mixture. Fractions 24–30 of the eluate were combined. Removal of the solvent left 421 mg (13.3%) of dicholesteryl formal, mp 190–2°C. After crystallization from hexane-acetone the product (308 mg) melted at 195–6°C; $[\alpha]_D^{26}$ −28.6°; λ 9.05 and 9.65 (C—O of ether) (no adsorption in the hydroxyl and carbonyl regions).

Proton magnetic resonance (pmr): 3.43 (broad multiplet, 3 $-\mathrm{O}\overset{|}{\underset{|}{\mathrm{C}}}\underline{\mathrm{H}}$), 4.77 (s, —OC$\underline{\mathrm{H}}_2$O—), 5.33 (broad doublet, 6 = $\overset{|}{\underset{|}{\mathrm{C}}}\underline{\mathrm{H}}$) ratio of integrations 1:1:1, respectively.

Kupchan et al. (*3*) reported an mp of 190.5°C, and $[\alpha]^{26}_D$ −30.8° (chloroform) for their dicholesteryl formal. Lunn (*4*) assigned a signal observed at δ 4.63 ppm in the pmr spectrum of 17β,17β′-oxymethylene-diandrost-4-ene-3-one to the —OCH$_2$O— hydrogens. The area of this peak, as in the case of 3A, was equal to that of the steroid

$$-\mathrm{O}\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{H}$$

protons (at the 17 and 17′ positions). He also suggested that the —CH$_2$OCH$_2$OCH$_2$— structure in some of his compounds was responsible for the intense absorption bands observed at 8.62, 9.09, 9.81, and 10.87 μ in their infrared spectra.

Dioxymethylene Dicholesteryl Ether. On combining fractions 33-40 of the eluate and removing the solvent, there remained 295 mg (9.0%) of a white solid melting at 134–42°C. One recrystallization from hexane–ethanol afforded 222 mg of dioxymethylene dicholesteryl ether, mp 148–9°C; $[\alpha]^{26}_D$ −29.8°; λ 8.99, 10.04, and 10.12.

Pmr: 3.38 (broad multiplet, 3 $-\mathrm{O}\overset{|}{\underset{|}{\mathrm{C}}}\underline{\mathrm{H}}$) 4.82 (s, —OC$\underline{\mathrm{H}}_2$O—), 5.33 (broad doublet, 6 = $\overset{|}{\mathrm{C}}\underline{\mathrm{H}}$) ratio of integrations 1:2:1, respectively.

Trioxymethylene Dicholesteryl Ether. Fractions 44–55 were combined, evaporated to dryness, and the residue was crystallized from hexane–ethanol. There was obtained 79.0 mg (2.3%) of trioxymethylene dicholesteryl ether, mp 174–7°C; $[\alpha]^{26}_D$ −34.2°; λ 8.87, 9.01, 10.23, and 10.86.

Pmr: 3.38 (broad multiplet 3 $-\mathrm{O}\overset{|}{\underset{|}{\mathrm{C}}}\underline{\mathrm{H}}$) 4.82 (s, —OC$_2\underline{\mathrm{H}}$O), 4.88 (s, central —OC$\underline{\mathrm{H}}_2$O—), 5.33 (broad doublet, 6 = $\underset{|}{\mathrm{C}}\underline{\mathrm{H}}$) ratio of integrations 1:2:1:1, respectively.

When fractions 63-76 were combined and evaporated to dryness, 2–3 mg of a white solid remained. This material was not identified but, because of the relationship of its thin-layer chromatographic spot to those of the formal, the polyoxymethylene ethers and cholesterol (R_f of 3A > 3B > 3C > this fraction > 2), it is quite possible that this product may be the next higher homologue, tetraoxymethylene dicholesteryl ether. Cholesterol, identified by thin-layer chromatography, was isolated from subsequent eluates.

