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141. Bicyclo[4.1.0]hept-3-ene-2,5-dione (Homo-*p*-quinone[1])) and its *Bamford Stevens* Reaction

by **Christopher B. Chapleo**[2]) and **André S. Dreiding**

Organisch-chemisches Institut der Universität Zürich, Rämistrasse 76, 8001 Zürich

(2. V. 74)

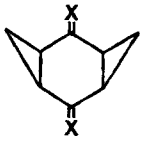
Zusammenfassung. Homo-*p*-chinon[1]) (**4** = Bicyclo[4.1.0]hept-3-en-2,5-dion) wurde hergestellt und auf seine Spektraleigenschaften untersucht. Die UV.-, IR.- und NMR.-Spektren sind charakteristisch für die darin enthaltene Endion- und *cis*-disubstituierte Cyclopropan-Substruktur, ohne eine starke Wechselwirkung zwischen den beiden zum Ausdruck zu bringen.

[1]) The prefix 'homo-' before a trivial name signifies that the system (chain or ring) has been enlarged by one carbon member. The special case of double bond to cyclopropane 'enlargement' has received individual attention in connection with *Winstein*'s homoconjugation concept. For this reason and for the sake of brevity we shall, in the following text, refer to compounds **1a** and **2a** as *syn*- and *anti*-bis-homo-*p*-quinone and to compound **4** as homo-*p*-quinone.

[2]) Post-doctoral fellow, University of Zürich, 1972–4.

Basische Thermolyse des Bis-*p*-toluolsulfonylhydrazons (**9**) von Homo-*p*-chinon ergab das bekannte 1,7a-Diaza-inden (**10**). Dies bestätigt den früher postulierten Mechanismus der *Bamford-Stevens*-Reaktion mit den zwei isomeren Bis-homo-*p*-chinonen (**1a** und **2a**).

1. Introduction. – Recently we reported [1] [2] the synthesis of *syn*-(**1a**) and *anti*-(**2a**) bis-homo-*p*-quinone[1]) of interest due to the rather rigid arrangement of two cyclopropane rings with respect to two carbonyl groups. A characteristically



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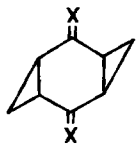

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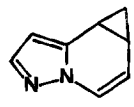

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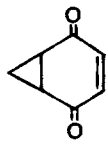
a: X = O

b: X = NNHTs

deepseated rearrangement of the corresponding bis-*p*-toluene-sulfonyl-hydrazones **1b** and **2b** was observed [3] under *Bamford-Stevens* conditions, which led to 4,5-dihydro-4,5-methano-1,7a-diaza-7a*H*-indene (**3**, 4,5-homo-1,7a-diaza-indene[1])). In this connection it appeared of interest to prepare and study the corresponding lower homologue, homo-*p*-quinone (**4**), for two reasons: 1. The diketone **4** combines the



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structural features of *p*-quinone and of bis-homo-*p*-quinone and 2. the *Bamford-Stevens* reaction of **4** could be a test case for the mechanism of the complicated rearrangement postulated [3] for the formation of **3** from **1** and **2** (see below).

2. Homo-*p*-quinone. – The mono(ethylene)acetal (**6**) of homo-*p*-quinone (**4**) (bicyclo[4.1.0]hept-3-ene-2,5-dione-mono(ethylene)acetal, (**6**) had already been observed [2] in connection with the attempts to add two methylene groups to the mono(ethylene)acetal (**5**) of *p*-quinone in order to obtain **1a**. The formation of the bis-adduct required a large excess of trimethyl-sulfoxonium iodide [2]; the use of

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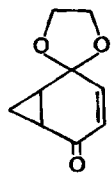


6

only two mol-equivalents of this reagent with **5** led to the mono-adduct **6** as the only product in 43% yield [2]. In the present work, the acetal **6** was hydrolysed in

88% yield to homo-*p*-quinone (**4**) as yellow needles, m.p. 47–49.5° and stable on standing, with the following spectral properties:

The IR.-spectrum shows four bands in the carbonyl region, two strong ones at 1685 and 1680 cm^{-1} as well as two weak ones at 1748 and 1645 cm^{-1}. It is worth noting that many *p*-quinones show multiple absorption in the carbonyl region, even in dilute solution, which is attributed mainly to *Fermi* resonance effects [4]. Enediones also show similar multiple absorptions [5]. The double bond gives rise to a very sharp band of medium intensity at 1610 cm^{-1}.

