Attempted Reduction of VI.—When VI was subjected to the conditions of Iselin[12] or Castrillón and Szmant,[13] decomposition of the substrate resulted. The former procedure provided 31% the starting material while the latter method produced a 6% yield of the desired thioether, mp 83–85°. A mixture melting point with authentic V was not depressed.

Attempted Reduction of III with Triphenylphosphine.—A mixture of 0.73 g (2.5 mmoles) of III and 0.78 g (3 mmoles) of triphenylphosphine in 75 ml of xylene was stirred under a gentle reflux for 0.5 hr, cooled, filtered, and concentrated *in vacuo* to 10 ml. The solution was applied to a 2.5 × 40 cm column of silica gel (100 g, 0.05–0.2 mm); elution was monitored by tlc (system D); and two major components were removed and purified. The higher mobility material was eluted from the column with chloroform and was recrystallized from ethanol to yield 100 mg (48%) of 1,1,2,2-tetraphenylethane: mp 210–212° (lit.[19] mp 210°). A mixture melting point with authentic material was not depressed and tlc (system D) mobility was identical. The mass spectra of both materials exhibited a parent ion at *m/e* 334 and successive fragments corroborated the assignment. The lower mobility component required ethyl acetate–chloroform (1:1) for elution and was recrystallized from *n*-hexane to produce 660 mg (80%) of triphenylphosphine oxide: mp 155–156° (lit.[20] mp 154°). Comparison of the infrared spectrum with a published spectrum of triphenylphosphine oxide[21] indicated that two materials were identical. No starting material or phenyl benzhydryl sulfide was observed.

Registry No.—IV, 13641-03-7; VI, 13641-04-8; VIII, 13641-05-9; XI, 13641-06-0; XII, 6297-53-6; XIII, 13698-40-3.

Acknowledgment.—We are indebted to Dr. Kurt L. Loening of the Chemical Abstracts Service for assistance in determining the nomenclature for the bisdisulfide derivatives.

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[19] W. T. Nauta and D. Mulder, *Rec. Trav. Chim.*, **58**, 1070 (1939).

[20] H. Straudinger and J. Meyer, *Helv. Chim. Acta*, **2**, 635 (1919).

[21] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 835 (1951).

The Synthesis of a Series of 1,1a,3,3a,4,5,5,5a,5b,6-Decachlorooctahydro-4′-Substituted Spiro[1,3,4-metheno-2H-cyclobuta[*c,d*]pentalene-2,2′-oxazolidin]-5′-ones

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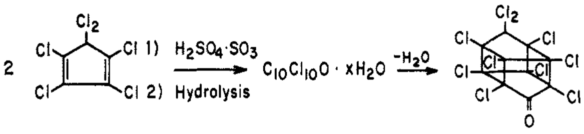
The reaction of hexachlorocyclopentadiene (I) with itself in the presence of fuming sulfuric acid or sulfur trioxide with subsequent hydrolysis gives $C_{10}Cl_{10}O$ (II)[1,2] (Kepone, Allied Chemical Corp; H-1 ketone, Hooker Chemical Corp.). The product is usually isolated as a hydrate with one to four associated water molecules. The parent ketone, mp 349°, can be obtained by azeotropic dehydration with toluene, xylene, etc. The chemistry of II has been reviewed recently[3]


(1)

$C_{10}Cl_{10}O$, II,
m.p. 349°C

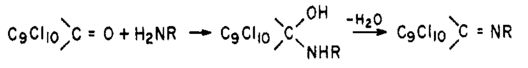
and the structure of the compound has been adequately proven[4,5]

Compound II is particularly effective against chewing insects (fire ants, roaches, soil insects in bait form, and chewing insects that prey ornamentals and potatoes)[6] with an LD_{50} of 126 mg/kg (rat).

