97. ¹³C-NMR. Spectra, Structure and Reactivity of Cyclic Oxocarbons[1])

by **Werner Städeli, Roger Hollenstein** and **Wolfgang von Philipsborn**

Institute of Organic Chemistry, University of Zurich, Rämistrasse 76, CH–8001 Zurich

In memory of the late Prof. *Hans Schmid*

(7. II. 77)

Summary

The structures of cyclic polyketones, their hydrates and reduction products were studied in different solvents by ¹³C-NMR. spectroscopy. In dimethylsulfoxide solution rhodizonic acid (**1**), croconic acid (**2**) and squaric acid (**3**) exhibit signal averaging. In anhydrous tetrahydrofuran **1** and **2** could be observed as non-dynamic species. The spontaneous reactions of dodecahydroxycyclohexane (**5**) and decahydroxycyclo-pentane ('leuconic acid') (**6**) and the sequence of formation of ring-contracted products were investigated. Key intermediates could be clearly identified which support the mechanism proposed earlier involving a benzylic acid type rearrangement followed by decarboxylation and subsequent redox reactions.

1. Introduction. – Rhodizonic acid (**1**) and croconic acid (**2**) are two well-known representatives of the class of oxocarbons prepared in the early nineteenth century. Their constitution, however, was elucidated much later. The analogous four- and three-membered compounds, squaric (**3**) and deltic acid (**4**), were synthesized only in recent years [2] [3]. Typical for these compounds is the enediol moiety and the varying number of vicinal carbonyl groups. In aqueous solution some of the carbonyl groups become hydrated and new compounds are formed. Rhodizonic acid dihydrate, for example, can be isolated as a crystalline solid (see section 2.1). Oxidation of the enediols **1**, **2** and **3** leads to another series of compounds formally represented by the structures **5**, **6** and **7**. The carbonyl groups, however, are fully hydrated in the crystalline state. In addition, water of crystallization may be present, as in the case of the 'oc-

Scheme 1

1	**2**	**3**	**4**
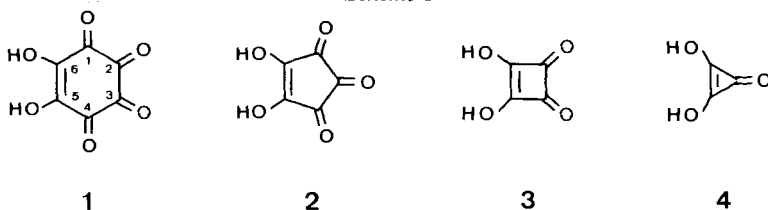
¹)   ¹³C-NMR. Spectroscopy, Part XVII; for Part XVI see [1].

Scheme 2

5   **6**   **7**
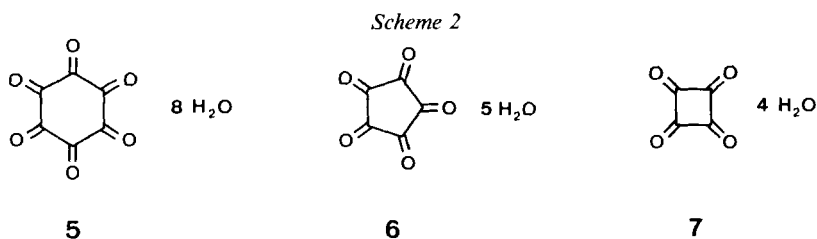
tahydrate' **5**. In solution, equilibria can be observed between the polyhydrates and partly dehydrated forms. For structural investigations of the solids, as well as in the case of the symmetrical dianions, e.g. 1^{2-}, IR. spectral data proved to be very informative. The dianions are also of interest from a theoretical point of view [4].

Scheme 3

1^{2-}
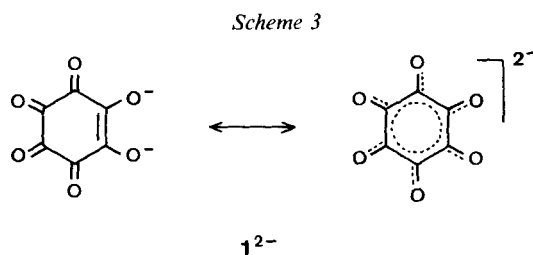
Several reviews have already been published on the synthesis and reactivity of oxocarbons [5]. However, the structures of the species present in solution, their spontaneous reactions and the sequence of the formation of new products have not yet been investigated in detail. ^{13}C-NMR. spectroscopy now offers an ideal tool to study such molecules, and our results are reported in the following.