The UV.-spectrum of **4** exhibits two symmetrical absorptions at 227 nm ($\varepsilon = 9650$) and at 347 nm ($\varepsilon = 180$) which are characteristic of the chromophore –CO–CH=CH–CO– [6]. The additional three-membered ring between the two carbonyl groups in **4** does not appear to add significantly to the conjugation. The mass spectrum shows the molecular ion (122 *m/e*) as well as fragmentation involving two consecutive losses of CO (94 and 66 *m/e*) followed by loss of CH_2 (54 *m/e*).

The ^{1}H-NMR.-spectrum of **4** can be interpreted fully as a A_2M_2XY-system: The olefinic hydrogen atoms (A_2) generate the triploid signal at 6.43 ppm with 1.5 Hz as the sum of the long range couplings. The M_2XY-portion of the spectrum is due to the *cis*-symmetrically disubstituted cyclopropane substructure with the two angular methine hydrogen atoms (M_2) producing the quartet-like signal at 2.56 ppm and the two methylene hydrogen atoms (X and Y) giving rise to the more complex signal at 1.9–1.6 ppm. The following parameters permitted the simulation of the M_2XY portion of the spin system: $\nu(M) = 252$, $\nu(X) = 173$, $\nu(Y) = 166.6$ and $J(XY) = 4.6$, $J(MX) = 8.8$, $J(MY) = 5.6$ Hz. The simulated signals exhibited excellent agreement

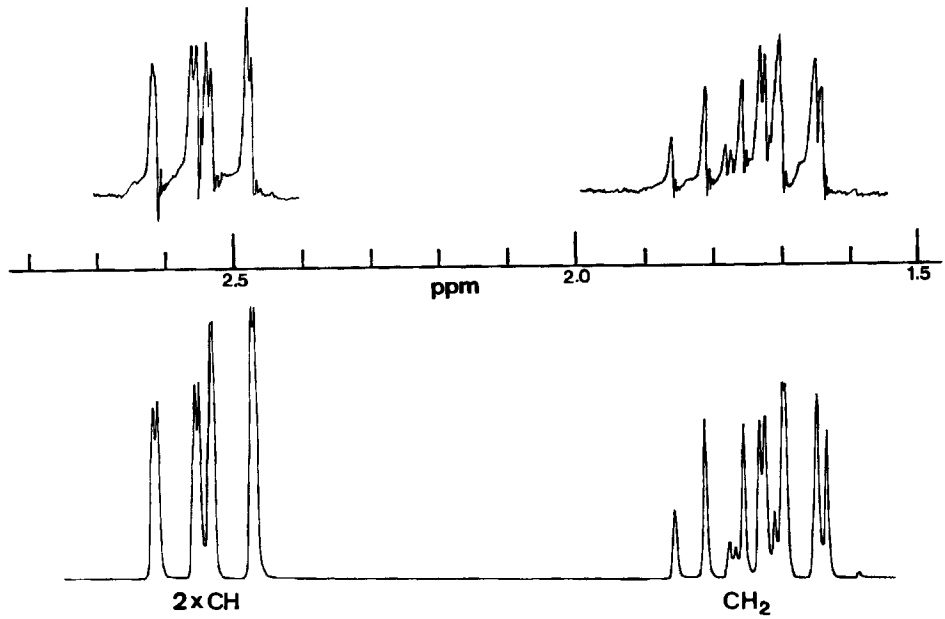
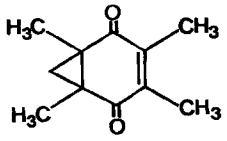


Fig. 1. Top: *100 MHz-NMR.-spectrum of homo-*p*-quinone* (**4**) with long range couplings removed. Bottom: *Spin-simulated spectrum of the cyclopropane portion of homo-*p*-quinone* (**4**)

with those in the observed spectrum, in which the long range couplings (with the two Y's) had been removed by spin decoupling. The observed spectrum and the simulated portion of the spectrum are shown in fig. 1.

