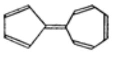
The Synthesis and Reaction of Sesquifulvalene-1, 4-quinone[1)]

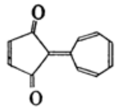
By Yoshio KITAHARA, Ichiro MURATA and Takashi ASANO*

(Received December 20, 1963)

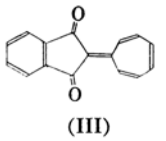
One of the non-alternant hydrocarbons, sesquifulvalene (I), has been synthesized recently by Prinzbach and Rosswog[2)] and found to be less stable than was expected from the molecular orbital theory.[3-6)] On the other hand, Roberts[7)] has pointed out that such



(I)



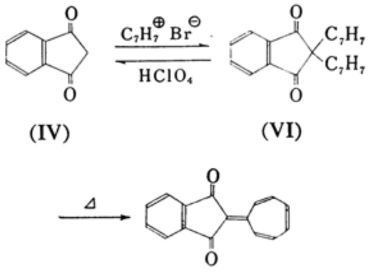
(II)



(III)

unsaturated cyclic hydrocarbons would be expected to form stable quinone derivatives. In this paper we will report on the synthesis and the chemical properties of the following five-membered ring quinone derivatives of sesquifulvalene; sesquifulvalene-1, 4-quinone (II) and 2, 3-benzosesquifulvalene-1, 4-quinone (III).

The reaction of indane-1, 3-dione (IV)[8)] with 2 mol. equiv. of tropylium bromide (V) in an aqueous solution afforded 2, 2-ditropylindane-1, 3-dione (VI)[9)] in a good yield. The two tropyl groups in compound VI were easily cleaved,[10)] by the action of perchloric acid, to yield IV and tropylium perchlorate. The thermal decomposition[11)] of VI gave 2, 3-benzosesquifulvalene-1, 4-quinone (III) as red needles.

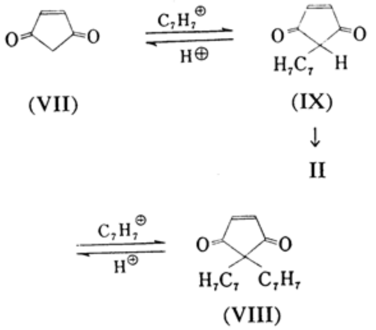


(IV) (VI)

(III)

When cyclopentene-3, 5-dione[12)] was allowed to react with 2 mol. equiv. of V, 4, 4-ditropylcyclopentene-3, 5-dione (VIII) was obtained in a very low yield; however, by adjusting the reaction mixture to pH 7 with sodium hydrogen carbonate, VIII could be obtained in an almost quantitative yield.

When an attempt was made to obtain sesquifulvalene-1, 4-quinone (II) by the thermal decomposition of VIII, the only product isolated was a reddish-brown resinous substance. This reaction will be discussed later. On the other hand, it is to be expected that II would be produced by the dehydrogenation of 4-tropylcyclopentene-3, 5-dione (IX). The preparation of this compound IX from VII was attempted, but even when 1 mol. equiv. of V was used, no monotropyl compound IX could be detected. The following equilibrium is supposed to be involved in the tropylation of cyclopentene-3, 5-dione (VII):



(VII) (IX)

(VIII)

---

* Present address: Santoku Chemical Co., Sendai.

[1)] Preliminary communication: Y. Kitahara, I. Murata and T. Asano, This Bulletin, **34**, 589 (1961).

[2)] H. Prinzbach and W. Rosswog, *Angew. Chem.*, **73**, 543 (1961).

[3)] J. F. Tinker, *J. Chem. Phys.*, **19**, 981 (1951).

[4)] B. Pullman, A. Pullman, E. D. Bergmann, H. Berthod, E. Fisher, Y. Hirshberg, D. Lavie and M. Mayot, *Bull. soc. chim. France*, **1952**, 73.

[5)] R. D. Brown, *Trans. Faraday Soc.*, **45**, 296 (1949); **46**, 146 (1950).

[6)] B. Pullman and A. Pullman, "Les Theories Electroniques de la Chimie Organique," Masson et Cie., Paris (1952).

[7)] J. D. Roberts, *Record of Chem. Progr.*, **17**, 107 (1956).

[8)] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston (1957), p. 127.