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LITERATURE CITED

(1) Boyd, R. H., *J. Polymer Sci.*, **50**, 133 (1961).
(2) Gresham, W. F., Brooks, R. E., U. S. Patent 2,449,469 (September 14, 1948).
(3) Kupchan, S. M., Casy, A. F., Swintosky, J. V., *J. Pharm. Sci.*, **54**, 514 (1965).
(4) Lunn, W. H. W., *J. Org. Chem.*, **30**, 2925 (1965).
(5) Montignie, E., *Bull. Soc. Chim.* [4], **47**, 467 (1930).
(6) Rosen, M. J., Kaye, I. A., U. S. Patent 3,092,618 (June 4, 1963).
(7) Walker, J. F., "Formaldehyde," 3rd ed., 1964, Reinhold Publishing Corp., New York, N. Y., pp 167–71.

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Behavior of 4-β-Hydroxyethyl-6,7,8,9-tetrachloro-1-oxa-4-azaspiro[4.4]nona-6,8-diene in Diels-Alder Reaction

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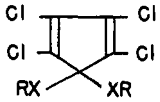
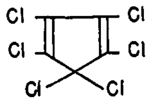
The formation of ketals (Ia) and mercaptals (Ib) of 1,2,3,4-tetrachlorocyclopentadienone from the condensation of hexachlorocyclopentadiene (II) with alcohols (*5*, *8*, *10*) or thiols (*9*) in the presence of strong bases has been known for some time. Although I and II add a variety of dienophiles to afford typical Diels-Alder adducts, neither undergoes the Diels-Alder self-dimerization characteristic of related cyclic dienes such as cyclopentadiene, cyclopentadienone or 1,2,3,4-tetrachlorocyclopentadienone. The 5,5-bis(dialkylamino)-1,2,-3,4-tetrachlorocyclopentadienes (IV) also do not self-dimerize and in fact decompose under Diels-Alder reaction conditions (*7*).

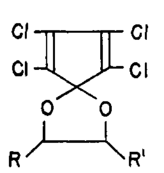


Ia, b
a, X = O
b, X = S

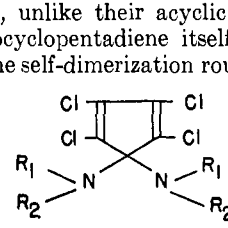


II

Vicinal glycols condense with II in the presence of bases to form cyclic ketals (III) which, unlike their acyclic counterparts Ia and Ib or hexachlorocyclopentadiene itself, readily afford Diels-Alder adducts via the self-dimerization route (*1*, *2*).



III
R, R'= H, alkyl

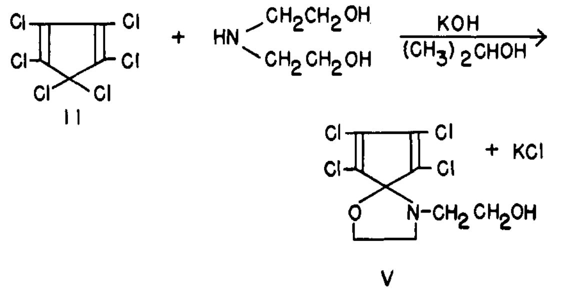


IV
R1, R2= alkyl

4-β-Hydroxyethyl-6,7,8,9-tetrachloro-1-oxa-4-azaspiro[4.4]nona-6,8-diene, a product of the reaction of hexachlorocyclopentadiene with diethanolamine, does not undergo Diels-Alder self-dimerization but does form adducts with certain common dienophiles under relatively mild reaction conditions. These observations suggest that the Diels-Alder behavior of this unusual spirodiene more closely resembles that of the acyclic ketals of 1,2,3,4-tetrachlorocyclopentadienone than it does that of either the counterpart cyclic ketals derived from 1,2-glycols or the related 5,5-bis(dialkylamino)-1,2,3,4-tetrachlorocyclopentadienes derived from secondary amines.

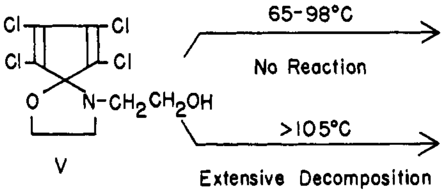
Chang has attributed the enhanced reactivity of the cyclic ketals to favorable steric factors which serve to expose the 1,4-positions of the diene by "pinning-back" the methylene groups through ring formation.

Kamal and Wicklatz (*4*) recently isolated the novel spirodiene 4-β-hydroxyethyl-6,7,8,9-tetrachloro-1-oxa-4-azaspiro[4.4]nona-6,8-diene (V) from the condensation of II with diethanolamine, but apparently chose not to study its reactions.



