

Wir sind daher der Ansicht, dass bei der Pyrolyse von **2** und **11** der von *Pines* & *Kozłowski* [2] für **1** vorgeschlagene Weg B durchlaufen wird. Diese Reaktionsfolge in Kombination mit intraannularen [1,5]-Wasserstoff- bzw. Deuterium-Verschiebungen führt bei **11** zu einer Verteilung der 6 Wasserstoffatome auf alle Stellen (vgl. *Schema 4*).

In Analogie zu den dargelegten Beobachtungen ziehen wir in Betracht, dass auch die Isomerisierung von **1** zu **3** über Weg B verläuft und dass keine [1,5]-Methylverschiebung vorliegt. Weitere Untersuchungen dazu sind im Gange.

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201. Tetrahalo-*anti*-bis-homoduroquinones¹⁾ by addition of dihalocarbenes to duroquinone

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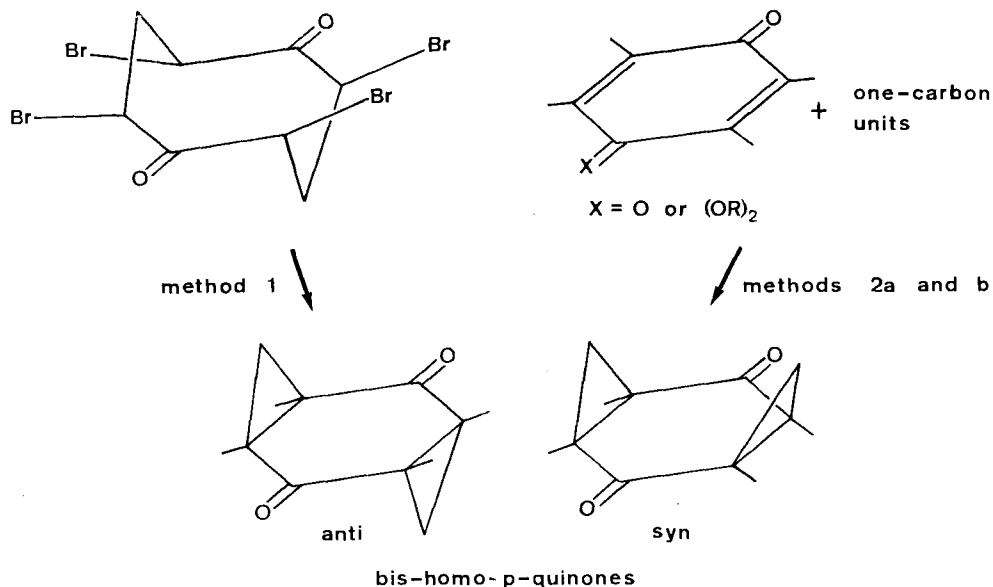
Zusammenfassung. Doppelte Anlagerungen von Dichlorcarben und von Dibromcarben an Durochinon (**1**) ergaben 4,4,8,8-Tetrachlor-(**3**) und 4,4,8,8-Tetrabrom-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octan-2,6-dion (**4**) (= Tetrachlor- und Tetrabrom-*anti*-bis-homodurochinon).

Die *anti*-Konfiguration der beiden Diketone **3** und **4** wurde aus einfachen röntgenographischen Daten abgeleitet: Zwei Molekeln in der Elementarzelle und die Raumgruppe $P2_1/n$ verlangen Zentrosymmetrie für die beiden Molekeln **3** und **4** im Kristallgitter, was die *syn*-Konfiguration ausschliesst.

1. Introduction. – The two principally different methods known for the preparation of bis-homo-*p*-quinones are: 1) Debrominative as well as dehydrobromi-

¹⁾ The systematic names according to the IUPAC rules are 4,4,8,8-tetrahalo-1,3,5,7-tetramethyl-*anti*-tricyclo[5.1.0.0^{3,5}]octane-2,6-diones and these names are included in the summary and the experimental section.

native cyclopropanisations of 2,4,6,8-tetrabromo-cyclooctane-1,5-diones yielding mostly the *anti*-isomer [1]. 2) Double addition of one-carbon units to *p*-quinone derivatives, which has been achieved in two ways: a) by the action of diazomethane [2] or diazoethane [3] on duroquinone followed by nitrogen elimination²⁾ and b) by the action of dimethylsulfoxonium methylide on a *p*-quinone-monoacetal [7] [8]³⁾.