The above parameters confirm structure **4** as follows: the two angular hydrogen atoms (M_2: $\delta = 2.56$ ppm) participate in a cyclopropane-*cis*- and -*trans*-vicinal coupling of $J = 8$ and 5.8 Hz with X and Y, respectively. These couplings are also seen in the signals of H(*exo*) (X: $\delta = 1.73$ ppm) and of H(*endo*) (Y: $\delta = 1.67$ ppm), which, in addition, couple with each other with $J = 5$ Hz as expected for geminal cyclopropane hydrogen atoms.

Of interest is the rather small difference ($\Delta\delta(exo-endo) = +0.06$ ppm) in the chemical shift of H(*exo*) and H(*endo*). In *anti*-bis-homo-*p*-quinone (**2a**) this value is +0.42 ppm, in the corresponding *syn*-isomer (**1a**) it is −0.52 ppm. Evidently the anisotropic effects which separated the resonance of H(*exo*) and H(*endo*) in opposite directions in the bis-homo-*p*-quinones (**1a** and **2a**) are modified in **4** so as to keep them roughly the same. This observation can be used to assign the chemical shift of the two methylene protons in homo-*p*-duroquinone (**7**) [7]. The difference in these chemical shifts has been found to be $\Delta\delta = 0.68$ ppm. No sign could be attached to



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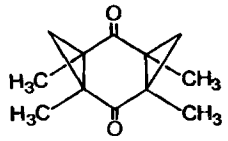

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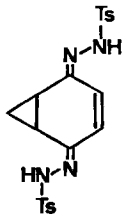
this value, however, since it was not known which of the two signals corresponded to H(*exo*) or H(*endo*). The effect of the angular methyl groups on the chemical shift difference ($\Delta\delta$) of such systems can be estimated as $\Delta\delta = -0.75$ ppm by comparing this value ($\Delta\delta(exo-endo) = -1.27$ ppm) in *syn*-bis-homo-*p*-duroquinone (**8**) [8][3]) with that ($\Delta\delta(exo-endo) = -0.52$ ppm) in *syn*-bis-homo-*p*-quinone (**1a**) [2]. If we add this 'methyl-effect' to the value ($\Delta\delta(exo-endo) = +0.06$ ppm) of our homo-*p*-quinone (**4**), we may calculate $\Delta\delta = -0.69$ ppm for **7**. Thus the observed [7] $\Delta\delta$-value in **7** must be negative, and the signal at $\delta = 1.05$ ppm can be assigned to H(*exo*) and the one at $\delta = 1.73$ ppm to H(*endo*).

The ^{13}C-NMR.-spectrum of **4** is in accord with the structure shown both with respect to the symmetry (4 signals) and with respect to chemical shifts (δ(C=C) = 137.0, δ(C=O) = 195.0, δ(CH) = 27.5 and $\delta(CH_2)$ = 19.6 ppm). For comparison we give here the corresponding values for *syn*-(**1a**)- and *anti*-(**2a**)-bis-homo-*p*-quinones, respectively. They are: δ(C=O) = 200.6 and 200.6; δ(CH) = 29.6 and 23.8; $\delta(CH_2)$ = 15.8 and 12.3 ppm.