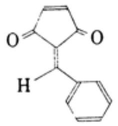
[9)] N. W. Jordan and I. W. Elliot, *J. Org. Chem.*, **27**, 1455 (1962).

[10)] K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

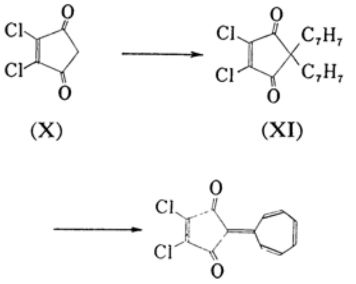
[11)] Cf. T. Nozoe, T. Mukai, K. Osaka and N. Shishido, This Bulletin, **34**, 1384 (1961).

[12)] C. H. DePuy and E. F. Zaweski, *J. Am. Chem. Soc.*, **81**, 4920 (1959).

This means that, if 1 mol. equiv. of acid were to be used in the reaction, even though VIII were formed, the action of the protons would be expected to cause cleavage in VIII and thus to shift the equilibrium towards the monotropyl compound IX. In fact, when the tropylation was carried out in the presence of a 1 mol. equiv. of hydrogen bromide, an oily substance resulted, and on dehydrogenation with chloranil in xylene, the oil gave II as red plates (m. p. 180$\sim$181°C). The possibility that the rearrangement to a benzene derivative might take part in the reaction was excluded by the finding reported below. The expected rearrangement product of II is 4-benzylidene-cyclopentene-3, 5-dione (structure shown below). This compound has already been synthesized by DePuy as pale yellow needles (m.p. 146$\sim$146.5°C[13]) and is obviously different from the product (II) (m. p. 180$\sim$181°C), obtained above.



The thermal decomposition of 1, 2-dichloro-4, 4-ditropylcyclopentene-3, 5-dione (XI), which was derived from 1, 2-dichlorocyclopentene-3, 5-dione (X),[14] gave 2, 3-dichlorosesquifulvalene-1, 4-quinone (XII) in a good yield.



(X)		(XI)

(XII)

All the sesquifulvalene quinone derivatives synthesized as above are red to reddish-orange crystals with high melting points; they are quite stable to air, heat and light.

It is noteworthy that the double bond at the 2, 3-position of the parent compound II is comparatively reactive. Thus, it reacted with bromine in chloroform to give a dibromide XIII as an adduct, and with cyclopentadiene in benzene, even at room temperature, a Diels-Alder reaction occurred to yield an adduct XIV; furthermore, by the action of diazomethane it afforded a pyrazoline derivative XV.

The highly unsaturated nature of the unsubstituted 2, 3-double bond in II accounts for the fact that, in the case of the 2, 3-benzo and 2, 3-dichloro derivatives where the 2, 3-position is substituted, the thermal decomposition of the ditropyl compounds, VI and XI, give III and XII respectively in good yields. Under the same conditions, however, only resinous products were obtained from VIII. This can be understood because, in the latter case, addition would occur between sesquifulvalene-1, 4-quinone and cycloheptatriene,[15] both of which would be formed during the thermal decomposition of VIII.

The ultraviolet absorption maxima[16] and the carbonyl-stretching frequencies[17] of the sesquifulvalene-1, 4-quinones and their 2, 3-adducts are shown in Tables I and II.

TABLE I. ULTRAVIOLET ABSORPTION MAXIMA: mμ (log ε)

	II	III	XII
	222 (4.35)	247 (4.43)	230 (4.20)
	253 (4.16)	257 (4.40)	255 (4.36)
	420 (4.37)	452 (4.57)	422 (4.42)
$\Delta\lambda$	0	+32	+2
	XIII	XIV	XV
	225 (4.30)	227 (4.27)	225 (4.33)
	267 (4.21)	264 (4.15)	266 (4.23)
	452 (4.43)	450 (4.42)	451 (4.42)
	+32	+30	+31

TABLE II. C=O STRETCHING FREQUENCIES: cm^{-1}; KBr-disk

	II	III	XII	XIII	XIV	XV
	1643	1645	1660	1627	1620	1618
$\Delta\nu$	0	+2	+17	−16	−23	−25

With reference to the 2, 3-adducts, XIII, XIV and XV it is significant that their ultraviolet absorption maxima at the longest wavelength show a bathochromic shift of about 30 mμ, and that their carbonyl-stretching frequencies, in the infrared spectra, are decreased by about 20 cm^{-1} compared with those of the 2, 3-unsaturated compounds, II and XII.