As in the case of many of the other highly chlorinated organic agricultural chemicals, II appears to have inherent residue and toxicity problems. That there is a high level of biological activity in the parent structure seems proven. That utilization of this activity may be of further interest seems apparent by the modifications of structure which have recently been described in the literature.[3,6]

Discussion

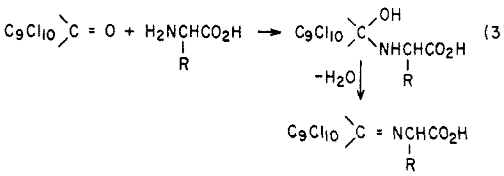
Attempts have been made to form typical ketone derivatives of $C_{10}Cl_{10}O$, oximes, hydrazones, phenylhydrazones, etc., and the initial addition to the carbonyl group takes place. Elimination of water to form the stable derivatives have, as presently known, required azeotropic distillation.[3]



$$C_9Cl_{10}{>}C{=}O + H_2NR \longrightarrow C_9Cl_{10}{>}C{<}^{OH}_{NHR} \xrightarrow{-H_2O} C_9Cl_{10}{>}C{=}NR \qquad (2)$$

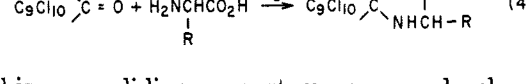
$R = -OH, -NH_2, -NH\phi$

We postulated that by using an amino group adjacent to a carboxyl group we might effect the dehydration to a stable imino structure, carrying also a solubilizing (salt-forming) carboxyl group. $C_{10}Cl_{10}O$ reacts under



$$\begin{array}{c} C_9Cl_{10}{>}C{=}O + H_2N\underset{R}{CH}CO_2H \longrightarrow C_9Cl_{10}{>}C{<}^{OH}_{NH\underset{R}{CH}CO_2H} \qquad (3) \\ \downarrow{-H_2O} \\ C_9Cl_{10}{>}C{=}N\underset{R}{CH}CO_2H \end{array}$$

azeotropic conditions with α-amino acids to give, with the loss of water, compounds of the type envisioned. However, structure determinations led us to the conclusion that, whereas the product isolated had indeed lost a molecule of water (from the original addition of the amino group to the carboxyl group), the actual loss had been from the reaction of the intermediate hydroxyl compound with the carboxyl group to form a lactone.



$$C_9Cl_{10}{>}C{=}O + H_2N\underset{R}{CH}CO_2H \xrightarrow{-H_2O} C_9Cl_{10}{>}C{<}\begin{array}{l} O-C{=}O \\ \qquad\;| \\ NHCH-R \end{array} \qquad (4)$$

This oxazolidinone system appeared chemically stable but did release a free amino group on boiling in

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[1] E. E. Gilbert and S. L. Giolito, U. S. Patent 2,616,928 (1952); see Reissue 24,435 (Feb 25, 1958) to Allied Chemical Corp.

[2] E. E. Gilbert and S. L. Gillito, U. S. Patent 2,616,825 (1952); see Reissue 24,749 (Dec 15, 1959) to Allied Chemical Corp.

[3] W. L. Dilling, M. P. Braendlin, and E. T. McBee, *Tetrahedron*, **23**, 1121 (1967).

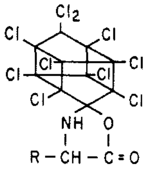
[4] E. T. McBee, C. W. Roberts, J. D. Idol, Jr., and R. H. Earle, Jr., *J. Am. Chem. Soc.*, **78**, 1511 (1956).

[5] D. H. Zijp and H. Gerding, *Rec. Trav. Chim.*, **77**, 682 (1958).

[6] E. E. Kenaga, *Bull. Entomol. Soc. Am.*, **12**, 161 (1966).

TABLE I

1,1a,3,3a,4,5,5,5a,5b,6-DECACHLOROOCTAHYDRO-4′-SUBSTITUTED SPIRO[1,3,4-METHENO-2H-CYCLOBUTA[*c,d*]PENTALENE-2,2′-OXAZOLIDIN]-5′-ONES



			% compn								
	%,		Carbon		Hydrogen		Chlorine		Nitrogen		
R	Yield	Mp, °C	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Registry no.
H-	78	270 dec	26.31	27.90	0.55	0.61	64.16	62.30	2.56	2.76	13422-72-5
CH_3-	71	195–196	27.50	27.80	0.90	1.08	62.80	63.00	2.50	2.39	13440-85-2
$(CH_3)_2CH$-	87	186–187	30.54	30.60	1.53	1.70	60.11	60.10	2.37	2.34	13440-86-3
$(CH_3)_2CHCH_2$-	53	204–205	31.82	32.05	1.84	1.86	58.72	58.20	2.32	2.19	13422-73-6
$CH_3(C_2H_5)CH$-	70	158–159	31.82	32.20	1.84	1.72	58.72	58.70	2.32	2.28	13422-74-7
$CH_3SCH_2CH_2$-[a]	38	155–157	28.97	29.10	1.46	1.60	57.02	57.00	2.25	2.16	13422-75-8
$C_6H_5CH_2$-	32	171–173	35.78	35.80	1.42	1.42	55.59	55.53	2.19	2.20	13422-76-9

[a] *Anal.* Calcd for S: 5.16. Found: 5.01.

aqueous alcohol for several hours or on standing in aqueous alcohol for several days at room temperature. This was shown by the positive ninhydrin reaction test after the indicated treatments, but no further work was done with this.

