plets centered at 4.75 and 4.63 ppm ($>C{=}CH_2$), a singlet at 2.16 ppm ($-CH_2\overset{|}{C}{=}$), a broad singlet at 1.77 ppm (ring protons), a broad partially resolved singlet at 1.62 ppm ($CH_3\overset{|}{C}{=}$), and a singlet at 1.43 ppm (-O-H).

Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59. Found: C, 79.07; H, 10.53.

Preparation of Isobutylmagnesium Chloride.[11]—Magnesium turnings (1.17 g, 0.048 g-atom) were placed in the reaction flask, and after the system had been swept with dry nitrogen for several minutes, a solution of 0.18 g (0.002 mole) of isobutyl chloride in 10 ml of sodium-dried ether was added. Initiation of the reaction was effected by the addition of several drops of ethyl bromide followed by warming on a water bath. To the moderately stirred mixture was added a solution of 4.44 g (0.048 mole) of isobutyl chloride in 25 ml of sodium-dried ether at a rate such that gentle refluxing was maintained. Stirring was continued for 2 hr after the addition of halide had been completed, and the reaction mixture was allowed to stand overnight.

Reaction of Isobutylmagnesium Chloride with Δ^2-Cyclohexenone.[12]—To the above suspension was added, in turn, 50 mg (0.51 mmole) of freshly prepared cuprous chloride,[8] and a solution of 1.92 g (0.020 mole) of Δ^2-cyclohexenone in 50 ml of sodium-dried ether. After employing the previously described isolation procedure, gas chromatographic analysis[9] of the crude reaction mixture revealed the presence of alcohol VI (35%) and ketone VII (63%, components listed in order of increasing retention time). The remainder of the product mixture (2%) was material of lower volatility which was not characterized.

A pure sample of the alcohol VI,[9] $n^{25}D$ 1.4708, exhibits infrared absorption[10] at 3625 (unassociated O-H) and 1645 cm^{-1} (*cis* CH=CH). The nmr spectrum[10] of the sample has a singlet at 5.54 ppm (-CH=CH-), a broad singlet at 1.64 ppm (ring protons), a doublet at 1.41 and 1.33 ppm ($-CH_2CH<$), a singlet at 1.27 ppm (-O-H), and a doublet at 0.97 and 0.88 ppm [$-CH(CH_3)_2$].

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.98; H, 11.87.

A pure sample of the ketone VII,[9] $n^{24.5}D$ 1.4527 (lit.[6] $n^{25}D$ 1.4525), exhibits infrared absorption[10] at 1715 cm^{-1} (C=O). The nmr spectrum[10] of the sample has a broad multiplet centered at 1.81 ppm (ring protons) and a doublet at 0.91 and 0.81 ppm [$-CH(CH_3)_2$].

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.72; H, 11.95.

In the absence of cuprous chloride, gas chromatographic analysis[9] of the crude reaction mixture revealed the presence of alcohol VI (97%) and ketone VII (3%, components listed in order of increasing retention time).

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[11] The apparatus was identical with that used for the preparation of β-methylallylmagnesium chloride.

[12] The procedure was identical with that for the reaction of β-methylallylmagnesium chloride with Δ^2-cyclohexenone.

Ozonolysis of 1,2,3,4,7,7-Hexachlorobicyclo[2.2.1]hepta-2,5-diene

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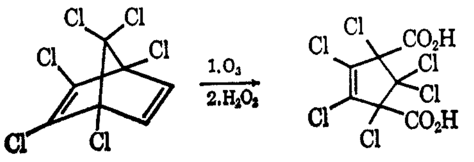
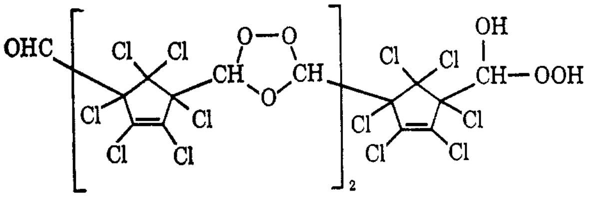
The present work was initiated with the desire of obtaining 1,2,2,3,4,5-hexachloro-4-cyclopentene-1,3-dicarboxylic acid (II) by oxidative ozonolysis[1] of 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]-2,5-heptadiene (I).



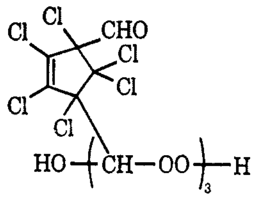
I II

There are numerous descriptions in the literature of this method for obtaining dibasic acids from cyclic aliphatic and aromatic olefins.[2-15] Although different intermediates can be isolated from ozonation in participating and in nonparticipating solvents, oxidation generally results in the same dibasic acid. In the present case the reaction did not give the expected high yields of II. However, several intermediate products were isolated which provide additional evidence for the Criegee[1b] mechanism of double bond ozonolysis.

