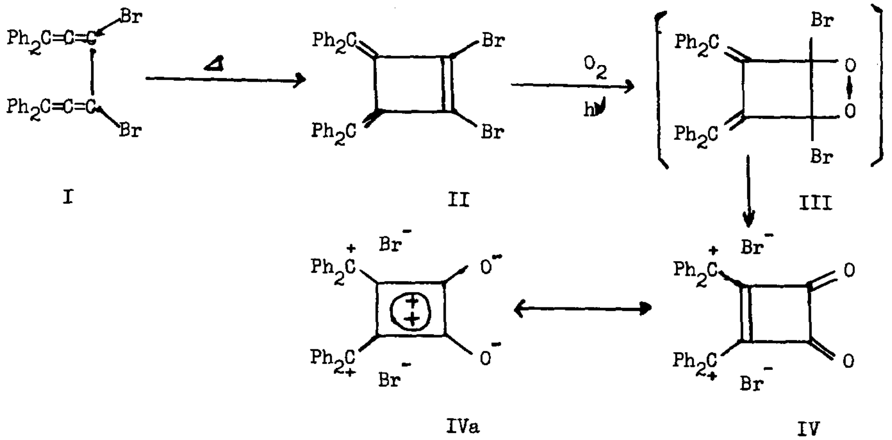
Since the first isolation of phenylcyclobutadienequinone,(1) a number of substituted cyclobutadienequinones have been prepared.(2) Although the cyclobutadienequinones have approximately the same ring strain as that of the cyclobutadienes, the former is remarkably more stable than the latter. We have isolated dibromocyclobutadienequinone (IV) of a new type having ionic structure, by a novel photooxygenation of dibromocyclobutene (II). We have also isolated a new dimethylenecyclobutane-1,2-dione (VI).

Intramolecular thermal cyclization of 3,4-dibromo-1,1,6,6-tetraphenylhexa-1,2,4,5-tetraene (I)(3) afforded 1,2-dibromo-3,4-bis(diphenylmethylene)cyclobut-1-ene (II) in quantitative yield, colorless needles; mp 190-191°. Anal. Calcd. for $C_{30}H_{20}Br_2$: C, 66.67; H, 3.70; Br, 29.58; mol. wt., 540. Found: C, 66.97; H, 3.49; Br, 29.41; mol. wt. (benzene), 551. $\nu_{max}^{CHCl_3}$, 1510 cm^{-1} (C=C); $\lambda_{max}^{CH_2Cl_2}$, 253 (34,400) and 287 mμ(ε, 42,800). Ultraviolet irradiation of a benzene solution of (II) under oxygen atmosphere at room temperature for 3 hr yielded the titled ionic dibromide (IV) in 51% yield, crimson prisms; mp 182-182.5°. Anal. Calcd. for $C_{30}H_{20}O_2Br_2$: C, 62.93; H, 3.49; Br, 27.92; mol. wt., 572. Found: C, 63.05; H, 3.50; Br, 28.39; mol. wt. (benzene). 568. $\nu_{max}^{CHCl_3}$, 1770 (C=O) and 1540 cm^{-1}(C=C); $\lambda_{max}^{CH_3CN}$, 260 (20,800), 270 (20,800), 346 (9,100) and 460 mμ (ε, 13,900). Its nmr spectrum showed only aromatic protons. Ionic nature of IV was suggested by the electronic absorption band at longer-wave length, 460 mμ which is not assignable to any structure having C-Br σ-bond. The spectrum is attributable to the contribution of cyclobutadiene dication structure (IVa) to the excited state. The suggestion was supported by the shaking of an acetonitrile solution of IV with aq. sodium chloride at room temperature to afford dichloro-analog easily, mp 169-170°.