The parent spiro structure of the products was substantiated as noted before. The nmr spectra displayed (see Experimental Section) two apparently unique features of the HN-CH coupling in these compounds. The first is observation of this coupling at all for an "amine." Slow exchange of the amine NH protons is implied ($\ll 2\pi \times J_{\mathrm{HNCH}} \approx 60\ \mathrm{sec}^{-1}$). Upon addition of a small amount of D_2O to the $CDCl_3$ and the pyridine solutions (R = H) the CH_2 doublet coalesces to a single line at its center (width at half-height ~1.8 Hz). This is attributed to replacement of the NH proton by deuterium. In pyridine solution where the spectrum was relatively strong, residual "satellite" lines at the original positions were seen and attributed to splitting by NH in equilibrium distribution of H and D among amine and water sites. The NH was not seen because OH lay at the same place in the spectrum. Thus, even with a significant amount of water present the NH exchange is slow. In DMSO-d_6 solutions, residual H_2O was seen separately, at approximately the same molar concentration. Very weak base character, if any, is implied. Rae has observed H-N-CH_3 splitting in N-methylbenzylamines when the pK_a values of the conjugate acid in water are less than 1.3.[7]

The second unusual feature is the size of the HN-CH coupling, 8.6–9.0 Hz. When R = *i*-C_3H_7, this coupling would be more reasonable for *cis* placement of the NH and CH protons on the five-membered ring (or, less likely, *trans* with dihedral angle closer to 180° than to 120°). When R = H, the 8.6-Hz coupling represents, strictly, the average value of the coupling of the NH proton to each CH_2 proton. This can come about in two ways, assuming that nitrogen is nonplanar: (1) fast inversion of the nitrogen occurs, so that the couplings (and chemical shifts) are the same on our time scale; (2) slow nitrogen inversion occurs, so that the HN-CH couplings differ, but appear to be the same (their average value) because of a small chemical shift and large coupling between the methylene protons. The first possibility seems more likely since there was no indication of deviation from the simple pattern with the solvent variation used.

The compounds in Table I were prepared and each was tested for insecticidal activity. The glycine reaction product showed good kills against the southern army worm, American cockroach, and confused flour beetle (*triboliam confusam*).

Experimental Section

Melting points are corrected (capillary) at 1.5°/minute. Infrared and nmr spectra were determined by Mr. R. A. Nyquist and by Dr. J. P. Heeschen, respectively. Mass spectrometry was obtained by M. Dilling, and elemental analysis was done by Mr. L. Swim.

Infrared spectra were recorded using a Beckman IR-9 spectrometer in the region 400–438 cm^{-1}. Solid-state spectra were recorded using the mull technique, and the mulling agents used were Nujol (400–1333 cm^{-1}) and Fluorolube (1333–3800 cm^{-1}). The nmr were determined on a Varian A-60 spectrometer with the probe at ambient temperatures (~25°) in $CDCl_3$. The chemical shifts are reported as shielding (parts per million) relative to internal tetramethylsilane. Mass spectra were obtained with a CEC-110 high resolution mass spectrometer with a direct probe inlet (120°).

A specific synthesis is given and is applicable with only minor variations to the preparation of the other compounds listed in Table I.

Preparation of 1,1a,3,3a,4,5,5,5a,5b,6-Decachlorooctahydro-4′-isopropylspiro[1,3,4-metheno-2H-cyclobuta[*c,d*]pentalene-2-2′-oxazolidin]-5′-one. A. Purification and Dehydration of Starting Material.—1,1a,3,3a,4,5,5,5a,5b,6-Decachlorooctahydro[1,3,4-metheno-2H-cyclobuta[*c,d*]pentalene]-2-one (500 g) (H-1 ketone from the Eastern Chemical Division of Hooker Chemical Corp.) was placed in a 5-l., single-necked, round-bottomed flask with 3000 ml of dried (magnesium sulfate) *m*-xylene. The flask was fitted with a Glas-Col heating mantle, a magnetic stirrer, and a reflux condenser. After refluxing for 0.5 hr the solution was decolorized with charcoal (Darco activated carbon, Atlas Powder Co.) and was filtered while hot into a dry 5-l. single-necked, round-bottomed flask equipped with a Glas-Col heating mantle, a magnetic stirrer, and a Dean-Stark phase separator. After the solution was brought to a boil, the solvent was recycled through the phase separator until all the water was removed; this process usually consumed 24 hr. The decolorization was repeated if needed; then the hot filtrate was chilled in an ice bath and the anhydrous ketone was allowed to crystallize. The large crystals were collected on a Büchner funnel, washed with small quantities of chilled *m*-xylene, transferred to a drying dish,

