TABLE I

RATES OF ALKALINE HYDROLYSIS OF ETHYL BENZOATE IN AQUEOUS DIMETHYL SULFOXIDE

Solvent, % by vol.	Temp., °C.	$k_2 \times 10^4$ l./mole/sec.	Rel. rate
85% aq. EtOH	25.0	7.0[a]	1
85% aq. DMSO[b]	25.0	2240 ± 80[c]	320
	20.0	1550 ± 50	
	15.0	1050 ± 15	
	10.0	735 ± 20	
80% aq. DMSO	25.0	1140 ± 34	160
	20.0	810 ± 20	
	15.0	550 ± 20	
	10.0	385 ± 30	
75% aq. DMSO	25.0	660 ± 27	94
	20.0	480 ± 8	
	15.0	350 ± 35	
	10.0	250 ± 15	
70% aq. DMSO	30.0	700 ± 28	
	25.0	500 ± 14	71
	20.0	350 ± 9	
	15.0	250 ± 6	
65% aq. DMSO	35.0	770 ± 10	
	30.0	535 ± 15	
	25.0	380 ± 26	54
	20.0	270 ± 7	
	15.0	180 ± 16	

[a] R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.*, 538 (1937). [b] Dimethyl sulfoxide. [c] One standard deviation unit.

TABLE II

THERMODYNAMIC ACTIVATION PARAMETERS FOR ALKALINE HYDROLYSIS OF ETHYL BENZOATE IN AQUEOUS DIMETHYL SULFOXIDE

Solvent	Mole fraction of organic component	ΔH^*, cal./mole	ΔS^*, e.u.
Aq. EtOH[a]	0.334	15,490	−19.2
	0.444	16,020	−19.0
	0.493	16,400	−17.0
	0.690[b]	17,320	−15.8
	0.850	18,420	−12.4
Aq. DMSO	0.320	11,700 ± 240[c]	−26 ± 3
	0.372	11,500 ± 120	−26 ± 1
	0.433	10,200 ± 300	−30 ± 3
	0.504	11,200 ± 400	−25 ± 4
	0.591	12,200 ± 250	−21 ± 3

[a] Obtained from data of ref. 10. [b] C. A. Burkhard and R. E. Burnett, *J. Am. Chem. Soc.*, **80**, 341 (1958). [c] One standard deviation unit from the mean.

solvation[5] with concomittant decrease in free energy of activation.

The data in Table II reveal that substitution of aqueous dimethyl sulfoxide for aqueous ethanol leads to both a reduced entropy and enthalpy of activation with the enthalpic change controlling the free energy of activation in agreement with the Hughes–Ingold theory of solvent effects on reaction kinetics.[9] Although the small differences in activation parameters provide only a slight basis for an anomalous dependency of activation enthalpy upon the mole fraction of dimethyl sulfoxide, such speculation is tempting. Further work is planned in this area to describe more adequately the solvation mechanism.

Experimental

Preparation of Materials.—Ethyl benzoate (n^{20}_D 1.5048) was purified by fractional distillation and analysis by g.l.p.c. gave only a single sharp peak. Dimethyl sulfoxide was dried over 4A Molecular Sieves and analysis by g.l.p.c. did not reveal the presence of any significant amount of impurity. The dimethyl sulfoxide–water—sodium hydroxide mixtures were prepared according to the following scheme: a weighed quantity of sodium hydroxide was dissolved in a measured volume of water which in turn was diluted with measured volumes of dimethyl sulfoxide to give, respectively, 65, 70, 75, 80, and 85% (by volume) aqueous dimethyl sulfoxide solutions approximately 0.05 *N* in sodium hydroxide. In all cases, mixing dimethyl sulfoxide with water produced a shrinkage of the total volume.