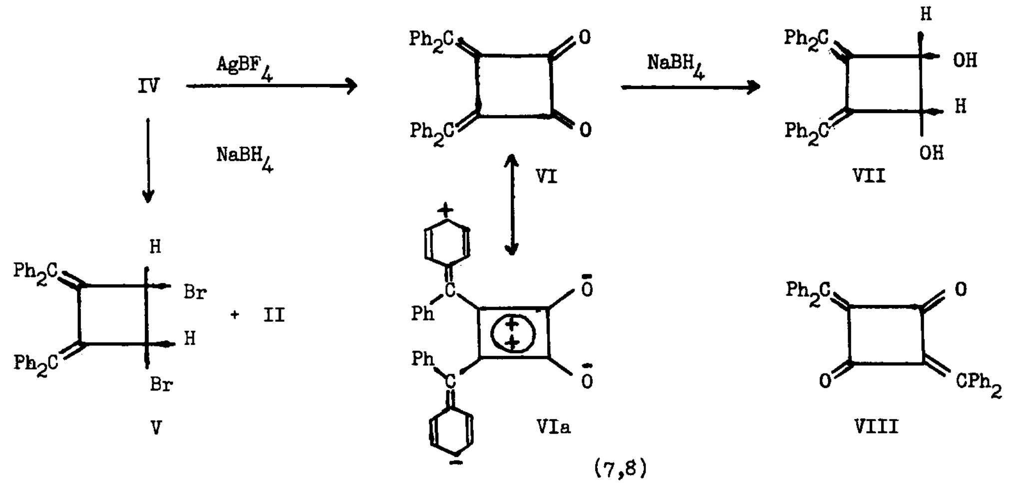
The photooxygenation reaction can be interpreted by the oxygenation at endo-double bond followed by the cleavage of carbon-bromine σ-bonds and 1,3-migration of the bromine atoms. This is the first example of the direct oxygenation of cyclobutene into cyclobutadienequinone, even though the oxygenation of tetraphenylcyclobutadiene with oxygen to afford the ring-opened product, cis-dibenzoylstilbene has been reported.(4) Diels-Alder type addition of oxygen(5) to II is unlikely since the reaction should involve an unfavorable cyclobutadiene intermediate.



The quinone (IV) was easily reduced at room temperature with sodium borohydride, yielding 1,2-dibromo-3,4-bis(diphenylmethylene)cyclobutane (V) and II in 55 and 22% yields, respectively. The structure of V was determined by comparing its physical data with those of an authentic sample prepared according to the reported method.(6) Mechanism of the anomalous reduction is not fully interpretable. Further studies on the reaction are in progress.

The treatment of IV in alcohol with two molar amounts silver fluoroborate afforded 3,4-bis(diphenylmethylene)cyclobutane-1,2-dione (VI) in 90% yield, green needles; mp 206-207°. Anal. Calcd. for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89; mol. wt., 412. Found: C, 87.15; H, 4.63; mol. wt. (benzene), 410. $\nu_{max}^{CHCl_3}$, 1750 with shoulders at 1770 and 1720 (C=O) and 1550, 1520 cm^{-1}(C=C); $\lambda_{max}^{CH_3CN}$, 252 (11,200), 274 (12,900), 315 (sh) (6,300), 465 (sh) (6,200), 499 (12,000) and 620 mμ (ε, 6,300). The nmr spectrum showed aromatic protons only.

The transformation of IV into VI can be interpreted by two-electrons reduction by fluoroborate anion of the dication derived from the reaction of IV and silver ion. The above result is in contrast to that of the reaction of IV with silver perchlorate or nitrate, which afforded an unidentified oxygenated product $C_{30}H_{20}O_3$ in 58% yield, red rhombics; mp 254°. $\nu_{max}^{CHCl_3}$, 1810 and 1765 (C=O), 1560 (C=C) and 950 cm^{-1}(unassignable); $\lambda_{max}^{CH_3CN}$, 308 (10,500) and 415 mμ(ε, 9,400). The difference between the two reactions is interesting, but not surprising since it has been known



that cyclobutadienes are easily oxidized by nitrous ion.(7,8) The electronic spectrum of VI suggests the contribution of the canonical structure (VIa) to the excited state.

The quinone (VI) is the first example of 3,4-dimethylenecyclobutane-1,2-dione system, even though, recently, 1,3-bis(diphenylmethylene)cyclobutane-2,4-dione (VIII) has been prepared.(9) For a compound obtained by partial ozonolysis of tetrakis(diphenylmethylene)cyclobutane, the structure (VI) has been assigned.(10) However, the reported physical data differ widely from those of the compound described in this paper. It has been also pointed out(9) that physical data of VIII(9) differ from those of a compound(10) reported as VIII, which was obtained from tetrakis(diphenylmethylene)cyclobutane by the same procedure.

Sodium borohydride reduction of VI afforded the dihydroxy derivative (VII) in quantitative yield, pale yellow needles; mp 222-223°. $\nu_{max}^{CHCl_3}$ (0.01 mole/l.), 3630 cm^{-1} (trans-diol); λ_{max}^{EtOH}, 262 (21,400) and 369 mμ (ε, 17,500); its diacetate, mp 197-198°. ν_{max}^{Nujol}, 1750 and 1230 cm^{-1} (O=C-O).

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