200. ^{17}O-NMR Spectra of Cyclopropenones and Tropone. Oxygen Exchange with Water

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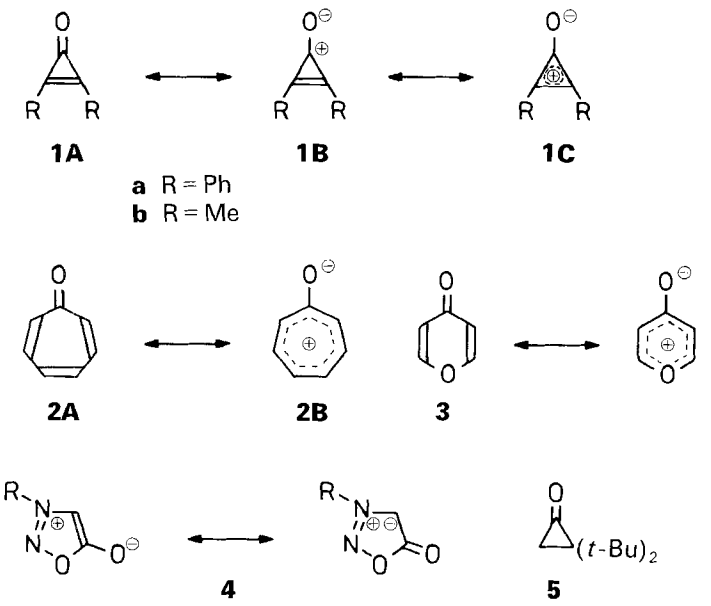
Whereas tropone (**2**) and a cyclopropanone **5** show rather normal ketone signals in their ^{17}O-NMR spectra, the two cyclopropenones **1a**, and **1b** exhibit exceptionally high shielding, indicating a structure closer to a $-O^-$ formula than to a ketone. For comparison, an enolate and several phenolates have been measured. In order to test the ketonic character, the nucleophilic addition of water was determined by the rate of isotopic O-exchange between ketone and water; **2** exchanged *ca.* 20 times slower than acetophenone, whereas **1a** reacted very much more slowly.

Introduction. – Cyclopropenones **1** [1] are quite stable compounds, in spite of their high ring strain (estimated at 67 kcal/mol [2]) and in contrast to the less unsaturated cyclopropanones and cyclopropenes; this has been attributed to resonance stabilisation by polar formulae **1B** and **1C** of which **1C** represents a pseudoaromatic *Hückel* $(2n+2)$ system ($n = 0$; see *Scheme*). The extent of aromaticity of **1**, however, is still controversial.

Scheme



On the basis of the relatively high dipole moment (4.80) and of an analysis of the IR spectra (in which, as a consequence of intense coupling, the normal order of C=C and C=O vibrations is inversed), the contribution of the aromatic form has been evaluated to *ca.* 30% only [3]. Thermochemical measurements point to a 'significant aromatic stabilisation' of *ca.* 16 kcal/mol, admitting the strain energy of 67 kcal/mol [2]. PE measurements (combined with calculations) gave a similar result [4]. On the other hand, ^{1}H-NMR (δ_H 9.1 ppm for **1** with R=H [5]) and ^{13}C-NMR data (δ_{CO} 155 ppm, δ_{CC} 160 ppm [6][7]) point to a situation intermediate between a (pseudo)aromatic cyclopropenylium ion (δ_H 11.1 ppm [8]; δ_C 177 ppm [9]) and a non-aromatic cyclopropene (δ_H 7.5 ppm [10]; δ_{CC} 108.7 ppm [11]), *i.e.* incomplete delocalisation of the π electrons. Furthermore, *Breslow et al.* [6][12], measuring the magnetic susceptibility anisotropy, found that the diamagnetic ring current in **1** is small, not bigger than in cyclopropene. Structure determination by microwave spectra [6] and X-ray analysis [13] have been interpreted as supporting the absence of resonance contributions (see, however, [14]). There have been, of course, numerous calculations on different levels, some of which have been interpreted in terms of resonance, while in others the stabilisation is attributed to a generalized interaction between π, p, and σ orbitals [15]. The most recent ones, made by *Schleyer* and coworkers [14], conclude to a resonance energy of 22 kcal/mol, which makes **1** a reasonably aromatic compound[1]). In this not quite conclusive situation, a further experimental test would not seem to be superfluous.

