# 80. Fluxional Isomerism in a Prebullvalene Lactone1)

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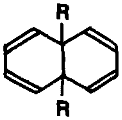
(20. III. 70)

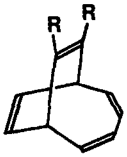
*Summary.* A prebullvalene lactone exhibits fluxional isomerism in solution. Analysis of proton NMR. spectra at 100 MHz and 220 MHz together with variable temperature studies show that the species existing in solution are **7**, **8** and **9**.

The photochemical conversion of *cis*-9.10-dihydronaphthalenes (**1**) into tetracyclo$[4.4.0.0^{2,10}.0^{5,7}]$deca-3,8-dienes (**2**), has recently been established for the parent hydrocarbon **1a** [2] and for a number of [4.4.3]propellane derivatives [3]. In the case of the imide **1c** and the N-methylimide **1d** the photoproducts **2c** and **2d** were stable and could be obtained as crystalline solids. In contrast, the ether **2e** was stable at temperatures below −20°, and the anhydride **2b** could only be observed as a fleeting intermediate even at −40°C.



**1**

**2**



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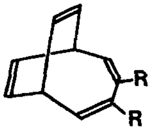

**4**

R, R: a, H; b, –COOCO–; c, –CONHCO–; d, –CONMeCO–; e, $-CH_2OCH_2-$

Compounds of type **2** underwent thermal rearrangement to bicyclo[4.2.2]-decatetraene derivatives ('prebullvalenes'). This thermal *retro-Diels-Alder* reaction was expected to give rise to compounds of structure **3**. In fact, the products isolated were all of type **4**. Subsequently, several investigations established that the prebullvalene system undergoes fluxional isomerism [4]. We now report the unique behaviour of the lactone member of this series.

The tetraenic lactone **5** was irradiated in methanol at 2537 Å while cooling with dry ice. The solvent was then evaporated at −50°, replaced by cooled deuteriochloroform and immediately transferred to the cooled (−42°) probe of an NMR. spectrometer. The spectrum of the product was clearly that of a mixture in which the allylic cyclopropyl protons of **6** could be observed at 1.6 and 2.0 ppm [3b]. However even at the low temperatures employed this signal disappeared rapidly. Workup of the reaction

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1) This paper is considered as Propellanes XI; X, see [1].

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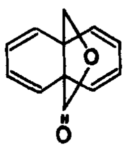
mixture and purification provided an analytically pure lactone as a sharp-melting solid in 60% yield.

This prebullvalene lactone was a pure substance by the usual criterion of constancy of melting point upon repeated crystallization. However, determination of its NMR.-spectrum in deuteriochloroform at 220 MHz and in tetrachloroethylene at 100 MHz revealed a striking example of fluxional isomerism.

The spectrum in deuteriochloroform at 220 MHz exhibits the best separation of the various types of protons. The spectrum consists of four major absorption regions: 1.45–2.1 ppm, 3.2–3.9 ppm, 4.5–5.0 ppm and 5.5–7.5 ppm. A first assignment of these regions can be made by a comparison with the chemical shift data of the anhydride **4b** and the ether **4e** (see Table). Accordingly the low field doublet (7.35 ppm) in the vinylic region must originate from a proton which is in the $\beta$-position of an $\alpha,\beta$-unsaturated lactone and in addition is probably deshielded by the coplanar carbonyl group as in the anhydride **4b**. This signal is of considerable diagnostic importance. The multiplet at 4.5–5.0 ppm (Fig. 1) must be assigned to the methylene protons of the lactone ring. The integral of this region serves as an integration standard. The complexity of the multiplet indicates the presence of more than one component in solution. It may be expected (see Table) that the region from 3.2 to 3.9 ppm contains the bridgehead methine protons; two pairs of multiplets can be recognized (Fig. 2), indicating the presence of two molecular species each having two methine protons. The high-field signals at 1.45–2.1 ppm have not been observed in the spectra of any of the other compounds (anhydride, ether, imides) of this series. This multiplet must originate from the cyclopropane protons of the fluxional isomer **8**.



