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Abstract

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Chemistry

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CYCLOPENTENE-4-DIONE-1,3

In 1957 a brief communication appeared (^{1}), and in 1959 a more detailed description (^{2}), of the preparation of cyclopentene-4-dione-1,3 (I).

Since I is, as it were, the simplest analogue of indandione-1,3 (II), it seemed advisable to us to study its properties more closely. We slightly modified the above-mentioned procedure and developed a more convenient method for preparing I. By using silver chromate, which possesses both halogen-binding and oxidizing properties (^{3}), we succeeded in converting 3,5-dibromocyclopentene-1 directly into I. This yellow substance (m.p. 36–37°), extremely unstable toward alkaline agents, forms the normal dioxime (III), condenses with *n*-nitrobenzaldehyde to form IV, and on bromination gives V. Addition of bromine to the double bond could not be achieved. Under the action of alkalis, V readily splits off bromine and liberates iodine from KI. Catalytic hydrogenation in the presence of skeletal nickel converts I and V into cyclopentanedione-1,3 (^{4,5}).

(I) (II) (III) (IV) (V)

(VI) (VII) $X =$

In 1897 Wolff (^{6}) reported the preparation, from dibromolevulinic acid, of a compound to which he assigned structure V. We repeated this synthesis and found that the substance obtained by Wolff differs sharply from V and, judging from its properties and IR spectra (Table 1), does not have structure V but, possibly, has a lactone structure (^{7,8}).

We were unable to acylate or alkylate I, but condensation of I with xanthydrol proceeds readily, which is characteristic of β-diketones (^{9,10}), including indandiones-1,3 ($^{11-13}$). As a result of xanthylation of I with an equimolar amount of xanthydrol, both the monoxanthyl derivative (VI) and the dixanthyl derivative (VII) are formed. Under the action of bromine on VI and VII, the xanthyl groups are readily eliminated.

IR spectra of I were recorded in CH_2ClCH_2Cl and CCl_4 (Table 1). In both cases bands of the stretching vibrations of the carbonyl groups were found at 1715 cm^{-1} and 1718 cm^{-1}, which lie within the range of cyclopentene-2-one-1-carbonyl frequencies ($^{14-17}$). The increase in the carbonyl frequency on going from CH_2ClCH_2Cl to the less polar CCl_4 is in accordance with the general rule (18,19). The second band at 1752 and 1751 cm^{-1} is of low intensity and arises from interaction of the vibrations of both carbonyl groups (20). The band of stretching vibra—

Table 1

IR spectra of cyclopentene-4-dione-1,3 and its derivatives

Compound	State of substance	$-NO_2$	phenyl ring	>C=C< and >C=N–	>C=O	Region 3000–3700 cm^{-1}
I	Solid[1]	–	–	–[2]	1715 (98)1752 (38)	~3390(weak)
I	In CH_2ClCH_2Cl8.3· 10^{-2} M	–	–	–	1748 (64)	Not recorded[4]
I	In CCl_4[3]2.3· 10^{-2} M	–	–	–	1718 (92)1751 (19)	–[4],[5]
I	In CCl_4[3]~4· 10^{-2} M	–	–	–	1718 (92)1751 (19)	–[4],[5]
VI	Solid[7]	–	1576 (51)1603 (36)	–	1695 (93)	–
VI	In CH_2ClCH_2Cl[7]4· 10^{-2} M	–	1580 (29)1605 (25)	–	1712 (79)	–
VII	Solid[7]	–	1577 (44)1599 (37)	–	1695 (84)	–
VII	In CH_2ClCH_2Cl[7]~4· 10^{-2} M	–	1580 (29)1602 (31)	–	1704 (67)	–
Xanthydrol	Solid[7]	–	1579 (37)1608 (40)	–	–	Not recorded
III	Solid[6]	–	–	1637 (74)	–	~3090 (50)~3180 (55)~3374 (40)