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[7] I. D. Rae, *Australian J. Chem.*, **19**, 409 (1966).

and dried in a vacuum oven at 80° for 24 hr. The yield of first crop was 260 g; upon evaporation of the filtrate a total of 430 g (86%) of pure ketone was obtained, mp 348–349.5°.

B. **Reaction of DL-Valine with II.**—Into a 2-l., single-necked, round-bottomed flask, equipped with a Glas-Col heating mantle, a magnetic stirrer, and a phase separator, was placed 245 g (0.50 mole) of II and 1400 ml of *m*-xylene. The mixture was heated to reflux and the solvent was recycled for 0.5 hr, then cooled slightly, and 58.5 g (0.50 mole) of DL-valine were added all at once. The reaction mixture was reheated to reflux and the solvent was recycled until all water was removed; this process usually consumed 48 hr. After the reaction was completed the solution was decolorized. The hot filtrate was chilled in an ice bath. The product was collected by suction filtration and washed with small quantities of chilled *m*-xylene. After drying in a vacuum oven at 45° for 24 hr the crude yield of 207 g (70%) was obtained. Evaporation of the mother liquor gave an additional 53 g of product giving a total crude yield of 88%, mp 178–186°.

The first and second crops were combined and dissolved in the minimum amount of refluxing toluene; a 10% excess of solvent was added and the solution was filtered while hot. The filtrate was allowed to cool to room temperature and then chilled in an ice bath. The white crystals were removed by suction filtration and dried in a vacuum oven at 45° for 24 hr to give a first, recrystallized crop of 208 g (70% yield). Evaporation of the toluene from the filtrate will give an additional 50 g of nearly pure material for a total recrystallized yield of 87%. The melting point of the pure lactone is 186–187°. The structure was confirmed by infrared spectra, nuclear magnetic resonance and elemental analysis (see Table I).

Spectra.—The reaction product from glycine (R = H) and Kepone gave an infrared spectra having the specific absorption at 2923 cm^{-1} ($\nu_{anti,sym\text{-}CH_2}$), 2850 cm^{-1} ($\nu_{sym\text{-}CH_2}$), 3320 cm^{-1} ($\nu_{NH}$), 3300 cm^{-1}, shoulder (ν_{NH}), 1821 cm^{-1} ($\nu_{C=O}$), and 1805 cm^{-1} ($\nu_{C=O}$). There are doublets for the ν_{NH} and $\nu_{C=O}$ due to crystal splitting. There are no absorptions inconsistent with the assigned structure where R = H.[4]

The mass spectra of the same compound showed the molecular weight to be 543 (calcd: 543). The Cl^{37}/Cl^{35} ratios show the presence of ten chlorine atoms for each molecule. The most abundant ions formed were $C_5Cl_6^+$ (*m/e* 270); this is characteristic of perchloropentacyclodecane derivatives.[8] These data and the rest of the fragmentation pattern are consistent with the proposed structure although some isomers cannot be ruled out.

The nmr spectra of the compound, when R = H, were run as saturated solutions in $CDCl_3$ and in DMSO-d_6 and 19.7% w/v in pyridine. Spectra were consistent with the proposed structure, plus toluene impurity. The integrals in pyridine solution agreed with assignment; the spectra in $CDCl_3$ and in DMSO-d_6 were too weak to give useful integrals, but appeared to be consistent. There was no observable evidence for nonequivalence of the CH_2 protons. The observed coupling between NH and CH_2 protons is 8.6 ± 0.2 Hz in pyridine and is approximately the same in the other solvents. The CH_2 group was a simple doublet in all solvents (J_{HN-CH_2} = 8.6 ± 0.2 Hz in pyridine, approximately the same in $ClCl_3$ and in DMSO-d_6), and the NH proton was a triplet with the same splitting, when seen (see Table II).