Tropone (**2**) is potentially the next-higher *Hückel* ($2n$+2) pseudoaromatic ketone. All experimental evidence, however, points to **2** being essentially an unsaturated ketone with little or no π delocalisation [16].

We have shown earlier [17] that the chemical-shift values in ^{17}O-NMR spectra are very clearly different for doubly (=O) and singly (–O–) bonded O-atoms and that both, but particularly the former, are very sensitive to electronic influences. Resonance effects are most important; *e.g.*, carbonyl O-atoms show signals at 580–550 ppm in aldehydes and ketones, at 350 ppm in carboxylic esters and at 300 ppm in carboxamides. Singly bonded O-atoms as in alcohols and ethers resonate at higher field, at *ca.* –50 to +100 ppm; carboxylate groups, intermediate between =O and –O–, show signals at *ca.* 250. As chemical-shift values can be easily determined to within ±0.5 ppm, the ^{17}O-NMR technique is a valuable tool to probe π-bond order or π-electron density around O-atoms, important factors influencing the paramagnetic screening at the O-atom [18].

A further test to evidence π delocalisation applicable to carbonyl compounds is their sensitivity towards attack by nucleophiles, the best investigated of which is H_2O addition in the reversible hydration [19] measured by the rate of isotopic exchange with water [20]:

$$\Big\{ > C=O + H_2{}^{17}O \rightleftarrows \Big\{ > C <^{^{17}OH}_{OH} \rightleftarrows \Big\{ > C={}^{17}O + H_2O$$

The rate of exchange is, of course, not a ground-state property, but involves an excited state; it may, however, furnish useful information. It has been shown, *e.g.*, that in *Leonard*'s medium sized ring ketones, the rate of exchange diminishes as transannular interactions modify the character of the carbonyl group [21]. With ^{17}O-NMR, one can follow the exchange reaction in an NMR tube.

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[1]) 'The difficulty lies, of course, in the selection of the proper reference compounds' [14].

Results and Discussion. – *^{17}O-NMR Data.* We have measured the ^{17}O-NMR chemical shifts of (mostly unenriched) diphenyl- and dimethylcyclopropenone (**1a** and **1b**, resp.) and of tropone (**2**; see *Table 1*) and compared these values with some reference compounds. The signal of **2** (516 ppm) is slightly upfield from that of other ketones (cyclic or acyclic, saturated or unsaturated, *cf. Table 1*), pointing to a small shielding by transfer of electrons towards the O-atom. This transfer is, however, smaller than *e.g.* that in 4*H*-pyran-4-one (**3**; δ_O 465 ppm [22]), confirming the ketonic character of **2**.

Table 1. *^{17}O-NMR Data of Ketones*

	δ [ppm]	Line width [Hz]
Diphenylcyclopropenone (**1a**)	248[a])	(680)
	246[b])	(500)
Dimethylcyclopropenone (**1b**)	233[a])	(140)
	234[b])	(190)
Tropone (**2**)	502[c])	(100)
[^{17}O]-**2**	516[d])	(80)
2,2-Di(*tert*-butyl)cyclopropanone (**5**)	524[e])	(240)
Acetone	569 [18]	
Acetophenone	554 [18]	
1-Penten-3-one	543 [18]	
Cyclohexenone	565 [22]	
4*H*-Pyran-4-one (**3**)	460 [22]	

[a]) In C_6D_6 at 66°. [b]) In CCl_4 at 66°. [c]) Pure liquid at 85°. [d]) Isotopically enriched, in CCl_4 at 78°. [e]) In $CDCl_3$ at 42°.