Compound	State of substance	$-NO_2$	phenyl ring	$>C=C<$ and $>C=N-$	$>C=O$	Region 3000–3700 cm^{-1}
IV	Solid	1509 (77)	1595 (72)	1622 (77)	1689 (90)1736 (43)	Not recorded
2-*n*-nitrobenzalindandione-1,3	Solid	1519 (84)	1593 (69)	1628 (65)	1692 (93)1734 (50)	Not recorded
V	Solid[6]	–	–	~1559 (62)1616 (68)~1643 (37) sh.	1692 (28)1731 (48)	–
V	In CH_2ClCH_2Cl[6] $3 \cdot 10^{-2}$ M	–	–	~1559 (62)1616 (68)~1643 (37) sh.	1692 (28)1731 (48)	Not recorded
Wolf bromination product (6)	Solid[6,7]	–	–	1548 (86)	1767 (96)1789 (87)	~3140(medium)

[1] Recorded in the interval 1490–1820 cm^{-1}. Almost monotonic absorption was observed up to ~1760 cm^{-1}, as a result of which it is impossible to distinguish individual bands. [2] On a double-beam IKS-14 instrument, in the spectrum of a concentrated solution of I, weak bands at 1646 and 1565 cm^{-1} were found. [3] Because of absorption by the solvent, the interval 1600–1820 cm^{-1} is accessible. [4] Recorded in the interval 2500–3700 cm^{-1}. [5] At an even higher concentration of I a weak band appears at ~3400 cm^{-1}. [6] Recorded in the interval 1490–1830 cm^{-1}. [7] Spectra were obtained with a less sensitive instrument than in the other cases, and the disappearance of some weak bands is possible.

Note. All spectra were recorded on a single-beam IKS-12 instrument, with a NaCl prism, in most cases in the intervals 1490–1760 cm^{-1} and 3000–3700 cm^{-1}. The spectra of solid substances were recorded in paraffin oil. Band positions are given in reciprocal centimeters; in parentheses are their intensities in absorption percent.

The stretching vibration of the double bond was not detected in the spectrum of I, probably because of the high symmetry of the molecule with respect to the double bond, which makes the vibrations of low intensity. Only in concentrated CH_2ClCH_2Cl solutions, using a double-beam instrument, were two weak bands found at 1646 and 1565 cm^{-1}. The latter of them probably belongs to vibrations of the double bond ([21]-[24]).

The IR spectrum of the dioxime (III) excludes the possibility of addition of NH_2OH at the double bond ([25]). In the spectrum of solid III the carbonyl frequency is absent; only a band at 1637 cm^{-1} is found, which may be assigned to the conjugated C=N bond. In the IR spectrum of solid IV two carbonyl bands are observed, 1689 cm^{-1} (strong) and 1736 cm^{-1} (weak), a band of vibrations of the conjugated double bond at 1622 cm^{-1} ([20],[26]), a band at 1595 cm^{-1}, assigned to the aromatic ring ([20],[26]-[28]), and a band at 1509 cm^{-1}, apparently belonging to antisymmetric vibrations of the nitro group ([29],[30]). The spectra of the structurally similar 2-benzal- ([20]) and 2-*n*-nitrobenzalindandiones-1,3 are analogous. In the spectrum of IV, bonds

with additional conjugation, the carbonyl frequency is lowered by 6 cm^{-1} in comparison with the 2-substituted derivatives, for example, VI and VII ([16,20,26]).

The IR spectrum of solid V shows strongly lowered frequencies of the vibrations of the carbonyl group and of the double bond, but in CH_2ClCH_2Cl normal values are observed. The band at 1731 cm^{-1}, assigned to the carbonyl groups of V, is raised by 16 cm^{-1} in comparison with the carbonyl frequency in I. It is of interest that this difference in the carbonyl frequencies of I and V is smaller than the values found for analogous compounds of the cyclopentanone and cyclopentenone systems ([31–33,15]). In the spectrum of V, unlike I, there is also an intense band at 1616 cm^{-1}, assigned to vibrations of the double bond. The reason for the appearance of such high intensity is not clear. The origin of another band, of lower intensity, in the form of a shoulder at 1643 cm^{-1} is likewise unclear ([34]).