Rate Measurements.—The kinetic experiments were carried out using both ester and sodium hydroxide in equal concentrations (about 0.05 *M*). The ester was weighed out in a volumetric flask, placed in a constant temperature bath (accurate to ±0.1°), and rapidly brought up to volume with the appropriate solvent mixture (pre-equilibrated to the reaction temperature, zero time was recorded as the time when one-half the solvent had been added). Aliquots were removed periodically; the reaction was quenched by addition to an excess of aqueous hydrochloric acid of known normality, and finally back-titrated with standardized aqueous sodium hydroxide to a bromthymol blue end point. The values of k_2 were calculated from the second-order reaction rate equation

$$k_2 = x/at\,(a - x)$$

where a is the initial concentration of each reactant and $a - x$ is the concentration of each reactant at time t. All of the measured reactions followed strictly second-order kinetic law, and consumed, within experimental error, 100% of the base present.

Treatment of the Kinetic Data.—The thermodynamic activation functions were obtained by IBM 1620 computer regression analysis of ln k/T *vs.* $1/T$.

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(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 345-350.

Preparation of Tetracyclopropyllead and a Study of Some of Its Cleavage Reactions

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Research in organometallic chemistry hasl ead to the discovery of many well-known aliphatic and aromatic lead compounds. Organometallic compounds containing small groups such as the vinyl and cyclopropyl have aroused much interest in the past few years. Tetravinyllead has been prepared[1]; moreover, vinyl metal compounds have been extensively studied with examples having been prepared for common metals in all the A families of the periodic table. Although larger cycloalkyllead compounds have been reported,[2,3] the preparation of tetracyclopropyllead could not be found in the literature. Only a few cyclopropylmetal compounds have been reported, among which are cyclopropyllithium,[4] cyclopropylmagnesium bromide,[5] and dicyclopropylmercury.[6] Recently, some cyclopropyl compounds of the group IV elements—silicon, germanium, and tin—have been prepared.[7]

We have prepared the last cyclopropyl organometallic compound of the group IV-A family, tetracyclopro-

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(1) E. C. Juenge and S. E. Cook, *J. Am. Chem. Soc.*, **81**, 3578 (1959).

(2) E. Krause and O. Schlottig, *Ber.*, **58**, 427 (1925).

(3) G. Gruttner, *ibid.*, **47**, 3257 (1914).

(4) H. Hart and J. M. Sandri, *Chem. Ind.* (London), 1014 (1956).

(5) J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 3176 (1951).

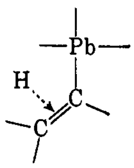
(6) G. F. Reynolds, R. E. Dessy, and H. H. Jaffe, *J. Org. Chem.*, **23**, 1217 (1958).

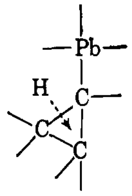
(7) D. Seyferth and H. M. Cohen, *Inorg. Chem.*, **1**, 913 (1962).

pyllead, from lead dichloride and cyclopropylmagnesium bromide. Tetracyclopropyllead, like tetraethyllead and tetravinyllead, was found to explode upon heating to elevated temperatures but could be distilled at reduced pressure without decomposition.

We have also found that cyclopropyllead salts can be prepared by reactions analogous to those used for the preparation of alkyl, aryl,[8] and vinyl[1] lead salts. Thus, tricyclopropyllead chloride and dicyclopropyllead dichloride were prepared from the reaction of tetracyclopropyllead with hydrogen chloride and chlorine, respectively.

The cyclopropyl group like the vinyl group was found to be more readily cleaved from lead than the ethyl group. Tetravinyllead has been reported to react more readily with acetic acid than tetraethyllead.[1] A mixture of equivalent amounts of tetracyclopropyllead and acetic acid with silica gel as catalyst gave, at room temperature, immediate but slow evolution of gas and formation of a solid within 24 hr. An equivalent mixture of tetracyclopropyllead and acetic acid when heated to 90° gave immediate formation of a white solid. It was shown that equivalent amounts of tetraethyllead and acetic acid with silica gel as catalyst showed, at room temperature, no sign of reaction or formation of solid after 24 hr.[1] Browne and Reid[9] have also shown that an equivalent mixture of tetraethyllead and acetic acid with silica gel as catalyst gave, when refluxed at 100°, slow evolution of gas and required about 30 min. to produce a good yield of triethyllead acetate. Similar cleavage tendencies were observed from more dilute solutions of tetraethyl, tetravinyl, and tetracyclopropyllead in acetic acid. At one dilution, precipitation occurred in 2 hr. with tetravinyllead, 10 hr. with tetracyclopropyllead, and not within 24 hr. with tetraethyllead. The ease of cleavage of vinyl and cyclopropyl groups may be associated with the π- and the partial π-character, respectively, of these groups permitting protonation at π-centers followed by rupture of the neighboring lead-to-carbon bond.