Inasmuch as the structural features of V are intermediate between those of the acyclic ketals, I, the cyclic ketals, III, and the 5,5-bis(dialkylamino)-1,2,3,4-tetrachlorocyclopentadienes, IV, we were interested in examining V's behavior under Diels-Alder conditions.

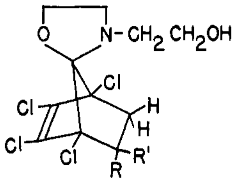
The spirodiene V was found to be storage stable for prolonged periods (a slight yellowing occurs, but the melting point is unaffected) in the solid state and to exhibit no tendency to dimerize when heated either in neat form just above its melting point (60–61.5°C) or in solution in polar or nonpolar solvents at temperatures up to 98°C for as long as 24 hr. By way of contrast, tetrachlorocyclopentadienone and its cyclic ketal derivatives III dimerize slowly in the solid state at ambient temperatures (*1*) and are completely converted to their dimers within two hours at steam bath temperatures. Evidently the single β-hydroxyethyl substituent in V is capable of shielding the ends of the diene grouping from approach by a second molecule in the same manner as do the two alkyl groups attached to the oxygen atoms in the acyclic ketals Ia.



Attempts to promote the dimerization of V by utilizing higher reaction temperatures were precluded by thermal instability of the diene at temperatures above about 105°C. In refluxing toluene or *n*-octane, for example, V rapidly decomposes with the evolution of hydrogen chloride and the formation of a carbonaceous mass. This observation is in accordance with the report of Kamal and Wicklatz that attempts to refine V by distillation resulted in vigorous decomposition accompanied by gas evolution (*4*).

We found that this decomposition occurs even under the conditions of attempted falling film distillation at short residence times and moderate temperatures (∼130°C). This decomposition could involve intermolecular nucleophilic attack of the tertiary nitrogen atom at one of the chlorine-bearing vinylic carbon atoms of the diene or, alternatively, intramolecular nucleophilic displacement of chloride from an adjacent carbon atom by the hydroxyl group with formation of a new six-membered ring. (This possibility of an intramolecular reaction was suggested by one of the reviewers.) That these vinylic positions are readily susceptible to attack by nucleophiles is well known in the acyclic ketal series I (*6*). The thermal stability of V is significantly greater than that of the aminals IV, which decompose even in boiling benzene.

Although V lacked the required reactivity for Diels-Alder dimerization and could not be subjected to temperatures exceeding 105°C, it did react with several common dienophiles to afford Diels-Alder adducts. Characterizable adducts were obtained from styrene (VI), acrylonitrile (VII), allyl alcohol (VIII), acrylamide (IX), and methacrylamide (X). Except in the case of the preparation of VIII, where excess allyl alcohol was used as the solvent, all of the adductions were carried out in refluxing isopropanol using reaction times of from 7 to 21 hours. Yields were reasonably good except in the case of X, where the reaction was very sluggish, product was not obtained pure (0.8% above theory in C), and insufficient material was available for further purification and reanalysis. Maleic anhydride reacted with V to afford a high-melting, uncharacterized solid whose infrared spectra indicated that both adduct formation and anhydride ring-opening had occurred. No adducts were isolated from reactions of V with dienophiles such as cinnamaldehyde, propargyl alcohol, cyclohexene, 2-hydroxymethylnorborn-5-ene(cyclol), *trans*-2,3-dicyanonorborn-5-ene, and crotonaldehyde.



