(2) Ferris, J. P.; Kuder, J. E.; Catalano, A. W. *Science*, **1969**, *166*, 765–766; Ferris, J. P.; Kuder, J. E. *J. Am. Chem. Soc.* **1970**, *92*, 2527–2533.
(3) Ferris, J. P.; Trimmer, R. W. *J. Org. Chem.* **1976**, *41*, 19–42.
(4) Koch, T. H.; Rodehorst, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 6707–6710.
(5) Ferris, J. P.; Trimmer, R. W. *J. Org. Chem.* **1976**, *41*, 13–18, and references therein.
(6) Hong, J. H.; Pownall, H. J.; Becker, R. S. *Photochem. Photobiol.* **1976**, *24*, 217–222.
(7) Becker, R. S.; Kolc, J.; Rothman, W. *J. Am. Chem. Soc.* **1973**, *95*, 1269–1273.
(8) Ferris, J. P.; Sanchez, R. A.; Orgel, L. E. *J. Mol. Biol.* **1968**, *33*, 693–704.
(9) Moser, R. E.; Fritsch, J. M.; Westman, T. L.; Kliss, R. M.; Matthews, C. N. *J. Am. Chem. Soc.* **1967**, *89*, 5673–5676.
(10) Ferris, J. P.; Donner, D. B.; Lotz, W. *J. Am. Chem. Soc.* **1972**, *94*, 6968–6974.
(11) The chemical shift assignments for the methyl groups in 1-methyl-4-methylamino-5-cyanoimidazole[12] may be in error.[13]
(12) deVries, L. *J. Org. Chem.* **1974**, *39*, 1707–1710.
(13) Private communication from Dr. L. deVries.
(14) Boyer, J. H.; Kooi, J. *J. Am. Chem. Soc.* **1976**, *98*, 1099–1103. Boyer, J. H.; Dabak, H. *J. Chem. Soc., Chem. Commun.* **1970**, 1204–1205.
(15) Boyer, J. H.; Dunn, J.; Kooi, J. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1743–1747.
(16) Moffat, J. B. *J. Chem. Soc., Chem. Commun.* **1975**, 888–890. Loew, G. H.; Chang, S. *Tetrahedron* **1971**, *27*, 2989–3001. Jameson, C. J.; Yang, W. *J. Theor. Biol.* **1972**, *35*, 247–257.
(17) Saltiel, J.; Curtis, H. C.; Jones, B. *Mol. Photochem.* **1970**, *2*, 331–339. For a general discussion see: Cowan, D. O.; Drisko, R. L. "Elements of Organic Photochemistry"; Plenum Press: New York, 1976, pp 103–109.
(18) Padwa, A. *Chem. Rev.* **1977**, *77*, 37–68.
(19) deVries, L. *J. Am. Chem. Soc.* **1977**, *99*, 1982–1984. deVries, L. *ibid.* **1978**, *100*, 926–933.
(20) Ferris, J. P.; Joshi, P. C.; Edelson, E.; Lawless, J. G. *J. Mol. Evol.* **1978**, *11*, 293–311.
(21) Pauly, H. *Z. Physiol. Chem.* **1904**, *42*, 517. Hais, I. M.; Macek, K. "Paper Chromatography"; Publishing House of the Czechoslovakian Academy of Sciences: Prague, 1963; p 786.
(22) Donner, D. B., Ph.D. Thesis, Rensselaer Polytechnic Institute, 1972.
(23) Ferris, J. P.; Ryan, T. J., *J. Org. Chem.* **1973**, *38*, 3302–3307.
(24) This compound was synthesized previously in the laboratory of Dr. J. H. Boyer and its properties were described to us in a private communication from Dr. Boyer.

Structures of Some Kepone Photoproducts and Related Chlorinated Pentacyclodecanes by Carbon-13 and Proton Nuclear Magnetic Resonance

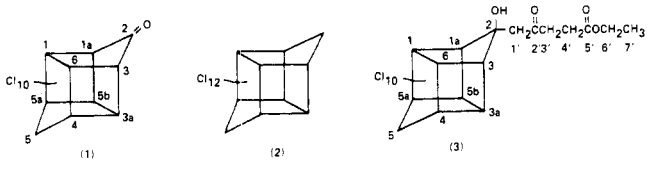
Nancy K. Wilson* and Robert D. Zehr

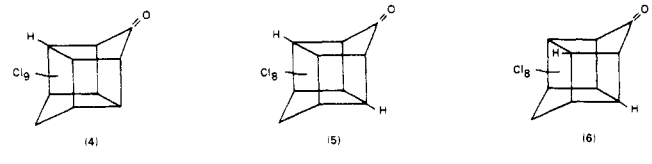
Health Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711