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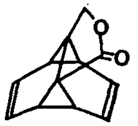
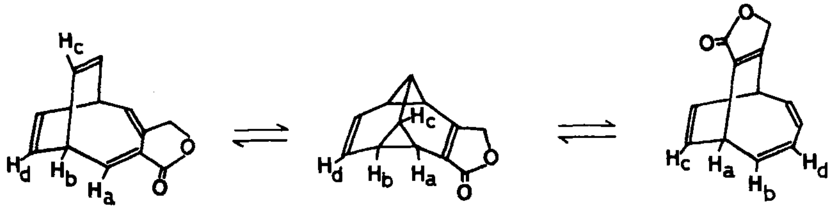


**6**



**7** **8** **9**

Variable temperature studies (27–180°) with the lactone (Fig. 3) reveal a drastic but completely reversible temperature dependence. This will be discussed below.

An expanded spectrum of the $-OCH_2$-region (Fig. 1) yields further information regarding the number of species in solution. This multiplet consists of two *AB* quartets and one closely-spaced doublet. The coupling constant $J_{AB}$ in both quartets is 17 Hz and is typical for a geminal interaction enhanced by the adjacent double bond. Comparison of the spectra at 220 MHz and 100 MHz shows that the doublet splitting

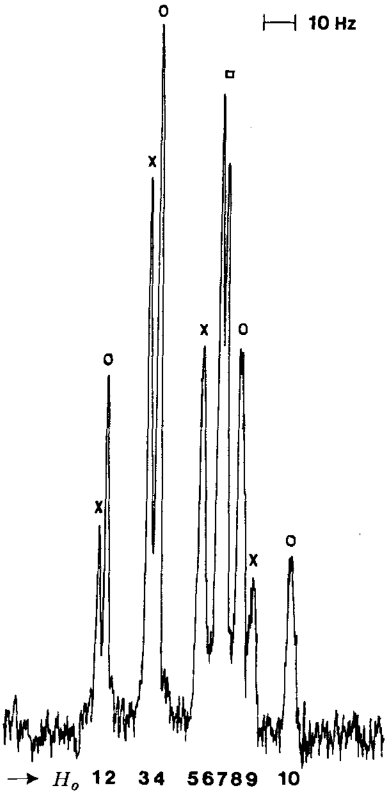


Fig. 1. *220 MHz NMR.-spectrum* ($CDCl_3$) *of the* $-CH_2O-$ *region of the lactone*
X = *AB*-quartet of **9**, O = *AB*-quartet of **8**, □ = $A_2$-singlet with fine splitting of **7**

*Proton NMR. Data*[a]

| Compound | Vinylic H–C(2) | $-OCH_2-$ | bridgehead methine | cyclo-propane |
|---|---|---|---|---|
| **4b** | 7.54 *d*[b]<br>$J_{1,2} = 9$ | – | 3.65 *m* | – |
| **4e** | 6.10 *d*<br>$J_{1,2} = 9$ | 4.49 *d*<br>$J = 2$ | 3.20 *m* | – |
| **7** | 7.35 *d*<br>$J_{1,2} = 9$ | 4.76[c] *q*<br>4.80[c] *q*<br>$J = 17$ | 3.3 *dt*<br>3.45 *dt* | – |
| **9** | < 6.35 |  | 3.6 *dd*<br>3.7 *dd* | – |
| **8** | – | 4.73 *d*<br>$J = 2$ | – | 1.45–2.1 *m* |
| **6** | – | 4.78 *s* | – | 1.6 *bs*<br>2.0 *bs* |

[a] Solvent deuteriochloroform; chemical shifts in δ (ppm), coupling constants in Hz.

[b] *d* = doublet, *dd* = double doublet, *dt* = double triplet, *m* = multiplet, *q* = quartet, *s* = singlet, *bs* = broad singlet.

[c] Centre of *AB*-quartet.

(2 Hz) is independent of the field strength. This small coupling must arise from allylic interaction with a neighbouring vinylic proton. The high-field components of both *AB* quartets are also broadened by small additional couplings. This analysis of the methylene region proves the presence of *three* fluxional isomers, two of which exhibit diastereotopic methylene protons whereas in the third isomer these protons are magnetically equivalent.

We now base further discussion on the three lactone structures **7**, **8** and **9**. **6** need not be considered further since it has already been shown to be very unstable thermally and to exhibit two distinct absorptions as broad singlets for the cyclopropane protons.