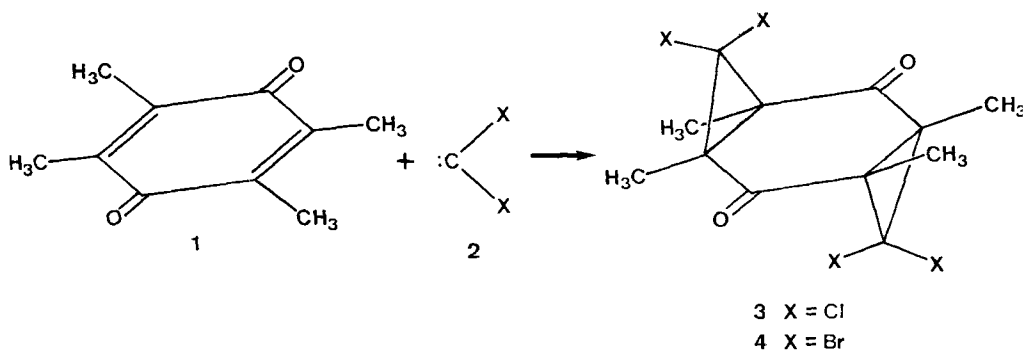


So far, the above mentioned additions of one-carbon units to *p*-quinone derivatives have afforded only the *syn*-isomers⁴⁾ and attempts to use carbenoids as such units have not met with success⁵⁾ ⁶⁾.

We report here the double additions of dichloro- and dibromocarbene to duroquinone (**1**) which resulted in tetrahalo-bis-homoduroquinones **3** and **4** exclusively in the *anti*-configuration.

- ²⁾ Bis-homo-*p*-quinones result from pyrolysis or photolysis of the bis-pyrazolines, which are the primary adducts of diazoalkanes at both double bonds of *p*-quinones. However, such bis-pyrazolines have been obtained in only few [2–4] of the many cases [5] [6] studied. The most frequently observed reactions of diazoalkanes with quinones involve: 1) attack at one of the carbonyl groups to give epoxides, carbinols, ethers and hydroquinone-derivatives [5], 2) attack at only one double bond to give mono-pyrazolines (convertible to mono-homo-*p*-quinones) [4] and 3) fast autooxidation of the primary pyrazolines to stable pyrazoles [6].
- ³⁾ Methods 1) and 2b) are suitable for unsubstituted bis-homo-*p*-quinone; method 2a) has been restricted to angularly alkylated derivatives.
- ⁴⁾ The configuration of the products from diazoethane and duroquinone were assumed [3] to be *syn* by analogy [2] with the diazomethane adduct.
- ⁵⁾ The *Simmons-Smith* and dichlorocarbene addition reactions with *p*-quinone monoacetal resulted in three methoxylated benzenoid products only [7].
- ⁶⁾ Carbenoid units have been added successfully to the unconjugated cyclohexa-1,4-diene. It is of interest to note that the resulting tricyclo[5.1.0.0^{3,5}]octanes (without the carbonyl groups) consisted exclusively (with dibromocarbene [9]) or predominantly (by *Simmons-Smith* [10] and by $\text{CH}_2\text{N}_2 + \text{CuCl}_2$ [11]) of the *anti*-isomers [12].

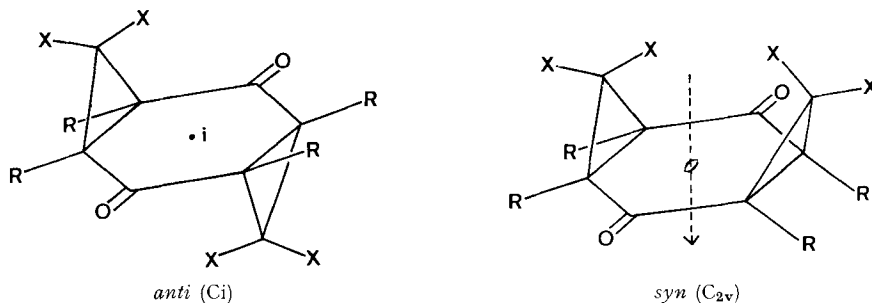
2. Tetrahalo-*anti*-bis-homoduroquinones. – The formation of tetrachloro-*anti*-bis-homoduroquinone (**3**), m.p. 256°, in 95% yield required a large excess of potential dichlorocarbene prepared *in situ* at room temperature from chloroform (55 fold excess) in the presence of 50% aqueous sodium hydroxide (41 fold excess) with triethylbenzylammonium chloride as a catalyst [13]. The same reaction with a two-fold excess of chloroform gave only a 3% yield of **3**. On the other hand, a similar procedure applied to the formation of tetrabromo-*anti*-bis-homoduroquinone (**4**), m.p. above 200° (dec.), required only a two fold excess of bromoform containing a small amount of ethanol [14] to give a 57% yield.