Received September 5, 1978

The pesticide Kepone, 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one, the related compounds mirex, kelevan, a monohydro photoproduct of kelevan, kepone alcohol, kepone hydrate, and the mono- and dihydro photoproducts of Kepone hydrate in hydrocarbon solution were examined by ^{13}C and ^{1}H nuclear magnetic resonance (NMR). The Kepone photoproducts were isolated directly from the photolysis products for the first time. Their structures were determined unequivocally to be 1,1a,3,3a,4,5,5,5a,5b-nonachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one (monohydrokepone) and 1,1a,3,3a,4,5,5,5a-octachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one (dihydrokepone). The NMR data indicate that the major monohydro photoproduct of kelevan is that with the hydrogen substituent at the 3a or 5b position, anti to the OH substituent. In solution, Kepone can exist as a carbonyl form and as its hydrate, a *gem*-diol. These do not equilibrate at ambient temperatures on the NMR time scale. Without stringent drying, only the *gem*-diol forms of Kepone and its mono- and dihydro photoproducts are observed. Variable temperature ^{1}H NMR studies of monohydrokepone *gem*-diol indicated that it does not form intramolecular hydrogen bonds, but forms intermolecular hydrogen bonds to other monohydrokepone molecules and to water. This results in dimer formation, with a rapid monomer–dimer equilibrium and proton exchange between monomers, dimers, and water at ambient temperatures.

The severe environmental contamination by the pesticide Kepone, 1,1a,3,3a,4,5,5,5a,5b,6-decachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalen-2-one[16] (1), in late 1975 led to our intense involvement in studies of the chemistry of and analytical methods for this compound and its derivatives.





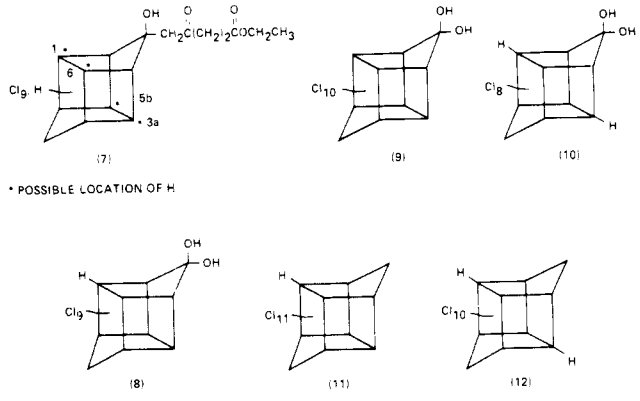
Kepone and the related pesticides mirex (2), dodecachlorooctahydro-1,3,4-metheno-2*H*-cyclobuta[*cd*]pentalene, and kelevan (3) have been the subject of several photochemical studies[1-6] performed to elucidate the mechanisms and products of the degradation of these compounds in the environment.[7]

Alley and his co-workers have photolyzed mirex, Kepone, and the dimethyl ketal of Kepone.[1,2] Using combined gas chromatography–mass spectrometry (GC–MS) and ^{1}H and ^{13}C nuclear magnetic resonance,[8] they characterized the photoproducts of mirex. Since they were unable to isolate the photoproducts of Kepone, the structures of these products were not fully determined. The GC–MS evidence did indicate only one possible structure for the monohydro photoproduct of Kepone (4), but two possible structures, 5 and 6, for the dihydro photoproduct.

To characterize the photolysis products of Kepone and to investigate means of synthesis of the photodegradation products for use in toxicological studies, we carried out a number of photolyses of pure Kepone, as its hydrate in hydrocarbon solution. The two major photoproducts, monohydrokepone and dihydrokepone, were isolated as their hydrates, and their structures were determined by GC–MS and ^{1}H and ^{13}C NMR.[9] Details of the isolation of the photoprod-

ucts and gas chromatographic data on these compounds are given elsewhere.[10]

For comparison of its NMR parameters with those of the Kepone and mirex derivatives, kelevan and its major monohydro photoproduct **7** were examined. The kelevan photoproduct **7** was hydrolyzed to give its Kepone analogue, monohydrokepone *gem*-diol **8**. These compounds too were characterized by ^{13}C NMR and GC–MS.



Experimental Section

Photolyses. Technical Kepone (Allied Chemical Corp.) was recrystallized several times from toluene and sublimed at 140 °C and 0.01 torr. Kepone was irradiated for 15–20 h in toluene or cyclohexane (Burdick and Jackson). Toluene was the better irradiation solvent because of the greater solubility of the Kepone hydrate **9** in this solvent. Since **1** rapidly picks up moisture to form **9** and since no special precautions were taken to protect the reaction mixture from atmospheric moisture, it is assumed that the diol **9** was the major form of the reactant in the solution.

A Hanovia 450-W mercury arc lamp in an Ace photochemical reactor was used. The reactor and the quartz immersion well were water-cooled. The solution was continuously stirred magnetically while nitrogen gas was passed through it.

Photoreactions were monitored with a Tracor MT-222 gas chromatograph equipped with a flame ionization detector and a 183 × 0.63 cm o.d. glass column (5% OV-1 on 80/100 Chromosorb W HP). Approximately 15% of the Kepone remained unreacted at the end of the experiment.