2. Compounds and Spectra. – 2.1. *Rhodizonic acid* (1). Rhodizonic acid dihydrate is a well-known compound which finds several applications. Two different constitutions, **1a** [5c] and **8** [6], were suggested.

Scheme 4

1a   **8**
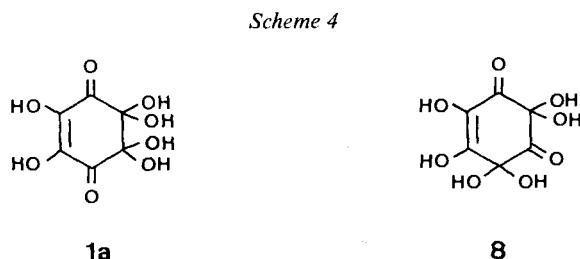
On the basis of the ^{13}C-NMR. spectra measured in different solvents (Table 1) only the symmetrical 1,4-diketonic structure **1a** can be considered.

Anhydrous, very hygroscopic rhodizonic acid (1) can be obtained from the dihydrate (**1a**) by extensive drying at 140° and 10^{-3} Torr. The ^{13}C-spectrum of 1 in very carefully dried THF-d_8 consists of three signals at $\delta = 175.0$ (C=O), 173.9 (C=O) and 148.9 ppm (C=C) (*Fig. 1*).

Table 1. ^{13}C chemical shifts [ppm,32°] of rhodizonic acid (1) and its hydrate (1a)

	Solvent	C(1), C(4)	C(2), C(3)	C(5), C(6)
1a	H_2O/D_2O	191.2	94.8	142.8
	DMSO-d_6	191.0	94.4	141.6
	THF-d_8	184.5	95.2	142.8
1	THF-d_8	173.9[b])	175.0[b])	148.9
	DMSO-d_6		165.6[a])	

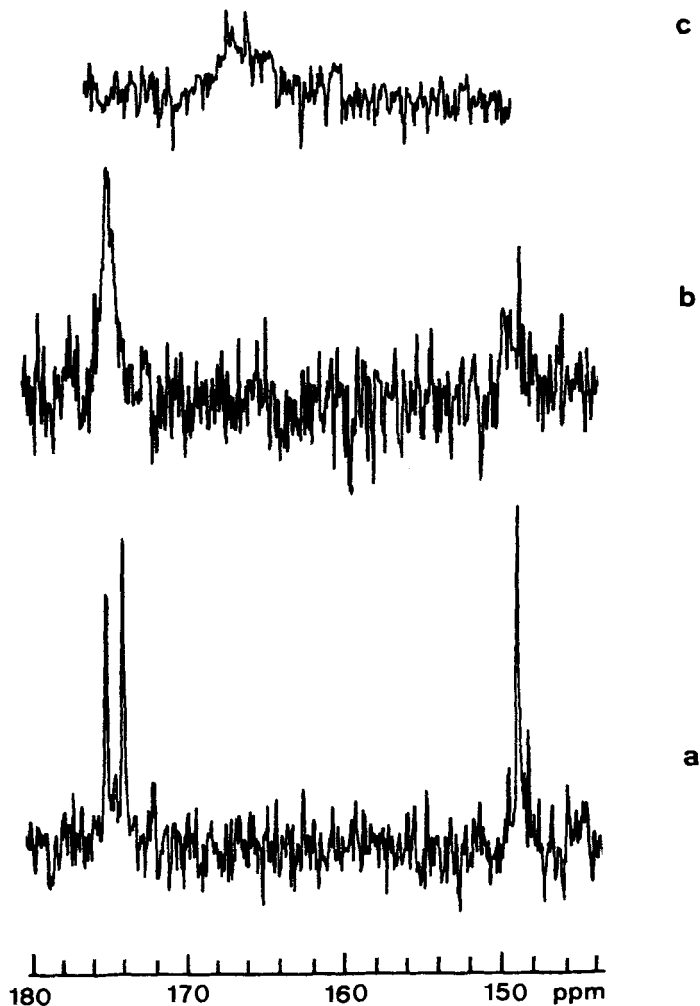[a]) Coalesced signal.   [b]) Tentative assignment.
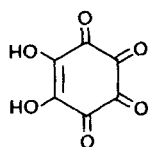
Fig. 1. ^{13}C-NMR. spectra of rhodizonic acid (1), a) in THF-d_8 at 30°, b) at 50°, c) in THF-d_8 with 5% DMSO at 30°

Upon addition of 5% dry DMSO to the THF solution the original spectrum disappears and one observes a very broad line at $\sim$ 166 ppm. This δ value agrees well with the averaged value (165.9 ppm) of the chemical shifts measured in THF solution.