As expected, the spectral properties of the tetrachloro-(**3**) and tetrabromo-*anti*-bis-homoduroquinones (**4**) are very similar: There is a single sharp carbonyl band in the solution IR.-spectra (CHCl_3) of both diketones **3** and **4**, namely at 1698 and 1695 cm^{-1} , respectively. This is in contrast to the bis-homo-*p*-quinones [1] and mono-homo-*p*-quinones [4] [15] which show two strong carbonyl absorptions in the solution IR.-spectra (when reported), the first in the range 1685–1712 cm^{-1} and the other in the range 1667–1686 cm^{-1} . A sole singlet can be seen for the four methyl groups at $\delta = 1.45$ and 1.44 ppm, respectively, in the $^1\text{H-NMR}$ -spectra of **3** and **4**. The mass-spectra of both products show the molecular weights (330 for **3**, resp. 508 for **4**) as well as fragmentations involving two consecutive losses of halogen, loss of halogen + CO and halogen + 2 CO. The base peak in these spectra corresponds to half the molecular weight (165 for **3**, resp. 254 for **4**). It is interesting to note that this fragmentation into two equal parts (68 *m/e*) is also quite strong (88 and 94%) with the parent compounds, *syn*- and *anti*-bis-homo-*p*-quinone (compare experimental section).

3. Determination of the *anti*-configurations. – The *anti*-configuration of the two tetrahalo-bis-homoduroquinones **3** and **4** was derived from simple crystallographic considerations as follows: The crystals of both compounds **3** and **4** are monoclinic with the lattice constants $a = 8.99$, $b = 9.41$, $c = 8.42$ Å, $\gamma = 104.84^\circ$ for **3**, and $a = 9.53$, $b = 9.31$, $c = 8.52$ Å, $\gamma = 105.22^\circ$ for **4**. The experimentally estimated crystal densities of about 1.6 for **3** and about 2.1 g/cm^3 for **4** agreed with the values obtained from the cell volumes and the assumed presence of *two* molecules in the unit cells, namely $d = 1.59$ for **3** and $d = 2.05$ g/cm^3 for **4**. The systematic extinctions show unambiguously that the crystal structures of both **3** and **4** conform

to the space group $P2_1/n$ with four general equivalent positions. Since both **3** and **4** contain only two molecules in the unit cell these molecules must occupy the only available two-fold special positions with the point symmetry $\bar{1}$ ($= C_i$). Thus both molecules **3** and **4** possess a configuration which permits a centrosymmetric conformation when packed in the crystal.



On this basis it is possible – without a full structure determination – to exclude the *syn*-configuration (group C_{2v}) for both compounds **3** and **4**. On the same basis one can exclude a boat conformation for the six-membered ring of both **3** and **4** in the crystalline state.

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Experimental Part

General. The abbreviations used in the experimental section have been described previously [15]. We thank the MS.-laboratory (direction Prof. *M. Hesse*) for the mass spectra and the micro-laboratory (direction *H. Frohofer*) for the elemental analyses and the IR. spectra.

4,4,8,8-Tetrachloro-1,3,5,7-tetramethyl-anti-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (3) (*tetrachloro-anti-bis-homoduroquinone*). To a vigorously stirred solution of 1 g (6.1 mmol) duroquinone (**1**) and 0.07 g triethylbenzylammonium chloride in 30 ml chloroform (337 mmol) was added 20 ml of 50% aqueous sodium hydroxide (250 mmol) over 10 min at room temperature. On completion of the addition the bright yellow mixture was heated to 45° for 90 min while it slowly changed to a brown viscous suspension. This was diluted with 20 ml of methylene chloride and after further heating for 90 min the mixture was poured into 250 ml water and extracted with chloroform. The combined extracts were washed with dilute hydrochloric acid and water, dried and evaporated to leave 1.95 g of a pale brown solid which on recrystallisation from chloroform yielded 1.92 g (95%) of *4,4,8,8-tetrachloro-1,3,5,7-tetramethyl-anti-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (3)* as white plates, m.p. 254–256°. – IR. (KBr): 3030 w; 3010 w; 3000 w; 2990 w; 2950 w; 1693 s; 1660 (w); 1458 m; 1390 m; 1375 m; 1285 w; 1255 s; 1068 w; 1045 m; 965 w; 922 m; 870 m; 810 m; 735 w; 710 w. – IR. ($CHCl_3$): 1698 s as the only band in the C=O region. – MS. (70 ev): 336/334/332/330/328 (0.02/0.04/0.25/0.75/0.5, M^+); 299/297/295/293 (1/5/15/16, $M^+ - Cl$); 271/269/267/265 (1/4/12/12, $M^+ - Cl - CO$); 262/260/258 (0.25/1.0/1.25, $M^+ - 2 \times Cl$); 243/241/239/237 (0.5/1.5/7/8, $M^+ - Cl - 2 \times CO$); 166/164 (60/100); 103 (17); 101 (84). – 1H -NMR. (60 MHz, $CDCl_3$): $\delta = 1.45/s$, presumably 12 pr ($4 \times CH_3$).