After being irradiated, solutions were concentrated on a rotary evaporator and applied to an EM Gel SI-200 column to remove polymeric materials formed in the photoreaction. Fractions were collected by eluting with cyclohexane with increasing proportions of benzene and were monitored by analytical gas chromatography.

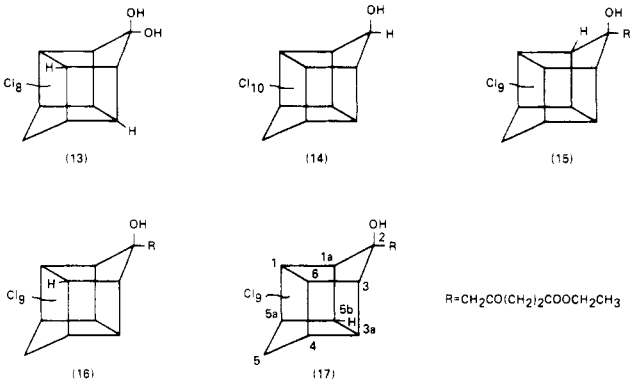
Fractions containing photoproducts were combined, washed with sulfuric acid, water, and saturated sodium chloride solution, concentrated, and subjected to preparative gas chromatography (GC).

Preparative GC was done using a 161 × 0.80 cm i.d. coiled stainless steel column (4% SE-30/6% OV-210 on 80/100 Gas Chrom Q). After repeated fractionations by preparative GC, dihydrokepone **9** (>98% pure, 1.6% yield) and monohydrokepone **8** (>98% pure, 1.6% yield) were obtained.

Dihydrokepone *gem*-diol **9** evolved a gas (water vapor) at 187–190 °C and melted at 218–222 °C: IR (CCl_4) 3570 (s), 3030 (w), 1340 (w), 1240 (sh), 1230 (m), 1210 (w), 1194 (m), 1170 (s), 1140 (m), 1112 (w), 1078 (w), 1068 (w), 1040 (w), 1019 (w), 1000 (m), 994 (sh), 986 (w), 968 (w), 955 (w), 870 (m, sh), 861 (m), 650 (w) cm^{-1}; MS *m/e* (rel intensity) 418* (0.25), 383* (3.2), 244 (3.3), 242 (21), 240 (68), 238 (100), 236 (61), 182 (21). (* Exact masses: calcd for $C_{10}H_2{}^{35}Cl_8O$ 417.7618, found 417.7614; calcd for $C_{10}H_2{}^{35}Cl_7O$ 382.7929, found 382.7925; calcd for $C_5H^{35}Cl_5$ 235.8523, found 235.8521.)

Monohydrokepone *gem*-diol **8** evolved a gas (water vapor) at 130 °C and melted at 276–277 °C: IR (CCl_4) 3575 (s), 3037 (w), 1345 (w), 1228 (m), 1187 (sh), 1180 (sh), 1171 (s), 1143 (s), 1112 (m), 1092 (w), 1079 (w), 1069 (w), 1032 (w), 1016 (m), 980 (w), 941 (w), 898 (w), 855 (m), 672 (m), 666 (m) cm^{-1}; MS *m/e* (rel intensity) 452* (1.2), 270* (54), 272 (100), 274 (87), 276 (39), 236 (24), 235 (23), 216 (11), 182 (21). (* Exact masses: calcd for $C_{10}H^{35}Cl_9O$ 451.7228, found 451.7224; calcd for $C_{10}H^{35}Cl_8O$ 416.7539, found 416.7536; calcd for $C_5{}^{35}Cl_6$ 269.8134, found 269.8131.)

Kelevan (**3**) was synthesized for us by Midwest Research Institute and photolyzed according to the procedure of Parlar et al.[6] The kelevan (3.362 g) was photolyzed in 450 mL of acetone (Burdick and Jackson) for 2 h with a Hanovia 450-W mercury arc lamp ($\lambda > 200$ nm) in an Ace photochemical reactor. The solution was concentrated on a rotary evaporator, and the residue was applied to a column of silica gel (50 g, Woelm activity grade I, 31 cm × 22 mm i.d.) in 3% acetone in cyclohexane. Fractions were collected while the acetone content of the eluting solvent was slowly increased, and they were monitored by thin-layer chromatography. Three products were detected. The fractions containing the major product (607 mg) were combined and rechromatographed similarly two more times to yield 248 mg of white solid, mp 132–136 °C. This material was recrystallized twice from methylene chloride/hexane to yield 189 mg of **17**.