It appears to be rather strange that, despite the decrease of conjugation due to the 2, 3-positions being saturated in the adducts, the absorption maxima are shifted towards longer

---

[13] C. H. DePuy and P. R. Wells, ibid., 82, 2909 (1960).

[14] B. T. McBee, C. W. Roberts and K. Dinbergs, ibid., 78, 489 (1956).

[15] The product from the thermal decompostion of VIII; it had the characteristic odor of cycloheptatriene, although none of this compound was actually isolated.

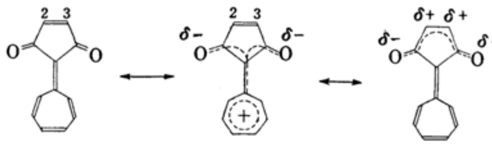
[16] The ultraviolet spectra were recorded on a Hitachi photoelectric spectrometer model EPU-2 and are for methanol solutions.

[17] The infrared spectra were measured on a Perkin-Elmer model 21 spectrometer and are for KBr-disks.

wavelengths. This apparent discrepancy could be explained as follows.

In sesquifulvalene (I), there appears to be quite a large contribution by the ionic structure Ib, a dipolar species possessing a positive seven-membered ring and a negative five-membered ring; for this reason a large dipole moment is expected.[4]


(Ia) (Ib)



(IIa) (IIb) (IIc)

A contribution by the ionic structure may also naturally be expected in II. However, in this case the negative charge is not delocalized over the whole five-membered ring, as is the case in the species Ib; rather, it is probably localized on the two more electronegative oxygen atoms and a charge distribution as depicted in IIb is obtained. The charge transfer between the seven-membered ring and the two oxygen atoms seems to be rather strongly inhibited by the charge transfer IIc which occurs between the double bond at the 2, 3-position and the oxygen atoms. Naturally, the conditions for the transfer of the charge from the seven-membered ring become more favorable when the 2, 3-double bond is removed by the addition of bromine, cyclopentadiene, or diazomethane. The shifts in the ultraviolet and infrared spectra are thus understandable. This speculation is also supported by dipole moment measurements.[18]

Experimental

2, 2-Ditropylindane-1, 3-dione (VI).—Tropylium bromide (3.4 g., 0.02 mol.) in water (50 ml.) was stirred in, drop by drop over a period of 10 min., into a solution of indane-1, 3-dione (1.46 g., 0.01 mol.) in acetonitrile (25 ml.) at room temperature; stirring was then continued for a further 5 hr. The crystalline deposit was filtered off (3.15 g., 97.2%, m. p. 164∼166°C) and recrystallized from ethanol to afford colorless prisms of VI (m. p. 167.5∼168°C).

IR ν_{max}^{KBr}: 3015, 1728, 1699, 1590, 765cm^{-1}. UV λ_{max}^{MeOH} mμ (log ε): 227 (4.69), 252 (4.31).

Found: C, 84.29; H, 5.41. Calcd. for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56%.

The Reaction of 2, 2-Ditropylindane-1, 3-dione with Perchloric Acid.—To a stirred solution of 2, 2-ditropylindane-1, 3-dione (0.65 g., 0.002 mol.) in 5 ml. of glacial acetic acid 60% perchloric acid (0.4 ml., 0.004 mol.) was added at room temperature; crystals were deposited almost immediately. After the mixture had been allowed to stand for 3 hr., the crystals of tropylium perchlorate (0.68 g., 89.4%) were filtered off. Its infrared absorption spectrum coincided with that of authentic tropylium perchlorate.

The filtrate was then diluted with water (300 ml.) and extracted with ether. The ether layer was washed with water, dried, and evaporated to yield crystals (0.25 g., 85.6%; m. p. 124∼127°C), which showed no depression on a mixed melting point test with indane-1, 3-dione.