VI-X

VI, R = phenyl, R' = hydrogen
VII, R = cyano, R' = hydrogen
VIII, R = hydroxymethyl, R' = hydrogen
IX, R = carboxyamido, R' = hydrogen
X, R = carboxyamido, R' = methyl

The thermal instability inherent in the spirodiene is noticeably absent in its adducts. Adduct VII, for example, was stable to distillation (falling film) at 185° C and adducts VI, VIII, and IX can be heated well above their respective melting points with no signs of discoloration or gas evolution. The enhanced stability of the chlorine atoms in these adducts toward bases is not unexpected; in fact, this behavior is characteristic of most Diels-Alder adducts (those from allylic alcohols which can form cyclic ethers by intramolecular attack at C_5

Table I. Adducts of 4-β-Hydroxyethyl-6,7,8,9-tetrachloro-1-oxa-4-azaspiro[4.4]nona-6,8-diene

Dienophile	Adduct[a]	Mol ratio, diene/ dienophile	Solvent	Reaction time, hr.	Reaction temp, °C	Yield, %	Bp, °C, mm.	n_D^{20}	Mp, °C (solvent)	Empirical formula
Styrene	VI	1/1	Isopropanol	21	82	83.1	...	...	154–154.5 (isopropanol)	$C_{17}H_{17}NO_2Cl_4$
Acrylonitrile	VII	2/1	Isopropanol	7	82	76.7	<184(0.01)[b]	1.5580	...	$C_{12}H_{12}N_2O_2Cl_4$
Allyl alcohol	VIII	20/1	Excess allyl alcohol	13	98	100[c]	...	...	132–133 (benzene)	$C_{12}H_{15}NO_3Cl_4$
Acrylamide	IX	1/1	Isopropanol	16	82	88.8	...	...	168.5–169.5 (isopropanol)	$C_{12}H_{14}N_2O_3Cl_4$
Methacrylamide	X	1/1	Isopropanol	16	82	25.6[d]	...	...	150.5–151.5 (benzene)	$C_{13}H_{16}N_2O_3Cl_4$

[a] Elemental analyses (C, H, N, and Cl) have been reviewed and are in accordance with theory except for C value (0.8% above theory) on Adduct X. [b] Refined on falling film-type molecular still. [c] Crude yield. [d] Diene conversion was only 57.5%.

Table II. Ir and Nmr Spectral Data on Adducts

Adduct no.	Structure	Ir spectra[a]	Nmr spectra[b]
VI	R = phenyl, R′ = hydrogen	2.93 μ (OH) 3.27 μ (aromatic C═C) 3.48, 3.55 μ (N—CH_2 or O—CH_2) 6.25 μ (Cl—C═C—Cl) 9.07, 9.42 μ (C—O—C) 12.33, 12.47, 13.63 μ (C—Cl)	3.22 ppm (OH proton) 3.88 ppm (C_2 exo; X portion of ABX pattern) $J_{H_x, 3H_x}$ (cis vicinal) = 9.2 cps $J_{H_x, 3H_n}$ (trans vicinal) = 4.2 cps 2.80 ppm (C_3 exo; B portion of ABX pattern) J_{H_x, H_n} (geminal) = 11.8 cps $J_{H_x, 2H_x}$ (cis vicinal) = 9.2 cps 2.25 ppm (C_3 endo; A portion of ABX pattern) J_{H_n, H_x} (geminal) = 11.8 cps $J_{H_n, 2H_x}$ (trans vicinal) = 4.2 cps 6.9–7.5 ppm (aromatic protons) 2.8–4.2 ppm (CH_2 from —CH_2CH_2OH and oxazolidine ring; A_2B_2 pattern)
VII	R = cyano, R′ = hydrogen	2.85 μ (OH) 3.50 μ (N—CH_2 or O—CH_2) 4.40 μ (CN) 6.26 μ (Cl—C═C—Cl) 9.30 μ (C—O—C)	3.50 ppm (OH proton) 3.78 ppm (C_2 exo; X portion of ABX pattern) $J_{H_x, 3H_x}$ (cis vicinal) = 9.2 cps $J_{H_x, 3H_n}$ (trans vicinal) = 4.2 cps 2.85 ppm (C_3 exo; B portion of ABX pattern) J_{H_x, H_n} (geminal) = 10.7 cps $J_{H_x, 2H_x}$ (cis vicinal) = 9.2 cps 2.11 ppm (C_3 endo; A portion of ABX pattern) J_{H_n, H_x} (geminal) = 10.7 cps $J_{H_n, 2H_x}$ (trans vicinal) = 4.2 cps 2.9–4.1 ppm (CH_2 from —CH_2CH_2OH and oxazolidine ring; A_2B_2 pattern)
VIII	R = hydroxymethyl, R′ = hydrogen	3.06 μ (OH) 3.52 μ (N—CH_2 or O—CH_2) 6.25 μ (Cl—C═C—Cl) 9.15, 9.25 μ (C—O—C) 9.50, 9.62 μ (C—OH) 12.65, 13.76, 13.9 μ (C—Cl)	3.50 ppm (OH protons − 2) ~2.80 ppm (C_2 exo; X portion of ABX pattern) obscured by methylene triplet at 2.95 ppm 2.46 ppm (C_3 exo; B portion of ABX pattern) J_{H_x, H_n} (geminal) = 10.2 cps $J_{H_x, 2H_x}$ (cis vicinal) = 8.4 cps 1.71 ppm (C_3 endo; A portion of ABX pattern) J_{H_n, H_x} (geminal) = 10.2 cps $J_{H_n, 2H_x}$ (trans vicinal) = 3.0 cps 2.95–4.05 ppm (CH_2 from —CH_2CH_2OH and oxazolidine ring; A_2B_2 pattern)
IX	R = carboxyamido, R′ = hydrogen	2.91, 3.01 μ (NH_2 and OH) 3.12 μ (NH_2) 3.54 μ (N—CH_2 or O—CH_2) 5.98, 5.15 μ (C═O) 6.24 μ (Cl—C═C—Cl) 9.14, 9.53 μ (C—O—C) 11.95, 13.12 μ (C—Cl)	... ...
X	R = carboxyamido, R′ = methyl	... ...	... ...