Monohydrokelevan **17** melted at 143–144 °C: IR ($CHCl_3$) 3400 (broad), 3040 (w), 2990 (w), 2940 (w), 2910 (w), 1731 (s), 1712 (s), 1420 (m), 1396 (w), 1373 (m), 1350 (m), 1340 (sh), 1325 (w), 1303 (w), 1265 (w), 1228 (m), 1186 (s), 1127 (w), 1110 (m), 1099 (w), 1079 (m), 1067 (sh), 1030 (w), 1014 (m), 984 (w), 969 (sh), 951 (w), 897 (w), 865 (w), 850 (sh) cm^{-1}; MS *m/e* (rel intensity) 596 (1.3, 9 Cl), 567 (25, 9 Cl), 551 (15, 9 Cl), 523 (9.7, 9 Cl), 507 (39, 7 Cl), 495 (6.9, 9 Cl), 319 (24, 6 Cl), 270 (5.7, 6 Cl), 259 (28, 4 Cl), 237 (100), 235 (70, 5 Cl), 225 (35, 3 Cl).

Anal. Calcd for $C_{17}H_{13}O_4Cl_9$: C, 34.01; H, 2.18; Cl, 53.15. Found: C, 34.25; H, 2.15; Cl, 53.13.

Oxidation of a portion of this material with chromium trioxide[11] yielded the corresponding monohydrokepone diol **8**.

Spectra. All NMR spectra were obtained on 50–100-mg samples dissolved in 3.5 mL of a deuterated solvent, usually benzene-d_6, chloroform-*d*, or acetonitrile-d_3. These were contained in 12-mm cylindrical sample tubes. Tetramethylsilane (~2%) was added to the samples to provide an internal reference.

Samples containing Kepone in the vacuum-sublimed carbonyl form **1** were prepared on a high vacuum line. Solvents were dried with Linde 3Å molecular sieves and vacuum distilled into the samples, which were then degassed and sealed under vacuum.

A Varian XL-100A-15 NMR spectrometer with a Nicolet TT-100A data system and a Nicolet MONA other-nuclei-observe accessory was used. Sweep widths of ±3 kHz with quadrature phase detection, flip angles of ~15° (90° pulse = 16 μs), pulse delays of 2–5 s, and 16K Fourier transforms were employed. Proton noise decoupling was used in some cases, with a noise bandwidth of 1.5 kHz and a decoupler power of ~10 W (<0.1 W reflected power).

Mass spectra were obtained by gas–liquid chromatography and 70-eV electron impact mass spectrometry on a Hewlett-Packard 5930A mass spectrometer with a Hewlett-Packard 5700 gas chromatograph. Exact mass measurements at high resolution were obtained on a Varian MAT311 mass spectrometer.

Infrared spectra were obtained on a Perkin-Elmer 257 grating infrared spectrophotometer.

Results and Discussion

The photoproducts of mirex (**2**) have been shown to be mono- and dihydromirex (**11** and **12**). The analogous Kepone photoproducts are monohydrokepone **4** and either 5b,6-dihydrokepone **5** or 3a,6-dihydrokepone **6**. These structures were supported by mass spectral data on the product mixture and on the photoproducts of Kepone dimethyl ketal, and by conversion of the ketal photoproducts to the mirex derivatives **11** and **12** by treatment with phosphorus pentachloride.[1,2]

As a first step in the characterization of the Kepone photoproducts, here isolated for the first time, ^{13}C NMR pa-

Table I. Carbon-13 Chemical Shifts of Some Chlorinated Pentacyclodecanes

compd	solvent[a]	δ_C C-1	C-1a	C-2	C-3	C-3a	C-4	C-5	C-5a	C-5b	C-6	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	C-7′
mirex (2)	B	77.19	83.11	92.23	83.11	77.19	83.11	92.23	83.11	77.19	77.19							
Kepone, carbonyl form (1)	B	74.75	73.92	190.87	73.92	74.75	85.79	89.36	85.79	74.75	74.75							
kepol (14)	A	75.17	79.40	81.53	79.40	78.00	84.52	92.82	84.52	78.00	75.17							
Kepone, diol form (9)	A	76.29	80.36	103.89	80.36	76.29	84.20	92.49	84.20	76.29	76.29							
monohydrokepone, diol form (8)	B	76.06	79.76	102.33	79.76	76.06	84.18	92.19	84.18	76.06	76.06							
dihydrokepone, diol form (10)	B	68.90	75.91	102.37	73.07	78.39	79.96	93.04	84.51	78.19	59.79							
kelevan (3)	A	71.94	74.69	104.12	74.69	71.94	79.43	94.49	79.43	60.34	60.34							
monohydrokelevan (17) (anti)	B	77.33	81.60	88.18	81.60	75.41	84.06	92.62	84.06	75.41	77.33	60.74	209.66	(38.12)	(38.20)	171.49	27.50	14.17
	B	(79.71)[b]	74.82	88.30	77.31	68.34	84.53	93.74	(81.99)	58.93	(78.42)	60.80	209.43	(37.91)	(39.55)	171.69	27.62	14.17

[a] A = acetonitrile-d_3; B = benzene-d_6. [b] Similar values in parentheses may be interchanged.

rameters were obtained for Kepone itself. In benzene solution, resonances for both the carbonyl form 1 and the hydrate, a *gem*-diol **9**, were observed. In acetonitrile and in acetone, only **9** was present. Hydration of **1** to form **9** occurs very quickly in the presence of small amounts of water, including atmospheric moisture. In solution, therefore, Kepone and its photoproducts are normally present as *gem*-diols, which may have several associated water molecules. In the gas chromatograph or the mass spectrometer, these convert, of course, to the carbonyl forms. Carbon-13 NMR parameters for both the carbonyl and the diol forms of Kepone are given in Table I.