Similar effects of the vinyl and cyclopropyl groups have been reported,[10] such as the high *ortho*-to-*para* ratios of nitration products of styrene and phenylcyclopropane. Comparison of ease of cleavage of tetravinyl- and tetracyclopropyllead is complicated by production of different products by reaction with carboxylic acids.

Products obtained in reactions of carboxylic acids with tetracyclopropyllead were generally not pure. Reaction of tetracyclopropyllead with equivalent amounts of acetic acid, monochloroacetic acid, and dichloroacetic acid yielded essentially dicyclopropyllead salts (I), while trichloroacetic acid yielded primarily tricyclopropyllead salts (II) with some dicyclopropyllead salts. It is reported[11] that the reaction of a plumbane with a carboxylic acid often yields a trialkyllead salt but that sometimes a dialkyllead salt or a mixture of these compounds is obtained. Thus, pure products are sometimes difficult to obtain,[9] and our work presents some further examples of the formation of dialkyllead salts by the reaction of plumbanes with carboxylic acids. Moreover, it is illustrated that the plumbane may be an important factor governing which salt is produced. Dithizone technique[12] was employed to determine the approximate content of di- and tricyclopropyllead salts produced. Carbon and hydrogen analyses obtained on the impure products seemed consistent with the dithizone results. In those reactions producing essentially pure products, a total lead per cent was also determined by dithizone technique (Table I).

TABLE I

DITHIZONE ANALYSES[12]

For reaction $Cp_4Pb \xrightarrow{RCOOH} \cdot \underset{I}{Cp_2Pb(OCOR)_2} + \underset{II}{Cp_3PbOCOR^a}$

Acid reactant	Dialkyllead salt (I), %	Trialkyllead salt (II), %	Total Pb, % calcd.	Total Pb, % found
CH_3COOH	95+[b]	Trace	50.9 (I)	49.2
$ClCH_2COOH$	95+[b]	Trace	43.5 (I)	42.6
Cl_2CHCO_2H	95+[c]	Trace	38.0 (I)	36.9
Cl_3CCO_2H	25	75		

[a] Cp = cyclopropyl. [b] C–H analysis was slightly high when calculated for dialkyllead salt. [c] C–H analysis was consistent for the dialkyllead salt.

The reactions between equivalent amounts of tetracyclopropyllead and mono-, di-, and trichloroacetic acids gave a white solid almost immediately at room temperature. Precipitation from ether solutions was slower with the rate of precipitation increasing with increased acidity of the chloro acid.

Seyferth and Cohen[7] reported that the most noticeable feature of the infrared spectra of many cyclopropylmetal compounds is the strong absorption near 900 cm.$^{-1}$. Moreover, this peak seems to be characteristic of the atom to which the cyclopropyl group is attached. Thus, in the IV-A family it has been shown that increased wave lengths for cyclopropylmetal compounds occur with increased atomic weights in the progression silicon, germinium, and tin. We have found that tetracyclopropyllead is consistent with this progression, absorbing at the highest wave length of the series (see Table II).

TABLE II

INFRARED ABSORPTION PEAKS OF CYCLOPROPYLMETAL COMPOUNDS

Compounds	Infrared absorption, cm.$^{-1}$
Cyclopropyltrimethylsilane	902
Cyclopropyltrimethylgermane	888
Cyclopropyltrimethyltin	875
Tetracyclopropyllead	865

Further work is planned to investigate the relative cleavage rates of cyclopropyllead and vinyllead compounds and to examine the products obtained in these reactions.