TABLE II

CHEMICAL SHIFTS TAKEN AS CENTERS OF PATTERNS

Proton groups	Chemical shifts, ppm In $CDCl_3$	In pyridine	In DMSO-d_6
NH	Not found	-5.61 ± 0.03	$-4.67 + 0.03$
CH_2	-3.78 ± 0.03	-4.05 ± 0.02	-3.77 ± 0.03

The nmr spectra of the compound, when R = *i*-C_3H_7 run as a 20.4% (w/v) solution in $CDCl_3$, is consistent with the assigned structure. Integration gave appropriate proton ratios. Chemical shifts, taken as the centers of the assigned structured groupings, were, ring CH, −3.78 ± 0.02 ppm; NH, −2.40 ± 0.03 ppm; isopropyl CH, −2.3 ppm; one isopropyl CH_3, −1.10 ± 0.02 ppm, other isopropyl CH_3, −1.05 ± 0.02 ppm. The isopropyl CH was relatively weak and overlapped the NH absorption, so that its position was not defined well. The NH lines were 3 Hz wide at half-height of the maximum peak. The observed coupling constants were J_{HNCH} = 9.0 ± 0.1 Hz; J_{HCCH} = 4.8 ± 0.1 Hz; J_{HCCH_3} = 6.8 ± 0.1 Hz.

Registry No.—II, 143-50-0.

Acknowledgment.—The authors wish to thank Mr. E. E. Kenaga for permission to use his results on the insecticidal properties of these compounds and Mr. N. DeHaas for some of the laboratory syntheses.

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[8] W. L. Dilling and M. L. Dilling, *Tetrahedron*, **23**, 1225 (1963); personal communication (M. L. D.).

2,2'-Thiobis(benzoxazole) and 3-(2-Benzoxazolyl)-2-benzoazolinethione

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Received May 4, 1967

In a recent publication,[1] we reported that the reaction of sodium 2-mercaptobenzoxazole with 2-chlorobenzoxazole in dimethylformamide at temperatures of 140–150° yielded 2,2'-thiobis(benzoxazole) (1). It was suggested by Gloede[2] that the product isolated in the above reaction was not 1 but its rearranged isomer, 3-(2-benzoxazolyl)-2-benzoazolinethione (2). They reported that the reaction of 2-mercaptobenzoxazole with 2-chlorobenzoxazole at 170–180° furnished 2 in 60% yield. Upon a more careful analysis based on infared and ultraviolet spectral data, the crude product isolated under our reaction conditions contained 75 and 19% of 2 and 1, respectively. However, by lowering the temperature to 80–90° and replacing the sodium 2-mercaptobenzoxazole with the potassium salt, we were able to obtain a crude product containing 92 and 6.5% of 1 and 2, respectively. Attempts to analyze a recrystallized sample of 1 (99.5%) by vpc at 260° resulted in rearrangement of 1 to 2. Moreover, 1 was converted to 2 by heating at 140–150° in dimethylformamide or without solvent at 170–180° (Scheme I). In contrast to the rearrangement of 2,2'thiobis(benzothiazole) to 3-(2-benzothizolyl)-2-benzothiazolinethione,[3] the conversion of 1 to 2 can be accomplished at much lower temperatures and without the use of a catalyst.

Experimental Section[4]

Analytical Methods.—Analyses of reaction products for 1 and 2 were made with a Perkin-Elmer Model 21 infrared spectrophotometer using 0.1-mm sodium chloride cells. Compound 1 had a 1506-cm^{-1} absorption band essentially free from interference from 2 while 2 had a 1028-cm^{-1} absorption band with only slight interference from 1. Calibration curves for 1 and 2 were prepared by measuring the absorbances of standard 5% (w/v) chloroform solutions covering the range of 0–100% for each compound. The reaction products were analyzed using the same procedure as in the calibration.

The ultraviolet spectra were determined using a Cary Model 11 spectrophotometer and matched 1-cm quartz cells. The ultraviolet spectra of 1, 2, 2-methylthiobenzoxazole (3), anp

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[1] J. J. D'Amico, *et al.*, *J. Org. Chem.*, **30**, 3618 (1965).

[2] H. Gross and J. Gloede, *Z. Chem.*, **5**, 178 (1965).

[3] J. J. D'Amico, *et al.*, *J. Org. Chem.*, **30**, 3628 (1965).

[4] All melting points were taken upon a Fisher-Johns block and are uncorrected.