In neat, dry DMSO the observed δ value is 165.6 ppm. At 60° this signal disappears and a new broad line occurs which is attributed to the coalesced signals of croconic
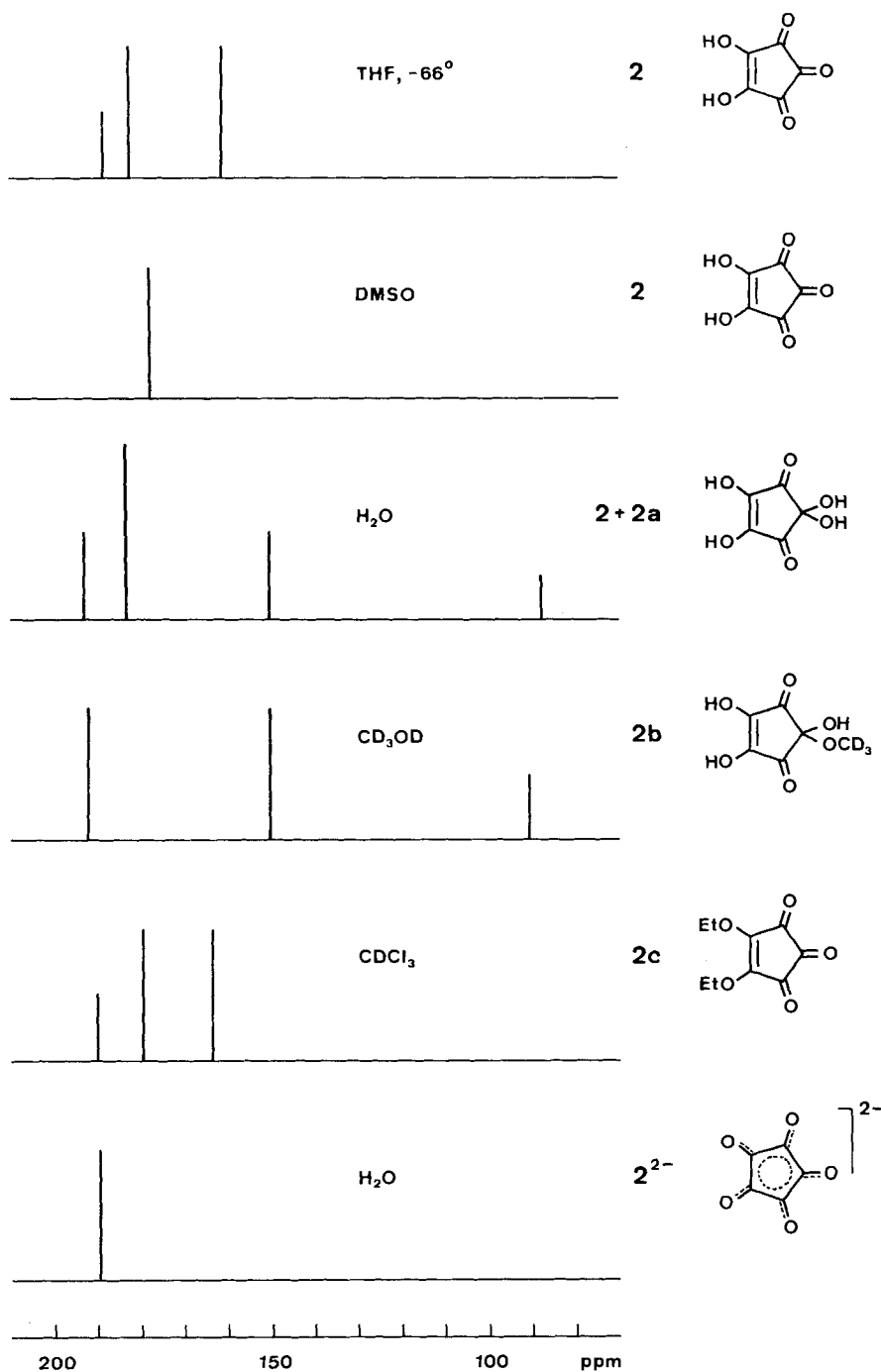
Fig. 2. *¹³C-NMR. spectra of croconic acid* (**2**) *and derivatives* (idealized peak heights). T = 30°, top spectrum at −66°

acid (**2**). This transformation is accompanied by a colour change of the solution from red to yellow. Since the three-line spectrum of rhodizonic acid could not be obtained in dry DMSO solution it may be concluded that the solvent not only has to be anhydrous to prevent hydration of the carbonyl groups but, in addition, must not be basic because intermolecular acid-base catalysed tautomerizations lead to an effective averaging of the carbon chemical shifts.