Carbon-13 resonances belonging to the diol **9** were identified by addition of tris(acetylacetonato)chromium(III), $Cr(acac)_3$, which both broadened these resonances and shifted them slightly. Comparison of the benzene data with data for Kepone in acetonitrile, in which only **9** was observed, confirmed the diol resonances.

The ^{13}C resonances of the carbonyl form of Kepone (**1**) were assigned as follows. Both the carbonyl, δ 190.87, and the dichloromethylene, δ 89.36, resonances could be assigned on the basis of their characteristic chemical shifts.[12] The four-carbon resonance at δ 74.75 was assigned to the four equivalent carbons C-1, -3a, -5b, and -6. Two two-carbon resonances, at δ 85.79 and 73.92, were assigned to carbons C-4 and -5a and C-1a and -3, respectively, on the basis of the greater shielding of the carbons α to the carbonyl group and the similarity of the shift of C-4 and -5a to that for C-4 and -5a in mirex (**2**).

For the diol form **9** of Kepone, chemical shifts in benzene and in acetonitrile are quite similar to each other and to the chemical shifts of **1** except for the oxygen-substituted carbon C-2. This *gem*-diol carbon resonance was at δ 102.33 in benzene and at δ 103.89 in acetonitrile. Carbons C-1, -3a, -5b, and -6 were assigned on the basis of their intensity (equals four carbons in the presence of $Cr(acac)_3$); C-5 was assigned on the basis of its typical dichloromethylene chemical shift. Resonances for carbons C-1a and -3 were distinguished from those for C-4 and -5a by the broadening and slight high-frequency shifts of the former resonances in the presence of $Cr(acac)_3$. Carbon-13 data for the monohydro photoproduct of Kepone are also given in Table I. Only the *gem*-diol form **8** was observed.

Several assignments for **8** could be based on the ^{13}C–^1H couplings observed in the ^{13}C spectrum. The coupling constants are 175.7 Hz for the direct C–H coupling at C-6, 13.5 Hz for the vicinal coupling to C-3a, 1.3 and 1.0 Hz vicinal coupling constants to C-5a and C-1a, respectively, and a 3.9-Hz geminal coupling constant to C-1. The vicinal coupling constants have an approximate Karplus angular dependence with the greatest coupling constant to C-3a, which has a C–H bond dihedral angle relative to H-6 of ~150°, and essentially zero coupling constants to C-2 and C-5, which have dihedral angles with H-6 close to 90°.

The resonance at δ 84.51 is assigned to C-5a on the basis of its chemical shift similarity to C-5a in mirex, Kepone, kepol, and monohydromirex. The resonance at δ 93.04 is characteristic of a dichloromethylene bridge carbon and is assigned to C-5. Of the remaining resonances at δ 73.07 and 79.96, the more shielded is assigned to C-3 because of its proximity to the *gem*-diol function and the less shielded to C-4.

For the diol form of the dihydro photoproduct of Kepone, two very similar structures, **10** and **13**, derived from the carbonyl forms **5** and **6** are allowed by the chemical and mass spectral evidence. However, these structures differ in symmetry. Whereas structure **13** has eight nonequivalent sets of carbons, structure **10** has only six sets because of its greater symmetry. The carbon-13 NMR spectrum of dihydrokepone diol exhibits only six resonances. Spectra in the presence of the lanthanide shift reagent $Yb(dpm)_3$, which would be expected to remove any accidental chemical shift equivalences, likewise exhibited only six resonances. Thus, the structure of this Kepone photoproduct is established as 5b,6-dihydrokepone diol (**10**).

Assignments of the dihydrokepone resonances were based primarily on the monohydrokepone assignments and the preceding arguments.

The asymmetric substitution of a hydrogen for a chlorine in Kepone diol to form **8** causes the two hydroxyl protons to become magnetically nonequivalent. Normally, one would expect proton exchange and hydrogen bonding to average the two resonances, so that only one OH resonance is observed in the ^1H NMR spectrum. However, for a carefully dried sample of **8** in benzene, we were able to see both of the diol OH resonances at 28 °C. These are shown in Figure 1. These resonances did not coalesce with increased temperature up to 65 °C, indicating that intramolecular hydrogen bonding and exchange were not occurring in the *gem*-diol. However, a strong temperature dependence of the two OH resonances was observed; at −58 °C, these resonances had moved to δ_H 4.32 and 4.28, displaced ~2 ppm toward higher frequency from their positions at ambient temperatures.