[a] All spectra taken as KBr pellets except adduct VII (CCl_4). [b] All spectra taken in deuterated acetone with TMS as reference.

represent an exception) of II and its various derivatives such as I and III (*2, 3, 10*).

Physical properties and analytical data on adducts VI–X are summarized in Table I. Infrared spectra on these adducts were in all instances consistent with the assigned structures; nmr spectra obtained for adducts VI–VIII not only supported the structural assignments, but also provided strong evidence from coupling constant data (*trans* vicinal relationship between the C_2 proton and the downfield C_3 *endo* proton) that the C_2 substituents in these adducts were present in the *endo* configuration. The nmr spectra did not, however, permit a decision regarding the position of the oxazolidine ring with respect to C_2 or the double bond. Ir and nmr spectral properties are summarized in Table II.

EXPERIMENTAL

Melting points were determined with a Mel-temp (Laboratory Devices, Inc.) capillary tube apparatus and are uncorrected. Microanalyses were performed by European Research Associates, s.a., Brussels, Belgium. Infrared spectra were obtained on a Perkin-Elmer Model 21 Spectrophotometer and nmr spectra on a Varian Associates Model A-60 instrument using tms as the internal standard and deutero-acetone as solvent. Falling film evaporative distillations were carried out with a Rota-film molecular still (Arthur F. Smith Co.) modified to utilize a refluxing solvent as heating medium in place of an electric mantle.

4-β-Hydroxyethyl-6,7,8,9-tetrachloro-1-oxa-4-azaspiro-[4.4]nona-6,8-diene (V). The preparative procedure described by Kamal and Wicklatz (*4*) was modified slightly to allow a 20-fold scale-up without a runaway reaction. The potassium hydroxide was dissolved in the isopropanol, the diethanolamine was added in one portion, and the hexachlorocyclopentadiene was fed in over a 30-min period with cooling to maintain the temperature below 50°C. It was necessary to charcoal-treat and recrystallize the crude gummy product three times in heptane solution to obtain material of good color. Consequently, our yield of white product, mp 60–61.5°C, was only 24.6%. Repetition of the reaction on this scale gave essentially the same yield again, whereas a run made with only one half of the usual quantity of diethanolamine afforded a gummy product which could not be induced to crystallize even after repeated treatments with decolorizing carbon present.

Our interest in this material as an intermediate to polyfunctional fire retardants for plastics waned when it became apparent that the preparation and isolation of the compound were not commercially attractive processes.

Preparation of Diels-Alder Adducts of V—General Procedure. The general procedure used to prepare the Diels-Alder adducts (VI–X) of V was to heat the spirodiene and the appropriate dienophile together in a solvent (usually 5–10 ml/0.01 mol of diene) under the conditions shown in Table I. The individual adducts were isolated as described below.