2.2 *Croconic acid* (**2**). At 30° and in THF-d$_8$ as solvent, croconic acid (**2**) shows two very broad ^{13}C-signals. Cooling to $-66°$ leads to the formation of the expected three lines at 188.4 ppm (C(2)), 182.4 ppm (C(1), C(3)) and 161.2 ppm (C(4), C(5)) (Fig. 2). The effect of fixation of the three individual shifts can also be achieved by transformation of the acidic OH groups into alkoxy groups. The corresponding resonance lines of diethyl croconate (**2c**) appear at 189.5, 179.3 and 163.4 ppm in CDCl$_3$ solution (Table 2). The chemical shift of **2** in DMSO solution is 177.9 ppm (averaged signal).

The ^{13}C-NMR. spectrum of croconic acid (**2**) has a lower coalescence temperature than that of rhodizonic acid (**1**) for which the following factors may be responsible:
1. $\sum_i (\delta_i - \bar{\delta})$ is larger for **1** (68.2 ppm) than for **2** (55.7 ppm); δ_i corresponds to the chemical shift of an individual carbon atom at the slow exchange limit;
2. **1** requires interconversion of six, **2** of only five tautomeric forms in order to achieve complete averaging of all carbon atom positions. This difference results in different overall exchange rates k_{total} for the two compounds. In addition, the rate constants of the individual tautomerization steps which make up k_{total} may be influenced by a difference in the acid strength of **1** and **2**.

In aqueous solution of croconic acid (**2**) an equilibrium between the triketone and its monohydrate (**2a**) is established. The signal of the triketone which exhibits fast exchange of the carbon atom sites appears at 183.3 ppm whereas the hydrate shows a typical low-frequency signal at 87.9 ppm (C(OH)$_2$) and signals at 150.4 ppm (C(4), C(5)) and 193.2 ppm (C(1), C(3)) (Fig. 2). In methanolic solution the equilibrium is shifted totally towards the hemiacetal (**2b**) which gives three lines at very similar positions like the hydrate, *i.e.*, 90.7, 150.5 and 192.3 ppm.

Croconic acid shows a larger δ value for the averaged carbon atom positions in aqueous solution than in dimethylsulfoxide. This finding may be a consequence of increased dissociation of the acid in water leading to a significant participation of the

Table 2. ^{13}C *chemical shifts* [ppm, 32°] *of croconic acid* (**2**) *and derivatives*

	Solvent	C(1), C(3)	C(2)	C(4), C(5)
2	THF-d$_8$[a])	182.4	188.4	161.2
	DMSO-d$_6$		177.9[b])	
2a	H$_2$O/D$_2$O	193.2	87.9	150.4
2b	CD$_3$OD	192.3	90.7	150.5
2c	CDCl$_3$	179.3	189.5	163.4[c])

[a]) At $-66°$.
[b]) Coalesced signal.
[c]) Further signals for the CH$_2$ and CH$_3$ carbon atoms at 70.8 and 15.9 ppm respectively.

monoanion and, possibly, also of the dianion 2^{2-} in the tautomerization reactions. It is well known that, for example, deprotonation of a carboxyl group leads to a high-frequency shift in the carboxylate anion. Correspondingly, the signal of sodium croconate $(Na^+)_2(C_5O_5)^{2-}$ is observed at even higher δ values (189.3 ppm) than croconic acid in water (Fig. 2).

