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NEW METHYLENECYCLOBUTENONES

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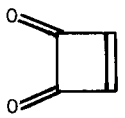
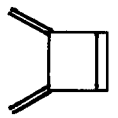
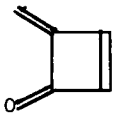
Although a number of dimethylene analogs of cyclobutadienequinone (I), dimethylenecyclobutenes (II), have been known,[1] no monomethylene analog of I, methylenecyclobutenone (III), has yet been reported.[2] We have isolated two derivatives of III (VII and XI), and studied their electronic spectra.



(I)

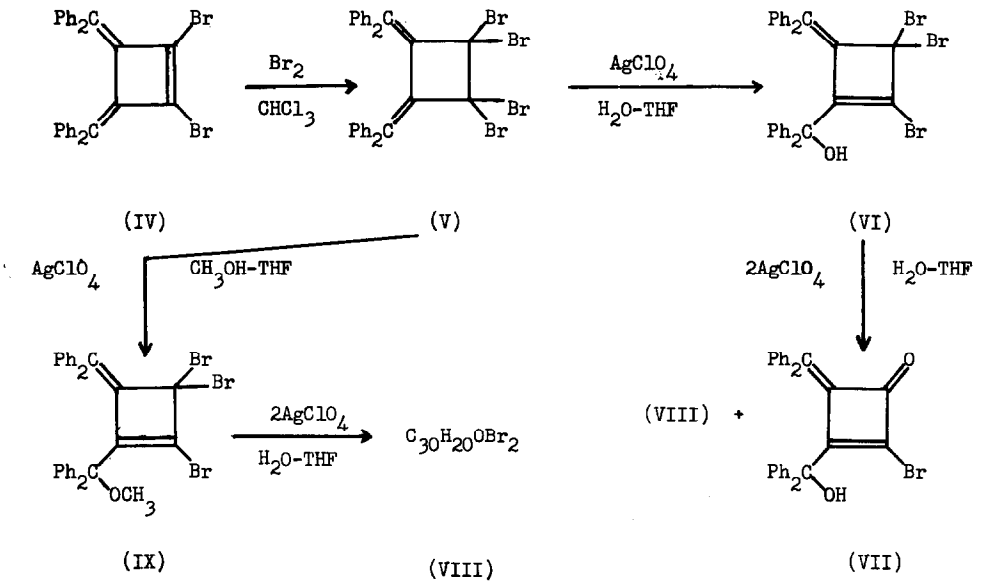


(II)



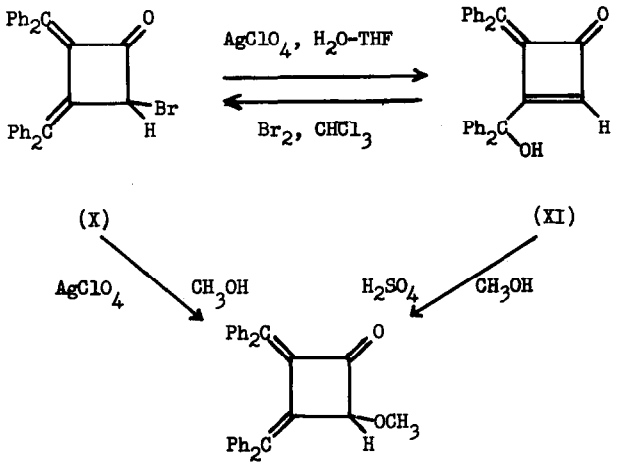
(III)

The treatment of a solution of 1,1,2,2-tetrabromo-3,4-bis(diphenylmethylene)cyclobutane (V),[3] prepared by the addition of bromine to 1,2-dibromo-3,4-bis(diphenylmethylene)cyclobutene (IV),[4] in 10% aqueous tetrahydrofuran (THF) with an equimolar amount of silver perchlorate ($AgClO_4$) at room temperature, afforded 1,2,2-tribromo-3-diphenylmethylene-4-diphenylhydroxymethylcyclobutene (VI) in 66% yield, colorless needles; mp 162-163°; IR 3480 (OH) and 1570 cm^{-1} (C=C); NMR 7.65-6.80 (m, C_6H_5, 20H) and 1.79δ (s, OH, 1H).[5] The electronic spectral data were summarized in Table 1 together with those of other compounds. Further treatment of VI with two molar amounts of $AgClO_4$ in 10% aqueous THF at room temperature afforded 2-bromo-3-diphenylhydroxymethyl-4-diphenylmethylenecyclobutenone (VII) and an unidentified compound ($C_{30}H_{20}OBr_2$) (VIII) in 15 and 10% yields respectively. The spectral data of VII (colorless prisms, mp 155-156°) were, IR 3450 (OH), 1790 (CO) and 1530 cm^{-1} (C=C); NMR 7.40-6.70 (m, C_6H_5, 20H) and 1.95δ (s,OH, 1H). However, the same treatment of IX, prepared by the reaction of V with $AgClO_4$ in MeOH-THF (1:10) in 60% yield, as that employed for VI afforded VIII in 54% yield. The spectral data of IX (colorless prisms, mp 134-135°) were, IR 1560 (C=C) and 1085 cm^{-1}(C-O-C); NMR 7.55-6.75 (m, C_6H_5, 20H) and 3.12δ (s, OCH_3, 3H).