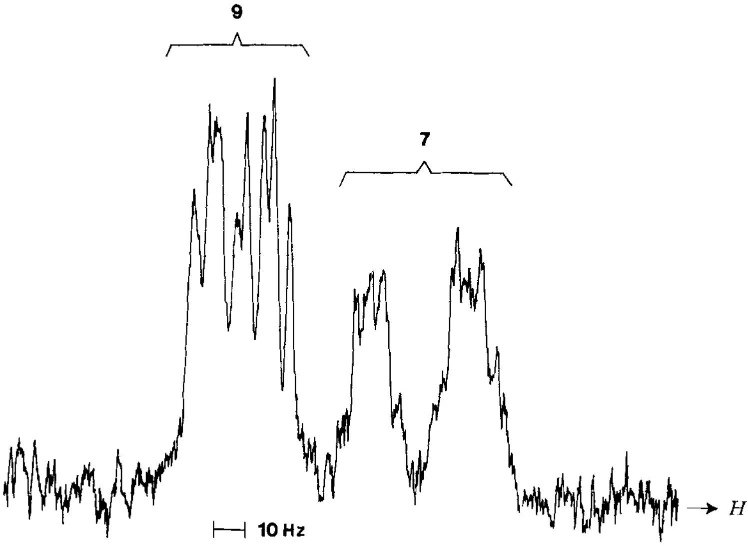


Fig. 2. *220 MHz NMR.-spectrum* ($CDCl_3$) *of the bridgehead methine protons of the lactone structures* **7** *and* **9**

**7** corresponds in structure to that of the model compounds of type **4** [3]. This lactone has $C_s$-symmetry and should exhibit equivalent methylene protons ($CH_2$-doublet). The vinylic proton in the $\beta$-position to the carbonyl group is expected to show a similar chemical shift as in the anhydride **4b**. This is indeed the case (7.35 ppm in **7**; 7.54 ppm in **4b**). Integration of this doublet relative to the $-OCH_2$-region reveals the presence of about 27% of isomer **7**. A second and probably more accurate value can be obtained from the integration of the expanded methylene region (Fig. 1). The integral of lines (5, 6, 7, 8, 9, 10) minus (1, 2, 3, 4) yields the area of lines (6,7) which corresponds to 23% of isomer **7**. This value is an average obtained from four integrations.

The ratio of the two isomers **8** and **9** is obtained from the integrals of the bridgehead methine protons (3.2–3.9 ppm) and of the high-field cyclopropane protons (1.45–2.1 ppm). At 220 MHz the methine protons give rise to four multiplets (Fig. 2). The two multiplets of lower intensity and similar pattern at 3.3 and 3.45 ppm can be assigned to isomer **7** on the basis of a decoupling experiment (100 MHz) with the doublet at 7.35 ppm. The low field part of the methine protons consists of two quartets

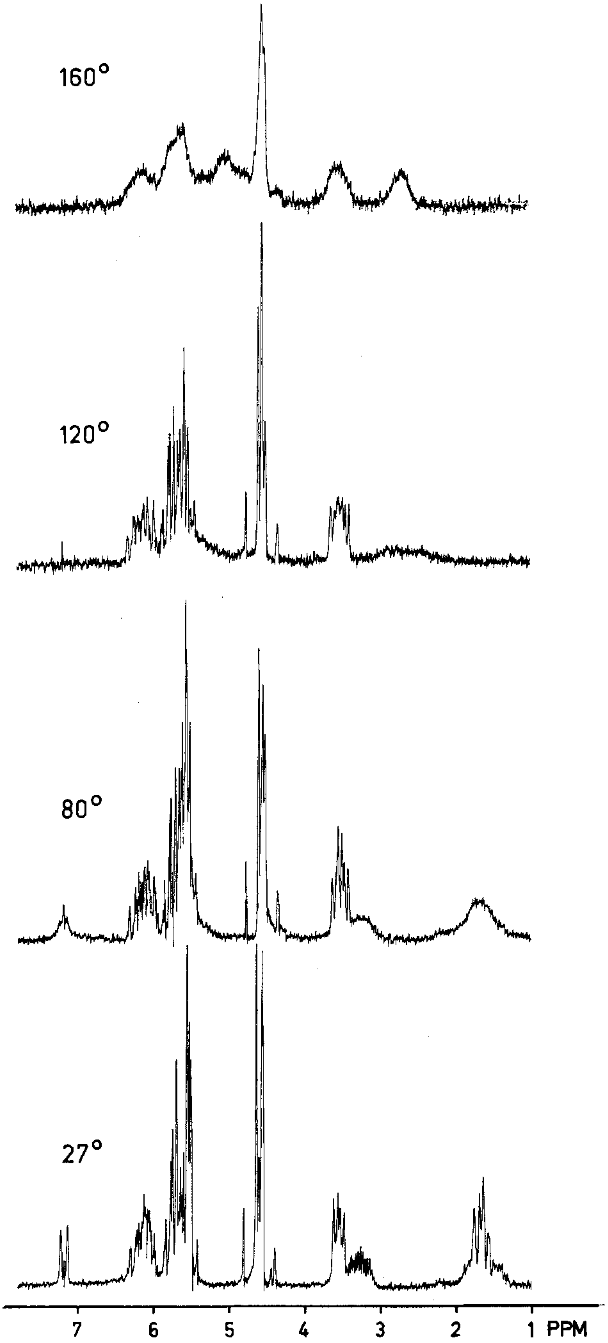
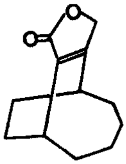