2.3 *Squaric acid* (3) *and deltic acid* (4). Squaric acid behaves similarly to 1 and 2. The averaged chemical shifts in DMSO and H_2O/D_2O are 189.5 and 195.3 ppm respectively. We were not successful in obtaining the ^{13}C-NMR. spectrum of the non-dynamic squaric acid (slow-exchange limit) for which two resonance lines would be expected. Since 3 is practically insoluble in THF the selection of a suitable solvent presented a problem. $CD_3OH/DMSO$ proved useful for temperatures as low as $-30°$. Nevertheless, the qualitative statement may be made that the coalescence point of 3 must be at a lower temperature than of 1 and 2. Dimethyl squarate can easily be obtained and it exhibits ^{13}C-lines at 189.4 and 184.7 ppm ($CDCl_3$) for the ring carbon atoms and a methoxy signal at 61.1 ppm. From these data an estimate for the individual chemical shifts of squaric acid can be made (*cf.* the δ_C values of 2 and 2c). The rather small difference of *ca.* 8 ppm[2]) between the two chemical shifts suggests a low coalescence temperature, particularly since the pK_a values for the first dissociation of squaric acid and croconic acid are comparable ($pK_a^1 \sim 0.5$). In this context a paper should be mentioned (*Reetz et al.* [7]) in which a fast isomerization of bis(trimethyl-silyl) squarate at $T > 80°$ is reported. The process is intermolecular and results in an averaging of the two types of ring carbon atoms.

The synthesis and some properties of deltic acid (4), its dianion 4^{2-} and of the diethyl and bis(trimethylsilyl) esters were recently described [3] [8] [9a]. There is a notable low-frequency shift for the two ring carbon atoms of diethyl deltate (137.4 ppm ($C=O$), 128.7 ppm ($C=C$) [9b]) in comparison with the corresponding values of dimethyl squarate. A similar effect is observed for the respective dianions 4^{2-} and 3^{2-} (see section 2.4).

2.4. *Dianions.* The δ values of the dianions of rhodizonic, croconic, squaric and deltic acid together with the averaged chemical shifts of the parent oxocarbon acids are given in Table 3.

The observed shifts of the dianions appear to depend somewhat upon substrate concentration as indicated by corresponding studies on different alkali salts of 1^{2-}. The dianions as well as the acids show increased shielding of the carbon atoms with increasing ring size. The smallest member 4^{2-} of the series drops out because of the three-membered ring effect and is not considered any further. The observed trend in the chemical shifts of the dianions suggests that the carbon-oxygen bonds become progressively less polarized in going from squarate to rhodizonate. In agreement with this reasoning the shortest C–O bond length (1.213 Å) was measured for rubidium rhodizonate [10]. For comparison, ammonium croconate [11] and potassium squarate [12] gave values of 1.262 and 1.259 Å respectively. Electron density calculations (HMO, PPP) on the oxocarbon acids [13] also indicate a higher carbonyl polarization in the lower members of the series. Similar calculations were performed on the

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[2])   Based upon the following assignment in the spectrum of dimethyl squarate: $\delta(C=O) = 189.4$ ppm, $\delta(=C(OMe)) = 184.7$ ppm.

Table 3. ^{13}C chemical shifts of the dianions (sodium salts) [ppm, H_2O/D_2O, 32°] and averaged values of the corresponding acids (in parentheses)

	1^{2-}	2^{2-}	3^{2-}	4^{2-}
δ_C	174.2 (165.9)[a]	189.3 (175.1)[a]	204.2 (186.0)[b]	140.0[c]
$\Delta\delta_C$	8.3	14.2	18.2	

[a]   Calculated from the spectra in THF at the slow exchange limit.
[b]   Estimated value by comparison with **2** and **2c**.
[c]   Lithium salt, from [3 b].

dianions [4], however, there appears to be no meaningful correlation with our ^{13}C chemical shifts. The chemical shift changes between acid and dianion ($\Delta\delta_C$) have the same direction as observed for the quaternary carbon atoms of pyrocatechol and its dianion. This high-frequency shift in the dianions may originate from the transformation of the enediol carbon atoms into carbonyl-type carbon atoms. In addition, it appears that the higher negative charge on the oxygen atoms in the squarate ion [4] creates more positive charge on the ring carbon atoms as compared to the higher members of the series. This may explain the variation in the $\Delta\delta_C$ values (Table 3).

3. Reactivity of the Hydrated Oxocarbons. – The instability observed for rhodizonic acid as well as for its alkali salts in water, *i.e.* their transformation into croconic acid and croconate ion respectively, is also typical for the polyhydrates of the cyclic polyketones **5**, **6** and **7**. We have found that the reactions of these compounds can be followed conveniently by ^{13}C-NMR. spectroscopy at room temperature in dimethylsulfoxide as solvent.