The large temperature dependences of the OH chemical shifts of **8** probably arise from participation of **8** in a monomer–dimer equilibrium. At high concentrations and at low temperatures, the dimeric form, which is stabilized by two strong hydrogen bonds, is predominant. The dimeric form is shown schematically in Figure 2.

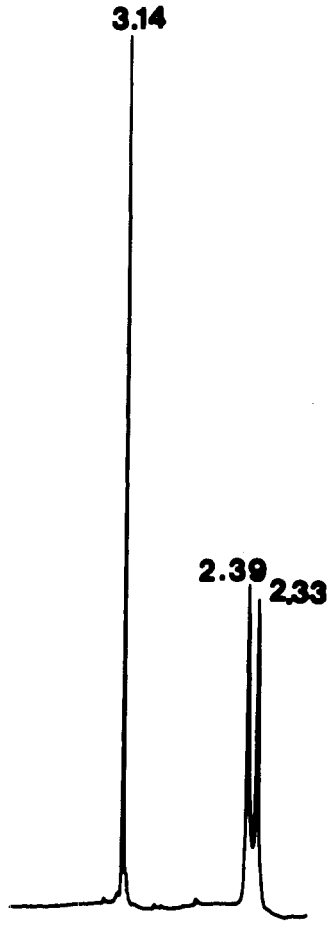


Figure 1. The ^1H NMR spectrum of monohydrokepone **10** at 28 °C. The peak at δ_H 3.14 is from H-1 and those at δ_H 2.39 and 2.33 are from the two nonequivalent hydroxyl protons.

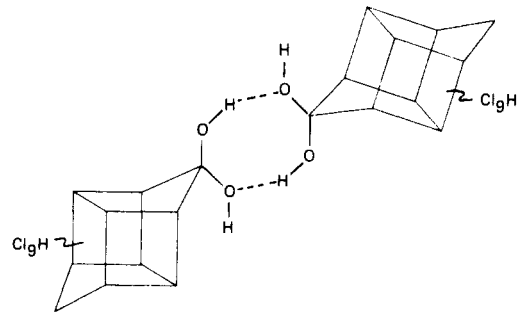


Figure 2. The postulated dimeric structure of the monohydro photoproduct of Kepone.

Table II. Predicted and Observed ^{13}C Chemical Shifts for Monohydrokelevan

observed chemical shift (δ_C), ppm	predicted chemical shift (δ_C), ppm	
	anti (**17**)	syn (**16**)
93.74	93.47	93.47
88.30	88.22	88.22
84.53	84.39	84.39
81.99	79.84	79.84
79.71[a]	*79.66*	*77.75*
78.42	*79.46*	*77.74*
77.31	*77.75*	*77.54*
74.82	74.91	74.91
68.34	*68.25*	*70.17*
58.93 (CH)	*59.14*	*61.06*

[a] Chemical shifts which are predicted to differ for **16** and **17** are italicized.

In the presence of small amounts of water, proton exchange takes place between **8** and water molecules. A minor component, constituting less than 10% of the sample, may be another monohydrokepone since it exhibits *gem*-diol OH peaks plus a singlet with δ_H nearly identical with that of the H-6 of **8**. It also exchanges protons with water. This minor component was not isolated or further characterized, however. We were not able to control the water content of the sample to give reproducible results for a further investigation of hydrogen bonding in this system.

Another Kepone derivative which we examined is the alcohol **14**, kepol, which we isolated from a human fecal sample.[13] Its ^{13}C NMR parameters are listed in Table I. The ^{13}C assignments are based on the following: first, the C–H couplings observed in the spectra (a direct coupling with J = 175 Hz to C-2, and long-range three-bond couplings with J = 3.9 Hz to C-3a and C-5b and with J = 2.8 Hz to C-1 and C-6); second, greater intensity in the partially relaxed $\{^1H\}$ ^{13}C spectrum for C-1a and C-3 than for C-4 and C-5a and for C-1 and C-6 than for C-3a and C-5b; third, agreement of these assignments with the chemical shift assignments for similar carbons in other compounds of this series; and finally, the characteristic chemical shift value, δ 92.82, for the dichloromethylene carbon.

The monohydro photoproducts of kelevan reported in the literature are **7**, in which the exact position of the proton substitution is not known, and **15**. With relatively short periods of irradiation, **15** has been reported to be the major photoproduct.[6] However, **7** can also be formed, and the distribution of the photoproducts is strongly dependent on the exact experimental conditions.[5] In our experiments, only minor amounts of **15** were formed, and the major product was **7**, which gave monohydrokepone diol **8** on hydrolysis. We show in this work that the structure of monohydrokelevan **7** is in fact **17**, with proton substitution at position 5b.