On the other hand, the cyclopropenones **1a** and **1b** (δ_O 248 and 233 ppm, resp.) show exceptionally high shielding of the carbonyl O-atom, even more than in esters (*ca.* 350 ppm) and amides (*ca.* 300 ppm). Only the exocyclic O-atom of sydnone (**4**; δ_O 232 ppm [23]) and related mesoionic compounds [24] which are currently formulated with $-O^-$ in the place of =O, shows a comparably high shielding. The pyridine-oxide signal appears at *ca.* 350 ppm [25][2]). The big difference between δ_O of **1** and normal ketones cannot be attributed to ordinary unsaturation: the values in *Table 1* show that it has only a slight influence. In order to test the influence of ring strain, we have measured the (relatively stable) 2,2-di(*tert*-butyl)cyclopropanone (**5**) [26] and found δ_O 524 ppm, close to an ordinary ketone. This small importance of the ring size has been found in other series too, *e.g.* cyclic ethers [27]. This means that special effects must be present in **1**.

The high shielding brings the δ_O for **1** not far from the range of two-bonded O-atoms (–O–), particularly those which are slightly deshielded by resonance effects: divinyl ether shows a δ_O of 129 ppm [25], the bridge O-atom of carboxylic esters of *ca.* 160 ppm [17], and the ring O-atom of **3** of 174 ppm [22]. As a closer model for comparison with **1C**, the phenolates and enolates would be interesting (*Table 2*); the δ_O of phenolate was found at 158 ppm, those of *o*-, *m*-, and *p*-nitrophenolate at 213, 166, and 210 ppm, resp. The Li-enolate of propiophenone, Ph–C(O^-)=CHMe Li^+, showed δ_O at 137 ppm, a value not far from those (100–120 ppm) for some (H-bonded) enols [28]. It is interesting to note

[2]) Taking into account the deshielding influence of the N-atom, estimated at *ca.* 100 ppm [24], these N^+-O^- compounds arrive at a δ_O corresponding to that of cyclopropenone.

Table 2. *^{17}O-NMR Data of Hydroxy Compounds and their Anions*

	Hydroxy compound δ [ppm]	Corresponding anion δ [ppm]
MeCOOH	254 [17]	282 [30]
PhCOOH	250 [31]	262 [32]; 264 (170[a]))[b])
PhOH	79 [33]	158 (170[a]))[b])
o-NO_2-C_6H_4-OH	87 [33]	213 (230[a]))[b])
m-NO_2-C_6H_4-OH		166 (290[a]))[b])
p-NO_2-C_6H_4-OH		210 [32]
Me-C(OH)=CHCOOEt	124 [28]	
Ph-C(OH)=CHCOOEt	109 [28]	
Ph-C($^{17}O^-$)=CHMe		113 (3700)[c]); 137 (3000)[d])

[a]) Line width in Hz.
[b]) Measured at 85° in H_2O depleted of ^{17}O and ^{18}O.
[c]) In hexane at −50° (*R. Hunma*).
[d]) In THF at −50° (*R. Hunma*).

that, in general, the deshielding effect on going from an acid to its conjugate base is small (for −COOH → −COO^-, $\Delta\delta$ *ca.* 10–30 ppm), but it increases with the extension of the conjugated system (*Table 2*).

Using estimated δ_o values of 520 ppm for formula **1A** (ketone) and 150 ppm for **1B,C** (enolate), it results that the shielding found in **1a,b** is *ca.* ¾ of that in an $-O^-$ situation. This contradicts earlier explanations [3] [29] assuming a nearly undisturbed carbonyl function and confirms its highly polarized character. On the other hand, the result does of course not permit to distinguish in **1** between true resonance (formula **1C**) and generalized interaction of σ,p, and π electrons.

O-Exchange with H_2O. Nucleophilic addition reactions would be expected to be absent or difficult with fully pseudoaromatic dipolar molecules like **1C**. Indeed, only very few such reactions are reported for cyclopropenones, *e.g.* with *Grignard* reagents [1]. Tropone (**2**) shows more reactions of this type, though conjugate additions seem to be important [34]. The acid-catalyzed isotope exchange with $H_2{}^{18}O$ has been used to prepare **1a** and **2** labelled at the carbonyl group [3].