3. Rearrangement of the bis-*p*-toluene-sulfonyl-hydrazone of homo-*p*-quinone. – The highly insoluble bis-*p*-toluene-sulfonyl-hydrazone (**9**) of homo-*p*-

[3]) H(*exo*) and H(*endo*) were assigned [8] on the following basis: 1. Proximity effect between the two H(*endo*)'s (compare [1]). 2. Nuclear magnetic resonance study of the two diastereoisomeric mono-keto-alcohols and their derivatives obtained from **8** by observing long range couplings between the methine proton and H(*exo*). 3. Nuclear *Overhauser* enhancements between H(*exo*) and CH_3.

quinone was obtained in 81% yield but lent itself to characterisation only by elemental analysis and the IR.-spectrum. When the sodium salt of **9** was subjected to



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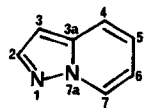
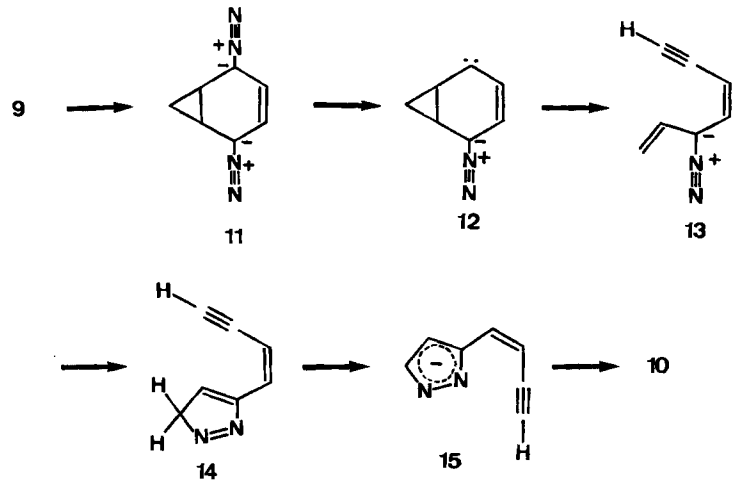


10

thermolysis at 180° in diglyme in the presence of sodium methoxide a 47% yield of a colourless oil was obtained, which was identified as 1,7a-diaza-indene (**10**) by the correspondence of its spectral properties (see experimental part) with those reported in the literature [9].

The formation of **10** from **9** can be formulated by the mechanism shown in *scheme 1*, which is analogous to that postulated [3] for the conversion of **1b** and **2b** to **3**. Since the product **10** is a known compound the presently observed reaction may be considered as further evidence for the reaction path previously postulated for the formation of **3**.

Scheme 1



This work was supported by the *Schweizerischer Nationalfonds zur Förderung der Wissenschaftlichen Forschung* and by *Sandoz* AG Basel. We thank Mr. *H. Hilpert* for technical assistance and Mr. *R. Hollenstein* for several of the NMR.-spectra and discussions on their interpretations.

Experimental Part

General. Melting points were taken in a sealed capillary tube in a heated oil bath apparatus; the temperatures are not corrected. The unqualified term 'dried' refers to the use of anhydrous magnesium sulfate. All compounds were analysed on thin layer chromatography (TLC.) plates prepared from *Macherey-Nagel* silica gel N–HR/UV_{254}.

The IR. spectra were measured on a *Perkin-Elmer* 21 or 421 spectrometer. They are recorded as follows: IR. (solvent or support): frequency in cm^{-1}, intensity as w = weak, m = medium and s = strong. The mass spectra were measured on a *CEC* 21-110 B or an *Atlas* CH-5 instrument. They are recorded as follows: MS. (energy in ev): molecular ions and/or fragment ions in *m/e* (intensities relative to base peak in %, interpretation when evident). Only the peaks with intensities higher than 5% are recorded. The electronic spectra were measured on a *Beckman*-spectrometer ACTA-111. They are recorded as follows: UV. (solvent): maxima and inflexions in nm (extinction ε). The proton resonance spectra were measured with an HA-100 instrument. They are recorded as follows: ^{1}H-NMR. (frequency and solvent): chemical shifts in ppm on the δ-scale (TMS internal = 0)/multiplicity with *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet and *m* = multiplet (splitting *J* in Hz), relative integration in pr units (interpretation). The protons are identified by the number of the carbon atoms to which they are attached; the numbering corresponds to that given on the formulae in the text. The spin-simulation spectrum was obtained with a *Varian* 620 L computer. The ^{13}C-NMR. spectra were measured on a *Varian* XL 100 instrument with *Fourier* transform. They are recorded as follows: ^{13}C-NMR. (frequency and solvent): chemical shifts in ppm on the δ-scale (TMS internal = 0) (interpretation). The chemical shifts are obtained from proton-noise decoupled spectra.