2, 3-Benzosesquifulvalene-1, 4-quinone (III).—2, 2-Ditropylindane-1, 3-dione (1.0 g., 0.00307 mol.), in a test tube fitted with a side arm which was connected via a dry-ice trap to a vacuum pump, was heated, under reduced pressure, in an oil bath at 175°C for 30 min. During this time an oil was observed to distil into the trap. After distillation of the oil had ceased, the pressure was kept at 2 mmHg for a further 10 min. The oil in the trap was then refluxed with maleic anhydride in xylene for 4 hr. The recrystallization of the crystalline product from carbon tetrachloride gave colorless rods (m.p. 98∼100°C). No depression in the melting point was observed when a mixed melting point test was carried with the maleic anhydride adduct of cycloheptatriene.

The residue which remained in the test tube after the above thermal decomposition was a red solid (0.70 g., 97.5%; m. p. 194∼200°C) which, after four recrystallizations from benzene, afforded red needles of III (m. p. 244∼245°C).

UV λ_{max}^{MeOH} mμ (log ε): 247 (4.43), 257 (4.40), 452 (4.57). IR ν_{max}^{KBr}: 1645, 1628, 1590, 760 cm^{-1}.

Found: C, 81.71; H, 4.13. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30%.

4, 4-Ditropylcyclopentene-3, 5-dione (VIII).—(a) Tropylium bromide (1.71 g., 0.01 mol.) in water (30 ml.) was stirred drop by drop during 10 min. into a solution of cyclopentene-3, 5-dione (0.96 g., 0.01 mol.) in water (20 ml.). After the reaction mixture had been allowed to stand for 3 hr. at room temperature, the resulting precipitate was taken up in ether. The ether layer was washed with water, dried over magnesium sulfate, and then evaporated. The residue, dissolved in benzene, was chromatographed on an alumina column (1× 10 cm.). From the combined yellow benzene eluates 0.55 g. of crystals was obtained (m. p. 118∼121°C). Recrystallization from cyclohexane gave yellow prisms (m. p. 121∼122°C).

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.17), 250 (3.90). IR ν_{max}^{KBr}: 3015, 1735, 1696, 740 cm^{-1}.

Found: C, 82.45; H, 5.84. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84%.

(b) Tropylium bromide (3.42 g., 0.02 mol.) in 75% ethanol (15 ml.) was added, in one lot, to a

---

[18] S. Katagiri, I. Murata, Y. Kitahara and H. Azumi, to be published.

stirred solution of cyclopentene-3,5-dione (0.96 g., 0.01 mol.) in ethanol (20 ml.) at room temperature. After being stirred for 10 min., the solution was adjusted to pH 6.5~7.0 with saturated aqueous sodium hydrogen carbonate. The precipitated crystals of 4,4-ditropylcyclopentene-3,5-dione (2.58 g., 93.5%; m. p. 118~120°C) were then filtered off.

Sesquifulvalene-1, 4-quinone (II).—To a stirred solution of cyclopentene-3,5-dione (1.92 g., 0.02 mol.) in water (40 ml.) 3.2 g. of 48% hydrobromic acid was added; then to this mixture, a solution of tropylium bromide (3.42 g., 0.02 mol.) in water (50 ml.) was stirred in drop by drop over a period of 30 min. The yellow oil which separated was extracted into ether, and the ether solution was washed with water, dried over magnesium sulfate, and then evaporated. The residual oil (3.7 g.), without further purification, was dissolved in xylene (40 ml.). Chloranil (4.8 g.) was added to the solution, and the solution was refluxed for 3 hr. and then allowed to stand overnight. The precipitated tetrachlorohydroquinone was filtered off, and the filtrate was concentrated under reduced pressure. The benzene-soluble fraction of the residue was chromatographed on an alumina column (2×15 cm.). The red benzene eluate yielded red crystals (0.37 g., 10% yield based on tropylium bromide; m. p. 172~175°C). Recrystallization from benzene afforded red plates of II (m. p. 180~181°C).

UV λ_{max}^{MeOH} mμ (log ε): 222 (4.35), 253 (4.16), 420 (4.37). IR ν_{max}^{KBr}: 3060, 1643, 1515, 1262, 849 cm^{-1}.

Found: C, 78.41; H, 4.26. Calcd. for $C_{12}H_8O_2$: C, 78.25; H, 4.38%.