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[8] G. Gruttner, *Ber.*, **51**, 1298 (1918).

[9] O. H. Browne and E. E. Reid, *J. Am. Chem. Soc.*, **49**, 830 (1927).

[10] R. Ketcham, R. Cavestri, and D. Jambotkar, *J. Org. Chem.*, **28**, 2139 (1963).

[11] R. Heap, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 658 (1951).

[12] M. E. Griffing, A. Rozek, L. J. Snyder, and S. R. Henderson, *Anal. Chem.*, **29**, 190 (1957).

Experimental[13]

Cyclopropyl bromide was prepared according to the excellent procedure described by Professor J. S. Meek, University of Colorado.[14]

Tetracyclopropyllead.—The cyclopropylmagnesium bromide was prepared from 5.08 g. of magnesium, 25 g. of cyclopropyl bromide, and 175 ml. of tetrahydrofuran as solvent.[5] The reaction was allowed to cool to room temperature and 42 g. of lead dichloride was added with constant stirring over a period of 25 min. The reaction mixture appeared green-brown in color, turning deep black from lead deposition near the end of the reaction. The system was then refluxed in an oil bath at 70–80° for 90 min. The tetrahydrofuran was then removed under slightly reduced pressures at an oil bath temperature of 40–45°. After the tetrahydrofuran had been removed, the system was connected to a cold trap (−80°), the pressure was reduced to about 0.1 mm., and the oil bath temperature was raised to 90°. After 30 hr., 10.4 g. of crude product had collected. The crude product (mol. wt. calcd., 371.5; found, 398) was redistilled, yielding 7.54 g. (29.8% yield) of colorless liquid boiling at 57–58.5° (0.1 mm.). A middle cut boiling at 58° (0.1 mm.), $n^{24}\text{D}$ 1.5505, was taken for analysis.

Anal. Calcd. for $C_{12}H_{20}Pb$: C, 38.79; H, 5.44. Found: C, 38.70, 38.48; H, 5.73, 5.62.

Tricyclopropyllead Chloride.—To a clean, dry test tube was added 215 mg. of tetracyclopropyllead and an equivalent amount of concentrated hydrochloric acid. A white precipitate formed immediately. The reaction was allowed to stand for 1 hr. with frequent stirring. The crystals were then washed with *n*-hexane and filtered. The yield was 186 mg. (84% yield) of colorless crystals, m.p. 173–174°.

Anal. Calcd. for $C_9H_{15}ClPb$: C, 29.55; H, 4.13. Found: C, 29.57; H, 4.21.

Dicyclopropyllead Dichloride.—A solution of 57.5 mg. of tetracyclopropyllead in 5 ml. of *n*-hexane was saturated with chlorine gas during which time precipitation occurred. The mixture was allowed to sit for 1 hr. with occasional addition of chlorine. The precipitate was collected, washed with *n*-hexane several times, and dried under vacuum at room temperature leaving 44.8 mg. (81%) of dicyclopropyllead dichloride, m.p. 250° dec.

Anal. Calcd. for $C_6H_{10}Cl_2Pb$: C, 20.00; H, 3.00. Found: C, 20.34; H, 2.82.

Dicyclopropyllead Bisdichloroacetate.—Tetracyclopropyllead (200 mg., 0.54 mmole) and 70 mg. of dichloroacetic acid (0.54 mmole) were mixed in 5 ml. of ether. After about 3 hr., precipitation began. After 20 hr., the white needles were collected, washed several times with 5-ml. portions of ether, and dried under vacuum at room temperature. The yield was 130 mg., m.p. 179–180° dec.

Anal. Calcd. for $C_{10}H_{12}Cl_4O_4Pb$: C, 22.03; H, 2.22. Found: C, 21.89; H, 2.48.

Other lead salts reported in Table I were obtained by similar reactions. Products in these cases were impure or mixtures, and dithizone analyses for them are reported in Table I also.