3.1. *Dodecahydroxycyclohexane* ('Octahydrate') (**5**). When the octahydrate **5** is dissolved in DMSO a yellow colour appears which is not stable. The ^{13}C-NMR. spectrum does not show one resonance line for the six equivalent $>C(OH)_2$ carbon atoms as expected for the hydrate **5** but instead, three lines which can be assigned to rhodizonic acid dihydrate (**1a**). The same transformation (**5** → **1** → **1a**) occurs when **5** is dried in high-vacuum at 78° and the rhodizonic acid formed under these conditions (yellow-orange solid) is dissolved in aqueous THF or aqueous DMSO. As already reported by *Eistert et al.* [14] prolonged heating of an ethanolic solution of **5** also yielded rhodizonic acid.

A kind of benzilic acid rearrangement followed by decarboxylation and a redox reaction between the ring-contracted product and remaining educt were proposed as a possible mechanism for the above transformation [14] [15].

Leuconic acid (**6**) formed as the second product in this reaction sequence is not stable under our conditions (DMSO) and can react further by the same mechanism (see section 3.2). In addition, the formation of tetrahydroxy-*p*-benzoquinone (**9**) as reduction product of **1a** is observed, the ^{13}C resonance lines of which appear as relatively broad signals at 180.6 and 134.4 ppm due to proton transfer (tautomerization). An aqueous solution of **5** is also unstable. In some experiments it proved possible to observe the expected single line at 95.7 ppm typical for the carbon atom of a hydrated carbonyl group. The variety of lines which appeared after some time could not be assigned.

Scheme 5
(Substituents not specified are always hydroxyl groups)
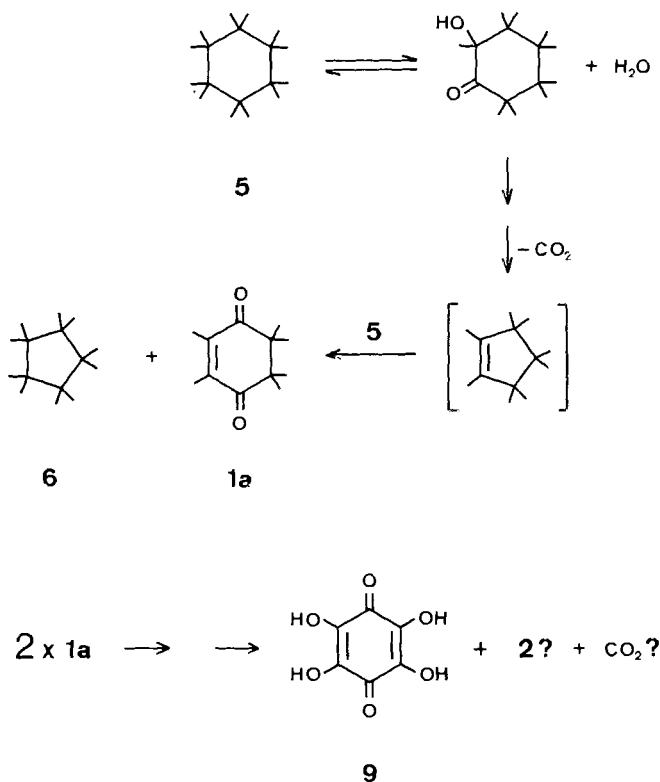
It should be mentioned that the number of products observed in the ^{13}C-NMR. spectra depends very much on the water content of the solvent used. When, for instance, **5** was dissolved at 50° in DMSO/H$_2$O 9:1 (v/v), the only observable product was **1a**.

3.2. *Leuconic acid pentahydrate* (**6**). The ^{13}C-NMR. spectrum of **6** in aqueous solution (H$_2$O/D$_2$O) can be best explained with the assumption of an equilibrium between the pentahydrate **6** and the tetrahydrate (monoketone) **10**.

The spectrum of the mixture consists of one line at 208.0 ppm (C=O) and of three lines at 96.9, 95.9 and 93.0 ppm for the three types of non-equivalent $>$C(OH)$_2$ carbon atoms. Also in this case these lines disappear with time and new, not identified resonances appear. If **6** is dissolved in dry DMSO an intense but transitory red colour appears and after a while the solution turns orange and, finally, yellow. The concomittant changes of the UV. spectrum can be read from Table 4. The absorptions at 388 and 327 nm can be assigned to croconic acid (**2**), the maximum at 270 nm to squaric acid (**3**). The absorption maximum at 462 nm agrees with the UV. spectrum of an α-diketone. The transitory red colour and an additional very weak maximum at 620 nm observed at the same time indicate the presence of the vicinal triketone **13** [16].