The IR spectra of VI and VII confirm their structure. In the solid state the carbonyl bands of both compounds are found at the same frequency: 1695 cm^{-1}. But in CH_2ClCH_2Cl they differ: 1712 cm^{-1} (VI) and 1704 cm^{-1} (VII). The small lowering of the frequency of VI, in comparison with the corresponding band in I (1715 cm^{-1}), is a normal phenomenon and is associated with the introduction of an additional alkyl substituent, which usually lowers the frequency of the carbonyl band ([35,36]). The comparatively low position of this frequency in VII is probably due to steric hindrance ([35,36]). In addition, in the spectra of VI and VII, both in the solid state and in solution, further bands associated with xanthyl groups are observed, since they also appear in the spectrum of xanthydrol.

Table 2

UV spectra of I

Solvent	K-band λ_{max}, mμ	K-band ε
Hexane	217.5	12220
C_2H_2OH (95%)	218.5	12280
Water	221.5	12900

In the literature, apart from ([1,2]), there are no data on the question of keto-enol equilibrium in cyclopentene-4-diones-1,3. On the basis of a study of their spectra, certain conclusions can be drawn. In the IR spectra of I, as well as of VI and VII, only normal unshifted carbonyl frequencies belonging to the diketo form were found. The band at ~ 1750 cm^{-1} also belongs to the diketo form. Other bands associated with a possible enol form were not detected. The weak band at 1646 cm^{-1}, found in the spectrum of a concentrated solution of I in CH_2ClCH_2Cl, cannot be ascribed to the enol form, since it may also arise in the case of dissociation of I or as an overtone (in the spectrum of solid I a strong band at 816 cm^{-1} was found).

The absence of the enol form is also confirmed by the spectra of I, VI, and VII in the region of the stretching vibrations of OH groups. In the spectra of VI and VII no bands are observed in this region, and the low-intensity band in the spectrum of I probably belongs to an overtone of the carbonyl frequency ([37]), since it is retained in CCl_4, where enolization of I is inconceivable. An analogous conclusion follows from the UV spectra of I, in which only one intense band at ~ 220 mμ, assigned to the K-band of the cyclopenten-2-one-1 system, was detected ([38,39]). The shift of this band as a function of solvent polarity corresponds to the general rule ([40,41]).

Consequently, the cyclopentene-4-dione-1,3 system is not tautomeric and is a new member of the series of non-enolized β-diketones, to which, evidently, the indandione-1,3 system also belongs.

Cyclopentene-4-dione-1,3 (I). To the mixture obtained by brominating 22.6 g of cyclopentadiene with 17.4 ml of bromine in hexane, 50 ml of acetone are added; with stirring, the solution is slowly added to a suspension of 150 g of silver chromate in 250 ml of 80% acetic acid at 28-30°, then a solution of 25 g of CrO_3 in 50 ml of 80% acetic acid is added at the same temperature, and the mixture is stirred until the temperature begins to fall. On the following day the precipitate of AgBr and Ag_2CrO_4 is separated and washed with acetone,

Water is added to the filtrate and it is extracted again with ether. The ethereal extract is concentrated in vacuo; ether is added to the dark residue, the mixture is filtered, and hexane is added to the filtrate. On strong cooling (below −50°), I crystallizes. After repeated crystallization from ether–hexane, the yield is 3.14 g (9.5%), m.p. 36–37°.

Dioxime (III). I + $NH_2OH \cdot HCl$ in an aqueous alcoholic solution at room temperature. White crystals (from alcohol + hexane), m.p. 243–245° (decomp.).

Found, %: N 22.33. $C_5H_6O_2N_2$. Calculated, %: N 22.22

Xanthylation of cyclopentene-4-dione-1,3.
0.12 g of I and 0.26 g of xanthydrol in 5 ml of a mixture of glacial acetic acid and alcohol (1:1) are left at room temperature. After 3–5 days the crystals are separated and boiled with alcohol. Yellow crystals VI precipitate from the filtrate, m.p. 191–192° (decomp.) (again from alcohol). Yield 0.16 g (44%).

Found, %: C 78.18; H 4.37
$C_{18}H_{12}O_3$. Calculated, %: C 78.25; H 4.38

The residue on the filter (0.05 g), after crystallization from acetic acid, gives yellow crystals VII, m.p. 241-242° (decomp.). When larger amounts of xanthydrol are used, VII is obtained chiefly. Xanthylation of VI also gives VII.

Found, %: C 81.47; H 4.66
$C_{31}H_{20}O_4$. Calculated, %: C 81.53; H 4.42

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