1, 2-Dichloro-4, 4-ditropylcyclopentene-3, 5-dione (XI).—Tropylium bromide (12.1 g., 0.0708 mol.) in acetonitrile (150 ml.) was stirred drop by drop into a solution of 1,2-dichlorocyclopentene-3,5-dione (5.5 g., 0.033 mol.) in acetonitrile (50 ml.) at room temperature. Pyridine (5 ml.) was then added, and stirring was continued for a further 30 min. The yellow crystals (11.2 g., 97.3%) which precipitated on the addition of water (500 ml.) had a m. p. of 98~100°C; recrystallization from methanol afforded yellow plates of XI (m. p. 103~104°C).

IR ν_{max}^{KBr}: 3020, 1757, 1712, 1584, 1200 cm^{-1}.

Found: C, 66.21; H, 4.20. Calcd. for $C_{19}H_{14}O_2Cl_2$: C, 66.11; H, 4.09%.

2, 3-Dichlorosesquifulvalene-1, 4-quinone (XII).—1,2-Dichloro-4,4-ditropylcyclopentene-3,5-dione (1.72 g., 0.005 mol.) was pyrolysed in a test tube with a side arm at 150°C under reduced pressure. During the reaction, the material in the tube melted, then began to bubble, and finally resolidified after about 10 min. Methanol was added to the residue, and the red crystals (1.1 g., 86.9%; m. p. 250°C (decomp.)) which were obtained in filtering the suspension were recrystallized from benzene to give reddish-orange scales of XII (m. p. 263°C (decomp.)).

UV λ_{max}^{MeOH} mμ (log ε): 230 (4.20), 255 (4.36), 422 (4.42). IR ν_{max}^{KBr}: 1660, 1615 cm^{-1}.

Found: C, 57.07; H, 2.59. Calcd. for $C_{12}H_6O_2Cl_2$: C, 56.95; H, 2.39%.

The Reaction of Sesquifulvalene-1, 4-quinone (II) with Bromine.—Bromine (0.08 g.) in chloroform (1 ml.) was added to a stirred solution of sesquifulvalene-1,4-quinone (0.09 g.) in chloroform (4 ml.) with ice-cooling. The crystalline orange precipitate (0.12 g; m. p. 80~95°C) which was produced was then filtered off and recrystallized from ethanol to yield golden-yellow scales of XIII (m. p. 148°C (decomp.)).

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.30), 267 (4.21), 452 (4.43). IR ν_{max}^{KBr}: 1627 cm^{-1}.

Found: C, 42.51; H, 2.42. Calcd. for $C_{12}H_8O_2Br_2$: C, 41.89; H, 2.34%.

The Reaction of Sesquifulvalene-1, 4-quinone (II) with Diazomethane.—Ethereal diazomethane was stirred into an ice-cold solution of sesquifulvalene-1,4-quinone (0.09 g.) in a mixture of benzene (4 ml.) and ether (50 ml.). Orange crystals began to be formed within a few minutes; the mixture was then allowed to stand for 30 min., after which time the crystals (0.08 g.; m. p. 290°C) were filtered off and recrystallized three times from ethanol to afford orange needles of XV (m. p. 290°C).

UV λ_{max}^{MeOH} mμ (log ε): 225 (4.33), 266 (4.23), 451 (4.42). IR ν_{max}^{KBr}: 1618 cm^{-1}.

Found: C, 68.67; H, 4.33; N, 12.08. Calcd. for $C_{13}H_{10}O_2N_2$: C, 69.01; H, 4.46; N, 12.38%.

The Reaction of Sesquifulvalene-1, 4-quinone (II) and Cyclopentadiene.—A solution of sesquifulvalene-1,4-quinone (0.09 g.) and freshly-distilled cyclopentadiene (0.07 g.) in benzene (6 ml.) was set aside for 24 hr. in a tightly-stoppered flask at room temperature. The residue remaining after the removal of the benzene was treated with light petroleum, and the insoluble residue (m. p. 182~183°C) was recrystallized from benzene; red prisms of XIV (m. p. 188~189°C) were obtained.

UV λ_{max}^{MeOH} mμ (log ε): 235 (3.82), 289 (3.83), 450 (4.43). IR ν_{max}^{KBr}: 1620 cm^{-1}.

Found: C, 81.51; H, 5.25. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64%.

The authors are indebted to Miss Yoko Endo and Miss Yukiko Endo of this Institute for their elementary analyses. They are also grateful to the Sankyo Co., Ltd., for its financial support in the present research.

The Chemical Research Institute of
Non-Aqueous Solutions
Tohoku University
Katahira-cho, Sendai