Scheme 6

6   **10**
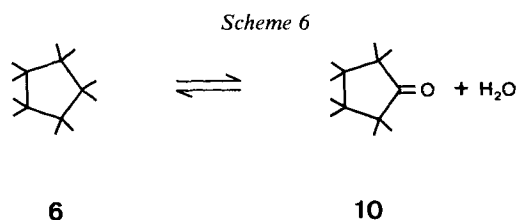
In the ^{13}C-NMR. spectrum there are, at the beginning, three intense lines at 204.3, 94.9 and 87.0 ppm and, depending upon substrate concentration and the time of measurement, three additional lines of lower intensity at 94.8, 92.1 and 91.8 ppm. All these resonance lines decrease with time and new signals appear at 179.1 ppm and

Table 4. *Time dependence of the UV. spectrum* ($E = -\log I/I_0$) *of a solution of* **6** *in DMSO* ($c = 2.33 \cdot 10^{-4}$)

| Time	E_{462}	E_{388}	E_{327}	E_{270}
0	0.089			
2.5 h	0.177		0.048	
8 h	0.244		0.154	0.241
23 h	0.279	0.189	0.280	0.253
2 days	0.291	0.233	0.357	0.260
3 days	0.297	0.258	0.399	0.270
4 days	0.299	0.274	0.427	0.274
5 days	0.295	0.290	0.452	0.269
9 days	0.275	0.301	0.476	0.258
13 days	0.262	0.306	0.484	0.252
28 days	0.194	0.300	0.486	0.209
39 days	0.157	0.301	0.485	0.188
56 days	0.118	0.299	0.482	

at 192.6, 148.8 and 88.5 ppm. The first of these signals originates from croconic acid (**2**) which is dynamic in DMSO solution (see section 2.2), whereas the other lines are assigned to its monohydrate **2a** (*cf.* Fig. 2). When the reaction proceeds new lines due to the formation of squaric acid (**3**) and octahydroxycyclobutane (**7**) (96.9 ppm) can be identified with certainty. Hence, the results from the ^{13}C-NMR. study and the UV. spectra are consistent. In analogy to the mode of reaction of the octahydrate **5** the following reaction scheme can be proposed. In a *first* step (dehydration reactions) a mixture of ketones is formed, the water content of the solvent increases and an
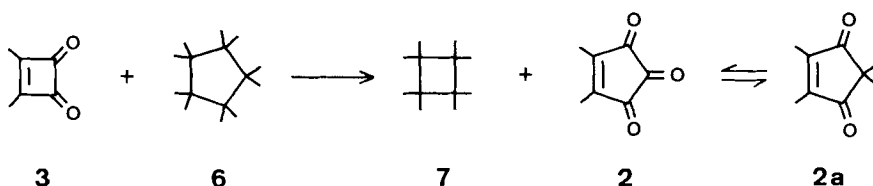
Scheme 7

6   **10**   **11**   **12**   **13**
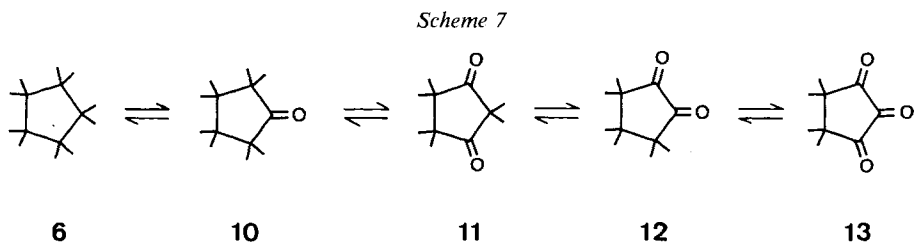
equilibrium between different species is established. On the basis of the initial ^{13}C-NMR spectrum the hexahydroxy-β-diketone **11** predominates.

The *second* step constitutes the benzilic acid rearrangement followed by decarboxylation leading to the ring-contracted product squaric acid (**3**).

Scheme 8

11   3

Scheme 9

3   6   7   2   2a
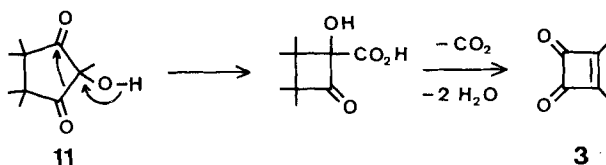
In the *third* step squaric acid reacts with the educt **6** in a redox reaction to form croconic acid (**2**), partly in form of its hydrate **2a**, and octahydroxycyclobutane (**7**).