Fig. 3. *100 MHz NMR.-spectra* ($C_2Cl_4$) *of the lactone at different temperatures*

(double doublets) at 3.6 and 3.7 ppm and can be assigned to the corresponding protons in **9**. These protons are coupled to two neighbouring vinylic protons with $^3J = 9$ Hz and 6 Hz respectively. The low field quartet shows additional broadening probably by long range homoallylic coupling to the methylene protons which is also observable in the methylene region (Fig. 1). On the other hand the two methine protons at higher field (3.3 and 3.45 ppm) give more complex multiplets (double triplets), and in **7** they are in fact expected to be coupled to three neighbouring vinyl protons two of which are equivalent. The ratio of the two quartets and the cyclopropane signals yields **8**:**9** = 1.4:1. This result agrees well with an analysis of the *AB* quartets in the $-OCH_2$-region. The ratio of **9** and **7** is obtained directly from the bridgehead methine signals as 1.4:1. We may therefore conclude that the composition of the fluxional isomeric mixture is 23% of **7**, 45% of **8** and 32% of **9**. The data for **8** and **9** are not expected to be more accurate than ± 3% absolute.

For the variable temperature studies the lactone spectra were measured in tetrachloroethylene with hexamethyldisiloxane as internal standard. Integration yields a somewhat different ratio of the three isomers with a lower percentage of the structure **8** ($\approx$ 30%). Spectra at 27°, 80°, 120° and 160° are illustrated in Fig. 3. From these 100 MHz spectra it can be seen that the characteristic signals of isomer **7** exchange with the cyclopropane protons of isomer **8** and that the coalescence point of the vinylic, bridgehead and cyclopropane protons is about 120°. On the other hand, no such behaviour can be observed for the corresponding protons of **8** and **9** which show only broadening above 140° but no coalescence up to 180°. A similar temperature dependence can be observed in the $OCH_2$-region. At 100° one of the *AB* systems and the signal with the small doublet splitting have already merged whereas coalescence with the second *AB* quartet takes place only above 160°. This leads to the conclusion that the isomerization reaction **7** $\rightleftharpoons$ **8** must be considerably faster than the reaction **8** $\rightleftharpoons$ **9**. After heating to 180° the solution was allowed to cool down to room temperature and the same spectrum was obtained as before heating.



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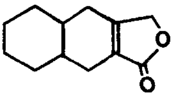

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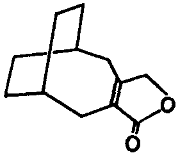

**12**

Chemical support for the presence of **7** and **8** in solutions of the prebullvalene lactone was obtained from catalytic hydrogenation which afforded crystalline **10** (42%) and **12** (57%). Structures were assigned to these compounds on the basis of the ratio of allylic to methylenic protons using the allylic ether protons as reference. The expected reduction product (**11**) of the fluxional isomer **8** was not observed. **11** is a more flexible molecule than **12**. Had it been formed, its NMR. spectrum would have been expected to change with the temperature. The NMR. spectrum (of **12**), however, exhibited no temperature dependence (– 50° to + 78°).