We chose to compare the rate of nucleophilic addition of water to **1a** and **2** with that of a normal ketone, acetophenone, by following in the ^{17}O-NMR spectra the isotopic exchange of ^{17}O between the ketone and water. As the equilibria are very much in favour of the carbonyl compounds [19], the rates of exchange are proportional to those of addition. The differences in rate between the three compounds were, however, so big that we had, for practical reasons, to measure acetophenone at lower temperature than **1a** and **2**. The easiest way of measuring isotopic exchange, *i.e.* reacting the ketone with a big excess of enriched water, is not available because the $H_2{}^{17}O$ peak deforms the base-line of the entire spectral range; we had thus to use a limited excess of $H_2{}^{17}O$ over ketone, giving second order kinetic conditions ([water]/[ketone] *ca.* 2) in dioxane solution in the presence of an acid catalyst. As in **1a** the substrate signal is much closer to that of water, the base-line deformation became critical even under these conditions. Therefore, we chose for **1a** the inverse procedure of following the reaction between (pre-exchanged) [^{17}O]-**1a** and ordinary water, measured in dioxane/acid as for the other compounds. Evaluation gave good 2nd-order plots for **2** and acetophenone: acetophenone (56°)

$k_2 = (3.4 \pm 0.2) \cdot 10^{-4}$ M^{-1}s^{-1}; **2**, (68°), $k_2 = (0.52 \pm 0.02) \cdot 10^{-4}$ M^{-1}s^{-1}. Tropone (**2**) reacts slower than acetophenone; if one takes into account the temperature difference, one can estimate that it is *ca.* 20 times slower, a slackening which can be explained by the conjugated unsaturation; a small contribution from a 'pseudoaromatic' formula **2B** cannot be excluded.

On the other hand, **1a** reacted so slowly that after 27 h, the system was still far from equilibrium (from the ratio of peak intensities we estimate that *ca.* 45% of the reaction had occurred); for technical reasons (decomposition, lack of long-time stability of the apparatus) the reaction had to be interrupted. For reason of scatter in this very slow reaction, a proper evaluation was not feasible. However, an estimation based on comparison of time for 45% exchange (under similar conditions, **1a** needed 27 h (68°), **2** 12 min (68°), and acetophenone 1.6 min (56°)) shows that **1a** reacts *ca.* 150 times slower than tropone, *i.e. ca.* 3000 times slower than acetophenone, a ratio which has to be attributed to the highly polar character of **1a**. The fact that nucleophilic addition persists at a measurable rate, however, shows that the polarisation cannot completely correspond to formula **1C**.

In order to verify, we submitted an activated phenol, 2,4-dinitrophenol, to our exchange conditions: no trace of reaction could be detected.

In the case of tropone, a different reaction path of exchange is conceivable (though less probable): 1,4 (or other conjugate) addition [34] followed by a 1,3-H shift and (conjugate) elimination, resulting in a change of position of the O-atom on the tropone cycle. We did not check the identity of the carbonyl C-atom after the reaction, but we made sure that the exchange of O was not accompanied by an H/D exchange with a D atom of the water used (most exclusively $D_2{}^{17}O$); this would have been the case with one of the more probable mechanisms of this particular reaction path.

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Experimental Part

General. See [35].

Diphenyl[^{17}O]cyclopropenone (**1a**). Diphenylcyclopropenone (1.34 g, 6.5 mmol, *Aldrich*), $H_2{}^{17}O$ (250 µl, 14 mmol; 10.2% ^{17}O, 37.8% ^{18}O), dioxane (1.0 ml), and conc. H_2SO_4 (1 µl; 'pH' *ca.* 1.5) were heated 27 h at 80°. After neutralization by $NaHCO_3$, the solvent was evaporated and the residue recrystallized 2 times in cyclohexane: 0.97 g (72%). M.p. 120° ([36]: 119–120°). CI-MS: **1a** non enriched: 209 (4.6, [M + 1] + 2); 208 (17.1, [M + 1] + 1); 207 (100.0, [M + 1]), **1a** enriched: 209 (36.1), 208 (26.2), 207 (100); tracer content: ^{18}O 31.5%, ^{17}O 9.1%.

Dimethylcyclopropenone (**1b**) was prepared following [12]. Purity control by GC. ^{1}H-NMR ((D$_6$)acetone): 2.25 (*s*).

[^{17}O]Tropone (**2**). Tropone (0.54 g, 5.0 mmol; prepared following [37]) and $D_2{}^{17}O$ (200 ml; 1.38% ^{17}O, *ca.* 10% ^{18}O) were submitted to exchange (24 h, 80° in the presence of H_2SO_4) following [3]. ^{1}H-NMR: identical with that of **2**. ^{2}H-NMR: no trace of incorporation of D. MS: **2** non enriched: 108 (0.5), 106 (100); enriched: 108 (9.9), 106 (100); practically quantitative ^{18}O-tracer incorporation.