$C_{12}H_{12}Cl_4O_2$	Calc.	C 43.67	H 3.67	Cl 42.97%
(330.04)	Found	„ 43.75	„ 3.74	„ 42.54%

When this reaction was performed with the same amounts of duroquinone, catalyst and aqueous sodium hydroxide, but with only 2.9 g (24.4 mmol = 2-fold excess) of chloroform, the yield of **3** was only 3%.

4,4,8,8-Tetrabromo-1,3,5,7-tetramethyl-anti-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione (**4**, *tetrabromo-anti-bis-homoduroquinone*). To a stirred mixture of 2 g (12.2 mmol) duroquinone (**1**), 14 g (55.3 mmol) bromoform, 0.1 g triethylbenzylammonium chloride and 0.3 ml ethanol was added with stirring 30 ml of 50% aqueous sodium hydroxide (375 mmol) over 10 min at 40–45°. The initially precipitated white solid gradually darkened until, 5 min after completion of the addition, it was dark brown in colour. At this stage 8 ml of methylene chloride was added because of the viscous nature of the reaction mixture. After 3 h at this temperature the mixture was poured into 200 ml water and extracted with chloroform. The combined extracts were washed with dilute hydrochloric acid and water, dried and evaporated to leave a pale brown solid which on recrystallisation from chloroform gave 3.55 g (57%) of *4,4,8,8-tetrabromo-1,3,5,7-tetramethyl-anti-tricyclo[5.1.0.0^{3,5}]octane-2,6-dione* (**4**) as white plates. During melting point determination the sample darkened above 200° and from 220° onwards it gradually shrank leaving a black powdery residue. – IR. (KBr): 3025 w; 3005 w; 2990 w; 2980 w; 2940 w; 1690 s; 1455 m; 1388 s; 1372 m; 1345 w; 1248 s; 1065 w; 1043 s; 870 w; 865 s; 782 m; 712 m; 702 w. – IR. (CHCl₃): 1695 s as the only band in the C=O region. – MS. (70 ev): 512/510/508/506/504 (0.4/1/1.2/1/0.4, M⁺); 431/429/427/425 (6/19/18/6, M⁺ – Br); 403/401/399/397 (4/10/10/4, M⁺ – Br – CO); 375/373/371/369 (2/6/6/2, M⁺ – Br – 2 × CO); 350/348/346 (22/42/22, M⁺ – 2 × Br); 322/320/318 (7/15/7, M⁺ – 2 × Br – CO); 307/305/303 (2/4/2, M⁺ – 2 × Br – CO – CH₃); 294/292/290 (12/22/13, M⁺ – 2 × Br – 2 × CO); 269/267 (92/97, M⁺ – 3 × Br); 256/254/252 (51/100/52); 241/239 (57/60, M⁺ – 3 × Br – CO); 225 (19); 223 (16); 213 (15); 160 (27); 147/145 (50/60); 133 (22); 132 (16); 118 (15); 116 (16); 91 (16). – ¹H-NMR. (60 MHz, Dioxane): δ = 1.44/s, presumably 12 pr (4 × ClI₃).

C ₁₂ H ₁₂ Br ₄ O ₂	Calc.	C 28.37	H 2.38	Br 62.92%
(507.87)	Found	28.48	2.54	62.42%

Crystal densities of 3 and 4. The crystal densities of **3** and **4** were estimated by the observations that a few crystals remained essentially floating in liquids of densities 1.6 and 2.1 g/cm³ respectively.

MS. (70 ev) of syn- and anti-bis-homo-p-quinones. Since the mass-spectra of these two diketones have not been reported completely [1], they are included here. *syn-Bis-homo-p-quinone*: 136 (59, M⁺); 108 (11, M⁺ – CO); 107 (17); 80 (26, M⁺ – 2 × CO); 79 (58); 68 (88, 1/2 M⁺); 39 (100). *anti-Bis-homo-p-quinone*: 136 (100 M⁺); 108 (11, M⁺ – CO); 107 (17); 80 (19, M⁺ – 2 × CO); 68 (94, 1/2 M⁺); 39 (45).

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