Spiro[2-phenyl-1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-ene-7,2′-(*N*-β-hydroxyethyl)oxazolidine] (VI). The adduct separated from the chilled reaction mixture as light tan, plate-like crystals whose melting point was unchanged after recrystallization from isopropanol for analysis.

Spiro[2-cyano-1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-ene-7,2′-(*N*-β-hydroxyethyl)oxazolidine] (VII). The dark reaction mixture was stripped free of volatiles by heating to 80°C/1 mm on a rotary evaporator. The reddish brown viscous residue (n_D^{20} = 1.5511) was purified by passing it through a falling film molecular still operated at 184°C/0.1 mm; this treatment removed a small quantity of low-boiling material and afforded a distillate unchanged in appearance from the crude product, but having n_D^{20} = 1.5580. Inasmuch as the adduct became glassy rather than crystalline on cooling, it was analyzed in the form of a viscous liquid.

Spiro[2-hydroxymethyl-1,4,5,6-tetrachlorobicyclo[2.2.1]-hept-5-ene-7,2′-(*N*-β-hydroxyethyl)oxazolidine] (VIII). The amber-colored solution was freed of excess allyl alcohol by heating to 90°C/1 mm on a rotary evaporator. The residue was a yellow solid melting from 104.5–11°C. Two recrystallizations of a portion of this crude material from isopropanol with water added until cloudiness developed afforded the purified product as fine white needles whose melting point of 134–6°C was unchanged by further recrystallization from benzene for analysis.

Spiro[2-carboxyamido-1,4,5,6-tetrachlorobicyclo[2.2.1]-hept-5-ene-7,2′-(*N*-β-hydroxyethyl)oxazolidine] (IX). The adduct separated upon cooling as a flocculent mass of cream-colored crystals melting from 157–60°C. Two recrystallizations from anhydrous isopropanol afforded the analytical sample as slightly off-white, very fine needles.

Spiro[2-carboxyamido-2-methyl-1,4,5,6-tetrachlorobicyclo[2.2.1]hept-5-ene-7,2′-(*N*-β-hydroxyethyl)oxazolidine] (X). The dark reaction mixture was stripped free of volatiles by heating to 90°C/1 mm on a rotary evaporator. The viscous, syrupy residue was extracted twice with 30-ml portions of hot hexane and once with a 10-ml portion of hot water. The hexane extracts on cooling yielded 1.3 grams of unreacted spirodiene V. The residue from the water extraction then solidified to a mass of brown colored crystals, mp 112–28° C. Several recrystallizations from hot benzene with decolorizing charcoal present afforded the still impure product (see foot-note, *a*, Table I) in the form of lemon colored crystals.

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LITERATURE CITED

(1) Chang, W. H., *Chem. Ind.*, **709**, 1491 (1964).
(2) Chang, W. H., *J. Chem. Soc.*, **1965**, 2305.
(3) Hoch, P. E., Stratton, G. B., Colson, J. G., *J. Org. Chem.*, **34**, 1912 (1969).
(4) Kamal, M. R., Wicklatz, J. E., *Can. J. Chem.*, **42**, 1500 (1964).
(5) Krynitsky, J. A., Bost, R. W., *J. Amer. Chem. Soc.*, **69**, 1918 (1947).
(6) McBee, E. T., Crain, D. L., Crain, R. D., Belohlav, L. R., Braendlin, H. P., *ibid.*, **84**, 3557 (1962); see also Lemal, D. M., Gosselink, E. P., McGregor, S. D., *ibid.*, **88**, 582 (1966).
(7) McBee, E. T., Stoffer, J. O., Braendlin, H. P., *ibid.*, **84**, 4540 (1962).
(8) Newcomer, J. S., McBee, E. T., *ibid.*, **71**, 946 (1949).
(9) Ordas, E. P., U. S. Patent 2,697,103 to Arvey Corp., Dec. 14, 1954.
(10) Ungnade, H. E., McBee, E. T., *Chem. Rev.*, **58**, 249 (1958); see also Chang, W. H., U. S. Patent 3,256,316 to Pittsburgh Plate Glass Company, June 14, 1966.

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