Bicyclo[4.1.0]hept-3-ene-2,5-dione-mono(ethylene)acetal (**6**), m.p. 32–35°, was prepared from cyclohexa-1,4-dione by the described method [2].

Homo-p-quinone (**4**, *Bicyclo[4.1.0]hept-3-ene-2,5-dione*). To a solution of 1.02 g (6.15 mmol) of **6** in 10 ml acetone was added 10 ml of 0.1 N hydrochloric acid and the resulting solution was allowed to stand for 8 h at room temp. The solution was concentrated under reduced pressure to 10 ml, diluted with 200 ml water and the product was extracted with chloroform. The extracts were washed twice with water, dried and evaporated to leave 0.66 g (88%) of *homo-p-quinone* (**4**) as a yellow solid, m.p. 42–48° which was shown to be pure by TLC. Sublimation at 0.2 Torr gave pale yellow needles, m.p. 47–9.5°. – IR. ($CHCl_3$): 1748 m; 1685 s; 1680 s; 1645 w; 1610 m; 1353 s; 1340 m; 1303 s; 1135 m; 1028 s; 1008 m; 938 m; 893 s; 835 m. – IR. (KBr): 3100 w; 1665 s. – MS. (70 eV): 122 (19, M^+), 94 (15, $M^+ - CO$), 68 (31), 66 (67, $M^+ - 2\times CO$), 65 (19), 55 (11), 54 (20, $M^+ - 2\times CO - CH_2$), 53 (14), 51 (6), 50 (8), 42 (18), 41 (5), 40 (58), 39 (100), 38 (28), 37 (15). – UV. (EtOH): Max. 347 (180); Max. 227 (9650). – ^{1}H-NMR. (100 MHz, $CDCl_3$ and spin-simulation): δ = 6.43/A_2 part of A_2M_2XY system (sum of *J* values = 1.5), 2 pr (2× =CH); 2.56/M_2 part of A_2M_2XY system (*J* = 0.75 & 5.8 & 8), 2 pr (2× CH); 1.73/*X* part of A_2M_2XY system (*J* = 5 & 8), 1 pr (H(*exo*)–CH_2); 1.67/*Y* part of A_2M_2XY system (*J* = 5 & 5.8), 1 pr (H(*endo*)–CH_2). – Spin-decoupling experiments: Irradiation at δ = 6.43 ppm (2× =CH) converted the signal at δ = 2.56 ppm (2× CH) to *d* × *d* (*J* = 5.8 & 8). – ^{13}C-NMR. (25.2 MHz, $CDCl_3$): δ = 195.0 (2× C=O); 137.0 (2× =CH); 27.5 (2× CH); 19.6 (CH_2).

$C_7H_6O_2$ (122.12) Calc. C 68.84 H 4.95% Found C 69.12 H 4.64%

^{13}C-NMR. (25.2 MHz, $CDCl_3$) of syn-(**1a**) *and* anti-(**2a**)*-bis-homo-*p*-quinones. syn*-Bis-homo-*p*-quinone (**1a**): δ = 200.6 (2× C=O); 29.6 (2× CH); 15.8 (2× CH_2). *anti*-Bis-homo-*p*-quinone (**2a**): δ = 200.6 (2× C=O); 23.8 (2× CH); 12.3 (2× CH_2).