The yield of croconic acid (**2**) was 9%, the theoretical maximum according to the above scheme being 50 mol percent. When an excess of squaric acid was added at the beginning of the reaction the yield of **2** could be increased to 24%. Assignment of the individual ^{13}C resonance lines has been achieved in most cases by addition of the corresponding compounds to the reacting solution and re-recording of the spectra.

Experimental Part

^{13}C-NMR. spectra were measured on a *Varian* XL-100-12 FT instrument. Typical pulse parameters involved a 25° pulse angle and pulse delays up to 1 s at an acquisition time of 0.7 s. In DMSO-d_6 and THF-d_8, TMS served as an internal standard, for H_2O/D_2O solutions dioxane was used. The conversion of the chemical shifts to TMS is given by $\delta_C(TMS) = \delta_C(dioxane) + 67.6$ ppm. UV. spectra were recorded on a *Beckman Acta III* instrument.

The solvents were dried carefully and the water contents thereafter were 0.1% and 0.2% for DMSO-d_6 and THF-d_8 respectively. DMSO-d_6 was stored in a stoppered flask over activated molecular sieves (*Union Carbide* Typ 4 Å, 4×8 mesh balls) for at least 24 h. Activation was achieved by heating in a round-bottom flask at 300–350° in high vacuum during 5 h. 1.5 ml THF-d_8 was treated with LiAlH$_4$ in a 5 ml round-bottom flask. The solvent was then distilled into the NMR. tube used for measurement.

Rhodizonic acid dihydrate (**1a**) *and rhodizonic acid potassium salt* were purchased in analytical purity from *Fluka AG*, Buchs SG.

Rhodizonic acid (**1**) was obtained from its dihydrate by drying in a round-bottom flask at 140° and 10^{-3} Torr for 3 h. Sublimation of **1** was not possible [17]. Dehydration was indicated by elemental analysis.

C$_6$H$_2$O$_6$ (170.08)   Calc. C 42.37 H 1.19%   Found C 41.99 H 1.47%

Alkali salts of rhodizonic acid. The lithium and sodium salts of **1** were obtained from the potassium salt by cation exchange. 15 ml of resin (*Dowex 50*, H^+ form) were loaded with a 2 N aqueous solution of the appropriate alkali chloride (pH 7–8), and 0.4 g of rhodizonic acid potassium salt in 250 ml of water were passed through the column (0.4 ml/min). The resulting solution was evaporated to dryness at 30°.

$C_6O_6Li_2$ (181.94)   Calc. C 39.61%   Found C 39.42%
$C_6O_6Na_2$ (214.06)   Calc. C 33.66%   Found C 33.81%

Tetrahydroxy-p-benzoquinone (**9**) was purchased in analytical purity from *Fluka AG*, Buchs SG.

Croconic acid (**2**), *croconic acid sodium salt and diethyl croconate* (**2c**). The preparation of croconic acid (**2**), its sodium salt (**2²⁻**) and of diethyl croconate (**2c**) followed the reaction schemes as worked out by *Sager et al.* [18] and *Malachowsky & Prebendowsky* [19]. The conversion of croconic acid barium salt to the free acid (**2**) has been changed with respect to *Sager's* original procedure. The barium salt was heated with exactly 1 mol-equiv. of dilute sulfuric acid. The $BaSO_4$ formed was filtered off, the filtrate evaporated to dryness at 50°. The yellow residue was boiled in THF with charcoal. After separating from the charcoal, the clear solution was then evaporated at 40° until crystallization began. The crystals were collected and washed with pure, cold diethyl ether. An analytical sample was recrystallized from THF/ether. By this procedure croconic acid monohydrate was obtained.

$C_5H_4O_6$ (160.09)   Calc. C 37.51   H 2.52%   Found C 37.76   H 2.55%

To obtain anhydrous **2**, the hydrate was dried at 100° and 10^{-3} Torr for 3 h.

Squaric acid (**3**) was purchased from *Fluka AG*, Buchs SG.

Squaric acid sodium salt was obtained by treatment of **3** with 2 mol-equiv. of dilute NaOH aq.

Dimethyl squarate (**3c**) was obtained according to the procedure given by *Cohen & Cohen* [20].

The polyhydrated species, 'octahydrate' **5**, leuconic acid (pentahydrate) (**6**) and octahydroxy-cyclobutane (**7**) were obtained by nitric acid oxydation of tetrahydroxy-*p*-benzoquinone (**9**), croconic acid (**2**) and squaric acid (**3**) respectively [18].

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