Carbon-13 NMR parameters for kelevan and monohydrokelevan **17** are given in Table II. The assignments for kelevan (**3**) were determined as follows. The keto ester substituent, R = $CH_2COCH_2CH_2COOCH_2CH_3$, had an ester carbonyl resonance at δ 171.49 and a ketone carbonyl resonance at δ 209.66.[14] The methyl carbon resonance at δ 14.17 and the resonance at δ 60.74 of the methylene carbon C-1′, substituted on the electron-withdrawing ring system, were easily identified. The two resonances at δ 38.12 and 38.20 were assigned to the similar methylene carbons C-3′ and C-4′; thus, the remaining methylene resonance could only be that of C-6′, at δ 27.50.

The ring carbon resonances of **3** were somewhat more difficult to assign. A single carbon resonance at δ 92.62 was assigned to C-5 because of its characteristic chemical shift and its low intensity and broadening resulting from the double chlorine substitution. The other single carbon resonance, at δ 88.18, then had to be for C-2, which was confirmed by the broadening of this resonance in the presence of $Cr(acac)_3$ and the much greater intensity of this resonance (from the dipolar interactions with ^1H nuclei on OH and R) relative to that of C-5 in the absence of $Cr(acac)_3$. Of the two-carbon resonances, that at δ 81.60 was assigned to C-1a and -3 because of its large relative intensity without $Cr(acac)_3$ and its broadening with $Cr(acac)_3$ in the sample. Carbons C-5a and -4 were assigned the resonance at δ 84.06 since they are less shielded than C-1a and -3 because of the α CCl_2, since they had low intensity because of their large distance from ^1H nuclei, and since their chemical shift is close to that for C-5a and -4 in mirex (**2**). The remaining two resonances were assigned to C-1 and -6 (δ 77.33) and C-3a and -5b (δ 75.41). The resonance due to C-3a and -5b

was more intense in partially relaxed spectra due to closer proximity to ^1H nuclei, was less shifted (1.2% less) by $Cr(acac)_3$ because these carbons are further from the OH site of $Cr(acac)_3$ complexation, and was less shifted by the lanthanide shift reagents $Eu(fod)_3$ (2.6% less) and $Yb(dpm)_3$ (52% less) than are C-1 and -6. Although the Eu and Yb compounds can complex at three sites in kelevan, at carbonyls C-2′ and C-6′ and at the hydroxyl-substituted carbon C-2, the preferred conformation, due to intramolecular hydrogen bonding between the OH and C=O (C-2′), places the site of shift reagent binding much further from C-3a and -5b than from C-1 and -6. Shift reagent bound at C-6′ has little effect on the relative chemical shifts of C-3a, -5b, -1, and -6. Preferential binding of the shift reagents at the C-2′ carbonyl and the hydroxyl group is indicated by the greater effects of the shift reagents on the chemical shifts of C-2 and C-2′ than on the chemical shift of C-6′.

The ^{13}C spectrum of monohydrokelevan **7** was partially assigned using the same techniques and considerations as for kelevan (**3**). The conversion by CrO_3 oxidation of **7** to monohydrokepone diol **8** showed that monohydrokelevan had either of the two structures **16** or **17**, which differ in the syn (**16**) or the anti (**17**) orientation of the ring hydrogen to the hydroxyl group. No doubling of the peaks in the presence of either $Eu(fod)_3$ or $Yb(dpm)_3$ indicated that only one of these isomers was present in the major product. The Yb shift reagent affected the chemical shift of the CH carbon somewhat less (8%) than it affected the chemical shifts of the carbons diagonally opposite it (C-1,6 in **17** or C-3a,5b in **16**).

To distinguish between these two possible structures, we estimated the effects of replacing a chlorine by a hydrogen at either the 5b or the 6 position on the δ_C values of **3** by calculating the additive substituent effects[15] [$\delta_C(8) - \delta_C(9)$, ppm] of this replacement in Kepone from the ^{13}C chemical shifts of Kepone diol **9** and monohydrokepone diol **8**. The predicted δ_C values for both syn and anti forms of **7** are given with the observed chemical shifts in Table II. Five chemical shifts should differ for the two forms; of these, the average deviation between predicted and observed shifts is 0.19 ppm for **17** but 1.40 ppm for **16**. These data thus show clearly that the anti form **17** is the major product of the photoreaction.

Acknowledgments. We would like to thank G. W. Sovocool and R. L. Harless for mass spectra and C. B. Bryden and S. T. Maher for technical assistance.

Registry No.—**1**, 143-50-0; **2**, 2385-85-5; **3**, 4234-79-1; **8**, 52171-96-7; **9**, 4715-22-4; **10**, 69069-44-9; **14**, 1034-41-9; **17**, 69069-45-0.