*Bis-*p*-toluene-sulfonyl-hydrazone of homo-*p*-quinone* (**9**). A solution of 0.30 g (2.46 mmol) homo-*p*-quinone (**4**) and 0.92 g (4.95 mmol) of *p*-toluene-sulfonyl-hydrazide in 12 ml ethanol was heated under reflux. After 5 min the product started to fall out of solution and after 60 min the precipitate was collected and washed with 200 ml ethanol. Due to its insolubility the *homo-p-quinone-bis-*p*-toluene-sulfonyl-hydrazone* (**9**) (0.91 g) could not be recrystallised; the yellow powder was dried under vacuum at 80°. During the m.p. determination, decomposition was observed to start at ~185° and to continue until blackening occurred; at 218° the sample suddenly effervesced. – IR. (KBr): 3225 w; 1660 w; 1600 m; 1400 m; 1343 s; 1180 m; 1165 s; 1065 s; 935 m; 905 m; 820 m; 810 m; 748 m; 665 s.

$C_{21}H_{22}O_4N_4S_2$	Calc.	C 54.98	H 4.84	N 12.22	S 13.98%
(458.57)	Found	,, 55.08	,, 5.12	,, 11.94	,, 13.79%

*Decomposition of bis-*p*-toluene-sulfonyl-hydrazone of homo-*p*-quinone* (**9**). *1,7a-Diaza-7a*H*-indene* (**10**, *pyrazolo(2,3a)pyridine*). A mixture of 1.00 g (2.18 mmol) bis-*p*-toluene-sulfonyl-hydrazone of homo-*p*-quinone (**9**) and 15 ml diglyme was heated with 0.60 g (11.1 mmol) anhy-

drous sodium methoxide under reflux (oil bath 180°) for 16 h. After cooling, 400 ml water was added and the product was extracted with ether. The extracts were washed six times with aqueous sodium chloride, dried and evaporated to give an oily residue which was purified by prep. TLC. (silica gel, ether/hexane 1:1) and distillation to give 0.12 g (47%) of 1,7a-diaza-7a*H*-indene (**10**) as a colourless oil, bp. 95–98°/22 Torr. – IR. (Film): 1648 s; 1520 s; 1462 m; 1438 s; 1375 s; 1340 s; 1255 s; 1228 s; 1180 m; 1145 m; 1010 m; 920 m; 890 m; 765 s; 740 m. – MS. (70 ev): 118 (100, M^+), 91 (27), 78 (16), 65 (5), 64 (21), 63 (13), 51 (5), 39 (6). – UV. (C_6H_{12}): Max. 338 (510); 310 (1800); 288 (3390); 223 (8340); 221 (8280). Infl. 322 (1380); 300 (1820); 280 (3020). – ^{1}H-NMR. (100 MHz, $CDCl_3$): δ = 8.48/*d*×*d* with fine splitting (J = 1 & 7), 1 pr (H–C(7)); 7.96/*d* with fine splitting (J = 2), 1 pr (H–C(2)); 7.52/*d*×*d* with fine splitting (J = 1 & 9), 1 pr (H–C(4)); 7.06/*d*×*d*×*d* with fine splitting (J = 1 & 7 & 9), 1 pr (H–C(5)); 6.72/*t*×*d* (J = 1.5 & 7), 1 pr (H–C(6)); 6.51/*d*×*d* (J = 1 & 2), 1 pr (H–C(3)). The blue-violet fluorescence in UV. light, the UV.- and the NMR.-spectra of this sample were in complete agreement with those already reported [9].

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142. Electronic States of 1,5-Cyclooctadiyne Radical Cation and of Related Systems: The Electronic Structure of *cis*-bent Carbon-Carbon Triple Bonds

by **Gerhard Bieri, Edgar Heilbronner, Else Kloster-Jensen**[1]**), Andreas Schmelzer** and **Jakob Wirz**

Physikalisch-chemisches Institut der Universität Basel, CH–4056 Basel
Klingelbergstrasse 80

Dedicated to Professor Pl. A. Plattner on his 70th birthday

(10. V. 74)

Summary. The photoelectron spectra of 1,5-cyclooctadiyne (**2**) and of 1,6-dithiacyclodeca-3,8-diyne (**3**) have been recorded. The first four (**2**) or six (**3**) PE. bands have been assigned as follows; in increasing order of ionization potentials:

[1]) Permanent address: Dept. of Chemistry, University of Oslo, Blindern, Norway.