Acknowledgment.—The authors gratefully acknowledge Mr. S. R. Henderson of Ethyl Corporation for analyses and to the Ethyl Corporation for samples of tetraethyllead used in these studies.

(13) Analyses were by Drs. G. Weiler and F. B. Strauss, Oxford, England.

(14) We are indebted to Mr. Dean Sinclair, Kansas State University, for bringing this excellent procedure to our attention.

Michael Addition of Hydroxylamines to Activated Double Bonds. A Convenient Synthesis of N,N-Dialkyl Hydroxylamines

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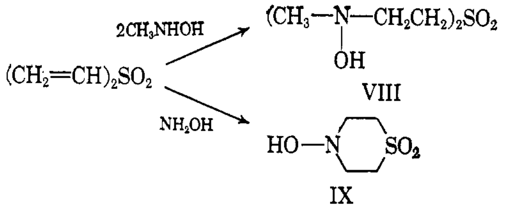
N,N-Dialkyl hydroxylamines have not been readily available, because attempts to synthesize them by dialkylation of hydroxylamine and by oxidation of secondary amines have given low yields, and the thermal decomposition of N-oxides have been restricted to the lower aliphatic members. We have found that a satisfactory route to these compounds lies in the addition of N-alkyl hydroxylamines to activated double bonds, a reaction not previously reported, although hydroxylamine itself has been used in addition reactions with methyl acrylate,[3] cinnamates,[4] mesityl oxide,[5] chalcones,[6] nitro olefins,[7,8] acrylonitrile,[9] 2-vinylpyridines,[10] diphenylmethylene carbamate,[11] and vinyl ketones.[12] In these cases, the products were generally the 1:1 adducts, which, on consideration of the difunctional character of the hydroxylamine, might not have been expected.

From the reaction of N-methylhydroxylamine with a number of vinyl compounds we obtained high yields of N-methyl-N-alkyl hydroxylamines (Table I). N,N-Dialkyl hydroxylamines were also produced by the reaction of hydroxylamine with vinyl sulfones and vinylpyridines (Table II), and in no case could the monosubstituted hydroxylamine, the 1:1 adduct, be isolated.

The expected product, bis(2-N-methylhydroxylaminoethyl) sulfone (VIII), was obtained when divinyl sulfone was allowed to react with N-methylhydroxylamine. However, in the reaction of divinyl sulfone with hydroxylamine, cyclization occurred and 4-hydroxytetrahydro-1,4-thiazine 1,1-dioxide (IX) was produced almost quantitatively. That IX is indeed the product, having arisen by intramolecular rather than intermolecular condensation, is indicated by the fact that it was also obtained, as the only product, from a high dilution experiment. Cyclic addition products have been isolated from the reaction of divinyl sulfones and primary amines.[13]



Experimental[14]

Vinyl Compounds.—The acrylamide, 2-vinylpyridine, 4-vinylpyridine, and divinyl sulfone used were the commercially available materials. Vinyl ethyl sulfone, b.p. 69–70° (0.7 mm.), was synthesized from 2-chloroethyl ethyl sulfone and triethylamine,[15] rather than by the dehydration of 2-hydroxyethyl ethyl sulfone[16] which was unsatisfactory.

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(1) To whom inquiries should be directed.

(2) Polaroid Corp., Cambridge, Mass.

(3) C. Harris and W. Harrmann, *Ber.*, **37**, 252 (1904).

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(5) C. Harris, *et al.*, *ibid.*, **36**, 656 (1903), and preceeding publications.

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(10) H. E. Reich and R. Levine, *J. Am. Chem. Soc.*, **77**, 5434 (1955); L. Bauer, A. Shoeb, and V. C. Agwada, *J. Org. Chem.*, **27**, 3153 (1962).

(11) S. R. Safir and R. J. Lopresti, *J. Am. Chem. Soc.*, **80**, 4921 (1960).

(12) D. J. Casey and C. S. Marvel, *J. Org. Chem.*, **24**, 1022 (1959).

(13) A. C. Bellaart, *Rec. trav. chim.*, **81**, 156 (1962).

(14) Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Analyses were by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.