References and Notes

(1) E. G. Alley, B. R. Layton, and J. P. Minyard, Jr., *J. Agric. Food Chem.*, **22**, 442 (1974).
(2) E. G. Alley and B. R. Layton, in "Mass Spectrometry and NMR Spectroscopy in Pesticide Chemistry", Plenum Press, New York, 1974, pp 81–90.
(3) E. G. Alley, D. A. Dollar, B. R. Layton, and J. P. Minyard, Jr., *J. Agric. Food Chem.*, **21**, 138 (1973).
(4) K. Knoevenagel and R. Himmelreich, *Z. Pflanzenkr. Pflanzenschutz*, **80**, 155 (1973).
(5) S. Begum, A. Gäb, H. Parlar, and F. Korte, *Chemosphere*, **2**, 235 (1973).
(6) H. Parlar, W. Klein, and F. Korte, *Chemosphere*, **1**, 129 (1972).
(7) D. A. Carlson, K. D. Konyha, W. B. Wheeler, G. P. Marshall, and R. G. Zaylskie, *Science*, **194**, 939 (1976).
(8) E. G. Alley, B. R. Layton, and J. P. Minyard, Jr., *J. Org. Chem.*, **41**, 462 (1976).
(9) N. K. Wilson and R. D. Zehr, presented at the 29th Southeastern Regional Meeting of the American Chemical Society, Tampa, Fla., Nov 9–11, 1977, Abstract 209.
(10) R. D. Zehr and N. K. Wilson, *J. Chromatogr.*, submitted for publication.
(11) A. Westlake, W. E. Westlake, and F. A. Gunther, *J. Agric. Food Chem.*, **18**, 159 (1970).
(12) N. K. Wilson and G. W. Sovocool, *Org. Magn. Reson.*, **9**, 536 (1977).
(13) R. L. Harless, D. E. Harris, G. W. Sovocool, R. D. Zehr, N. K. Wilson, and E. O. Oswald, *Biomed. Mass Spectrom.*, **5**, 232 (1978).
(14) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972.
(15) N. K. Wilson and R. D. Zehr, *J. Org. Chem.*, **43**, 1768 (1978).
(16) Bayer names for some compounds in this paper are as follows: **1**, 1,2,3,4,6,7,8,9,10,10-decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one; **9**, 5,5-dihydroxy-1,2,3,4,6,7,8,9,10,10-decachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane; **4**, 1,3,4,6,7,8,9,10,10-nonachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one; **8**, 5,5-dihydroxy-1,3,4,6,7,8,9,10,10-nonachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane; **5**, 1,3,4,6,7,9,10,10-octachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decan-5-one; **10**, 5,5-dihydroxy-1,3,4,6,7,9,10,10-octachloropentacyclo[5.3.0.0^{2,6}.0^{3,9}.0^{4,8}]decane.

Carbon-13 Nuclear Magnetic Resonance Studies of Allylic Hydroxysterols. Assignment of Structure to 5α-Cholest-8(14)-ene-3β,7α,15α-triol, an Inhibitor of Sterol Synthesis[1]

Mitsuhiro Tsuda, Edward J. Parish, and George J. Schroepfer, Jr.*

Departments of Biochemistry and Chemistry, Rice University, Houston, Texas 77001

Received September 5, 1978

5α-Cholest-8(14)-ene-3β,7ξ,15ξ-triol, a potent inhibitor of sterol biosynthesis in animal cells in culture, has been shown to be formed in 53% yield upon treatment of 3β-benzoyloxy-14α,15α-epoxy-5α-cholest-7-ene with refluxing aqueous ethanolic KOH [G. J. Schroepfer, Jr., E. J. Parish, H. W. Chen, and A. A. Kandutsch, *J. Biol. Chem.*, **252**, 8975 (1977)]. Detailed analyses of the ^{13}C nuclear magnetic resonance spectra of this compound and of other steroidal allylic alcohols and their derivatives have permitted the establishment of configurations of the 7 and 15 hydroxyl functions as α. The resonances of the individual carbon atoms have been determined for six allylic hydroxysterols as well as a number of carbamate and acetate derivatives. Treatment of 5α-cholest-8(14)-ene-3β,7α,15α-triol with acid gave 15-oxo-5α-cholest-8(14)-en-3β-ol in 87% yield. Also described herein are syntheses of 3β-benzoyloxy-8α,14α-epoxy-5α-cholestan-7α-ol, 3β-benzoyloxy-8α,9α-epoxy-5α-cholestan-7α-ol, 7-oxo-5α-cholest-8-en-3β-ol, 5α-cholest-8(14)-ene 3β,15α-diacetate, 5α-cholest-8(14)-ene 3β,15β-diacetate, 5α-cholest-8(14)-ene 3β,7α,15α-triacetate, and 7α,15α-diacetoxy-5α-cholest-8(14)-en-3-one.

Over 20 years ago Barton et al.[2,3] reported that treatment of 3β-acetoxyergosta-7,14,22-triene with perphthalic acid in ether gave, upon washing of the ether solution with dilute aqueous sodium hydroxide, the sodium salt of the half phthalate ester of 3β-acetoxyergosta-8(14),22-dien-7ξ,15ξ-diol. The product was not characterized as such but, upon

0022-3263/79/1944-1282$01.00/0