*2,2-Di-(*tert*-butyl)cyclopropanone* (**5**) was prepared following [26].

The *Li-Enolate of Propiophenone*, PhC([^{17}O]Li) = CHMe [38], was prepared from the corresponding ^{17}O-enriched trimethylsilyl ether [39] (^{17}O-NMR (hexane): 71 ppm (200 Hz)) following the general method [38].

^{17}O-NMR Spectra. – The spectra were recorded on a *Bruker-WH-360* spectrometer operating at 48.8 MHz. The temperature was stabilized by a *Bruker B-VT* unit and controlled by a *Hewlett-Packard 2802 A* thermistance Pt thermometer placed in the interior of the 10-mm sample tube. Shimming of the magnetic field was done with a D_2O lock; the spectra were recorded with sample spinning and without lock. The instrumental settings were: 40 kHz

spectral width; 2 K data points; 90° pulse length 33 μs; quadrature phase detection; acquisition time $T_{acq} \geq 4\ T_2$; preacquisition delay Δt 50 μs; no relaxation delay T_d; zero filling up to 8 K before FT; *ca.* 10^6 scans for non-enriched samples. The signal-to-noise ratio was improved by applying 100–200 Hz exponential broadening factor to the FID prior to FT. The chemical shift error was ±0.2 ppm. The chemical shifts are reported relative to $\delta(H_2O)$ 0.00 ppm; dioxane (δ 0.0 ppm) was used as an external reference standard [40].

Kinetics. – The soln. containing one of the two exchange reactants (see below) in a 10-mm NMR tube was thermostatted to the chosen reaction temp. inside the preheated NMR probe. After 10 min, the background spectrum was recorded. The second exchange reactant was added and recording started. With the aid of a microprogram on the *Aspect 2000*, the FID were measured automatically at prefixed time intervals. In order to avoid to change the intensities at each point measured, it is important to apply no left shifts, to utilise the same line-broadening factor, and to apply the same number of data points prior to FT, the same phase constants ($AI = 1$), and identical base-line correction. The error on peak integration is estimated at ±5%. The peak intensities of the ketone and water were both recorded; for **2** and acetophenone, their sum stayed constant at each moment (deviation < 5%). For evaluation, the intensity of the [^{17}O]ketone peak was plotted in the case of **2** and of acetophenone. The data were treated using an equation of degenerate reversible second order kinetics for reactants of unequal initial concentration:

$$kt = \frac{1}{c_o + w_o + w_o^*} \ln \frac{1}{1 - \frac{x(c_o + w_o + w_o^*)}{c_o w_o^*}}$$

with c_o, w_o, w_o^* = initial concentrations of unlabelled ketone, unlabelled water, and labelled water, resp.; x = time-dependent concentration of labelled ketone; evaluation by non-linear regression[3]).

Acetophenone. $H_2{}^{17}O$ (250 μl, 13.9 mmol; 10.2% ^{17}O), dioxane (0.96 ml), and conc. H_2SO_4 (0.96 μl) were warmed to 56° ± 1° in the preheated probe. After 10 min, acetophenone (0.75 g, 6.2 mmol) was added.

Tropone (**2**). $H_2{}^{17}O$ (250 μl, 13.9 mmol; 10.2% ^{17}O), dioxane (1.0 ml), and conc. H_2SO_4 (1.0 μl) were preheated to 68° ± 1°; **2** (0.69 g, 6.5 mmol) was added.

Diphenyl[^{17}O]cyclopropenone. [^{17}O]-**1a** (0.87 g, 4.2 mmol; 5.8% ^{17}O), dioxane (0.65 ml), and conc. H_2SO_4 (0.60 μl) were thermostatted to 68° ± 1°. H_2O (160 μl, 8.9 mmol; ^{17}O natural abundance) was added. Because of very slow reaction, the scatter of data points was very important. After 27 h, the ratio of peak surfaces was H_2O/**1a** = 0.93.

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