The authors would like to thank Dr. *J. K. Becconsall, ICI* Runcorn, England, for the 220 MHz spectra. This work was supported by the «*Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*».

**Experimental.** – *Photolysis of 11-oxo-12-oxa[4.4.3]propellane.* A solution of the tetraenic lactone **5** [5] (100 mg) in methanol (50 ml) was irradiated at –78° at 2537 Å for five hrs. as described previously [3]. The solvent was removed in a high vacuum while maintaining the temperature at – 50°, the residue was taken up in deuteriochloroform and the solution was transferred to the probe of the NMR.-spectrometer maintained at – 42°.

After 30 min at room temperature the spectrum remained unchanged. The solution was transferred to an *Erlenmeyer* flask, concentrated, and crystallized from benzene-pentane. Several crystallizations from this solvent mixture yielded the analytical sample (60 mg, 60%) of the prebullvalene lactone, m.p. 93.5–95°. UV. (methanol): $\lambda_{max}$ 257 (*sh*), 263, 270 (*sh*), 310 nm (*sh*); $\varepsilon$, 2200, 2500, 2100, 600. IR($CHCl_3$): 1760 $cm^{-1}$ (CO).

$C_{12}H_{10}O_2$ Calc. C 77.40 H 5.41% M.W. 186.20 Found C 77.13 H 5.81% $M^+$ 186

*Catalytic hydrogenation of the prebullvalene lactone.* A solution of the lactone (200 mg) in ethyl acetate (50 ml) containing platinum oxide (20 mg) was hydrogenated at room temperature and atmospheric pressure for 1.5 hr. The catalyst was removed and the solution analyzed by glc (5′ × 1/4″ SE-30, 120 ml helium/min, 180°). Peaks were observed at 20 min (trace), 22.5 min (42%), 24 min (*ca.* 1%), and 29.5 min (57%). The two major compounds were isolated by preparative-scale gas-liquid chromatography (glc.).

The first compound eluted was *3-oxo-4-oxatricyclo[5.4.2.0$^{2,6}$]trideca-2-ene* (**10**). Crystallization from hexane afforded the analytical sample (54 mg; 26%), m.p. 80°. UV. (methanol): $\lambda_{max}$ 222 (10100), end absorption 208 (5000) nm ($\varepsilon$). IR. ($CHCl_3$): 1750, 1684 $cm^{-1}$. NMR. ($CDCl_3$): 4.75 ppm (2H, –$CH_2$O–); 2.93 ppm (*br*, 2H, allylic C*H*); 1.2–2.1 ppm (*m*, 12H, $CH_2$).

| | | | | | |
|---|---|---|---|---|---|
| $C_{12}H_{16}O_2$ | Calc. | C 74.97 | H 8.39 | O 16.65% | M.W. 192.25 |
| | Found | ,, 74.83 | ,, 8.26 | ,, 16.97% | $M^+$ 192 |

The second major component was *4-oxo-5-oxatricyclo[7.2.2.0$^{3,7}$]trideca-3-ene* (**12**). Crystallization from hexane afforded the analytical sample (88 mg, 44%), m.p. 91°. UV. (methanol): $\lambda_{max}$ 218 (15000), end absorption 208 (11300) nm ($\varepsilon$). IR. ($CHCl_3$): 1750, 1675 $cm^{-1}$. NMR. ($CDCl_3$): 4.55 ppm (*br*, 2H), 2.47 ppm (*br*, 4H), 1.1–2.3 ppm (*m*, 8H). The NMR.-spectrum at 78° was unchanged.

| | | | | | |
|---|---|---|---|---|---|
| $C_{12}H_{16}O_2$ | Calc. | C 74.97 | H 8.39 | O 16.65% | M.W. 192.25 |
| | Found | ,, 74.89 | ,, 8.21 | ,, 16.84% | $M^+$ 192 |

Attempts to isolate the minor components of the reaction mixture in pure form were unsuccessful.

The proton NMR.-spectra have been obtained with *Varian HR* 220 (MHz) and HA-100 (MHz) spectrometers equipped with a V 4343 unit for variable temperature control (±3°). Tetramethylsilane and hexamethyldisiloxane have been used as internal standards for deuteriochloroform and tetrachloroethylene solutions respectively.

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