The halogen-free derivative of VII, 3-diphenylhydroxymethyl-4-diphenylmethylenecyclobutenone (XI) was easily obtained by the treatment of 2-bromo-3,4-bis(diphenylmethylene)-cyclobutanone (X)[6] with an equimolar amount of $AgClO_4$ in 10% aqueous THF at room temperature in 28% yield, colorless prisms; mp 163-164°; IR 3470 (OH), 1765 (CO), 1530 (C=C) and 835 cm^{-1} (=CH-); NMR 7.40-6.70 (m, C_6H_5, 20H), 6.37 (s, =CH-, 1H) and 1.89δ (s, OH, 1H). The structure of XI was further confirmed by the following reactions. The addition of bromine to a chloroform solution of XI afforded X quantitatively. The heating under reflux of a solution of XI in methanol containing a catalytic amount of concentrated sulfuric acid for 30 min gave 2-methoxy-3,4-bis(diphenylmethylene)cyclobutanone (XII) in almost a quantitative yield. The structure of XII, orange needles with mp 178-180°, was identified by the comparison of its electronic spectrum with that of X (Table 1), and by the following spectral data, IR 1755 (CO), 1545 (C=C) and 1070 cm^{-1} (C-O-C); NMR 7.30 (d, C_6H_5, 10H), 6.84 (d, C_6H_5, 10H), 5.26 (s, CH, 1H) and 3.25δ (s, OCH_3, 3H). However, when the reaction of X with $AgClO_4$ was carried out in 10% MeOH-THF, XII was isolated as a sole product in 80% yield.

As shown in Table 1, the electronic absorption bands of VII and XI (277 and 280 nm) are comparable to those of VI and IX (271 and 275 nm) rather than to those of X and XII (429 and 453 nm). The data suggest the absence of the full-conjugation between the diphenylmethylene

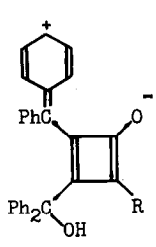


(XII)

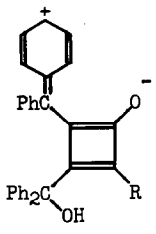
and the carbonyl through the endo-double bond in the compounds VII and XI. The data also suggest that a considerable conjugation system in VII and XI is 1,1-diphenylbuta-1,3-diene. The nonexistence of the full-conjugation in VII and XI may be due to the disadvantage of the contribution of the antiaromatic cyclobutadiene structure (XIII) to the resonance.[7] The electronic spectral data of VII and XI can be interpreted reasonably by assuming the contribution of the cyclobutenyl structure (XV) to the resonance. The contribution of the antiaromatic cyclobutadiene structure (XIV) to the resonance may also be unfavorable.

Table 1. Electronic Spectra

Compound	Solvent	λ_{max} (nm), ($\varepsilon_{max} \times 10^{-2}$)		
X	$CHCl_3$	274 (303)	342 (95)	453 (133)
XII	EtOH	272 (232)	330 (78)	429 (139)
VI	EtOH	275 (131)		
IX	EtOH	271 (158)		
VII	EtOH	277 (103)		
XI	EtOH	280 (154)		
IV	$CHCl_3$	290 (364)		
V	$CHCl_3$	295 (135)		400 (162)



(XIII)



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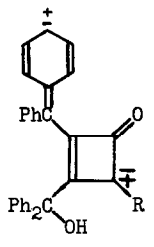
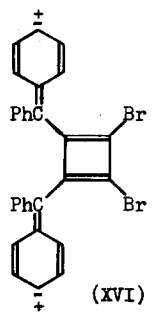
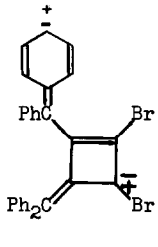


(XV)



(XVI)



(XVII)

By the same manner as above, the difference of the electronic spectra of IV and V can be interpreted. It has been pointed out that dimethylenecyclobutene (II) is better viewed as a cross-conjugated diene rather than as a conjugated triene, since the electronic spectrum of II shows maxima in the same region as that 1,2-dimethylenecyclobutane does,[8] even though the calculated delocalization energy of II, 1.21β is almost equal to that of cyclobutadienequinone (I), 1.24β.[9] We also have reported that a possible conjugated system in IV is to be 1,1-diphenylbuta-1,3-diene, since IV absorbed at much shorter wavelength region, 290 nm than did V, 400 nm, and since the band of IV at 290 nm is comparable to that of 1-phenylbuta-1,3-diene, 305 nm. The absence of a full-conjugation in IV can be interpreted by assuming a contribution of XVII rather than that of unfavorable XVI to the resonance. This interpretation is more reasonable than to assume such a puckered structure of IV[3] that one diphenylmethylene group is out of the plane containing the diphenylmethylene and the endo-double bond.

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