Ozonation of I in either carbon tetrachloride at 0° or pentane at −78° gave a white solid which was determined to be the trimer III by the infrared spectrum (which has carbonyl and hydroxyl bands), nmr spectrum, elemental analysis, molecular weight determination, active oxygen determination, and polarogram. The polarogram shows two half-wave potentials (Table I) which probably correspond to reduction of the ozonide and hydroperoxide, respectively. The aldehyde would not be expected to give a half-wave poten-



III



IV

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[1] For reviews on ozonation, see (a) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958); (b) R. Criegee, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **18**, 111 (1957); (c) R. Criegee, "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, pp 29-39.

[2] A. Rieche, *Ber.*, **63**, 2642 (1930).

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[7] R. H. Perry, Jr., *J. Org. Chem.*, **24**, 829 (1959); R. H. Perry, U. S. Patent 2,963,487 (Dec 6, 1960).

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[9] A. Maggiolo, M. Tumolo, and A. L. Tumolo, U. S. Patent 3,023,233 (Feb 27, 1962).

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[14] (a) P. S. Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956); (b) J. P. Wibaut and T. J. DeBoer, *Koninkl. Ned. Akad. Wetenschap., Proc., Ser. B*, **59**, 421 (1956); (c) W. F. O'Connor, W. J. Schmitt, and E. J. Moriconi, *Ind. Eng. Chem.*, **49**, 1701 (1957); (d) P. S. Bailey and S. B. Mainthia, *J. Org. Chem.*, **23**, 1089 (1958).

[15] P. S. Bailey, S. S. Bath, F. Dobinson, F. J. Garcia-Sharp, and C. D. Johnson, *ibid.*, **29**, 697 (1964).

tial in the range of this determination (+0.9 to −1.5 v) since most aldehydes which have been reported are reduced at less than −1.5 v. A positive test for peroxide was obtained with starch–iodide paper and also lead tetraacetate, the latter indicating the presence of hydroperoxide.[1a] The other probable structure (IV) for the polymer was ruled out by the nmr spectrum. Structure IV requires a ratio of aldehyde to total protons of 3:8; a ratio of about 1:7 was found.

TABLE I

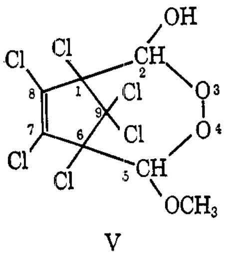
HALF-WAVE POTENTIALS *vs.* SCE[a]

Compd	$E_{1/2}$, v
III	−0.04, −1.18
V	−1.05
VI	−1.07
X	−1.05

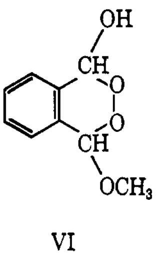
[a] Dme with medium of 0.3 M LiCl in 1:1 absolute methanol and benzene.

Structure III is similar to that proposed for the products from ozonation of phenanthrene[14d] and norbornylene[7] in nonparticipating solvents. In the case of norbornylene, however, the product was difficult to purify and conclusive elemental analyses were not obtained. Because of the similarity between I and norbornylene, the present work lends support to Perry's proposed structure for the ozonation product[7] of norbornylene. However, unlike Perry's work, our oxidation of the trimer III with hydrogen peroxide did not provide a high yield of the desired dibasic acid II but gave instead a mixture consisting of at least seven components. Further work-up was not attempted.

Ozonation of I in participating solvents provided a different set of reaction products, as would be expected.[1] Ozonation in methanol at 0° gave a white crystalline material, 1,6,7,8,9,9-hexachloro-2-hydroxy-5-methoxy-3,4-dioxabicyclo[4.2.1]-7-nonene (V). This structure was verified by the infrared spectrum (which showed a hydroxyl but no carbonyl band), elemental analysis, molecular weight determination, and polarogram. The polarogram showed a half-wave potential of −1.05 v compared with −1.07 v for the known compound 4-methoxy-2,3-benzodioxan-1-ol (VI)[15] (Table I). Starch–iodide gave a weakly positive test for peroxide whereas the lead tetraacetate test for hydroperoxide was negative.[1a]

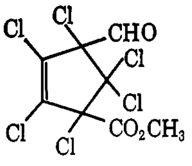


V

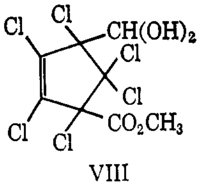


VI

When V was treated with 50% hydrogen peroxide in formic acid at 70° or above, a new compound resulted which gave peaks at 3545, 3440, 3250, and 1730 cm^{-1} in the infrared spectrum. Upon drying the compound *in vacuo* over phosphorus pentoxide, the bands at 3545, 3440, and 3250 disappeared and the carbonyl absorption shifted to 1745 cm^{-1} with a shoulder on either side. From the nmr spectrum (which gave only two peaks, 3.93 and 9.5 ppm, in an approximate area ratio of 3:1, respectively) and the elemental analysis, the latter compound was assigned the structure of methyl 1,2,2,3,4,5-hexachloro-3-aldehydo-4-cyclopentene-1-carboxylate (VII) and the former was given structure VIII, that of the hydrate of VII.

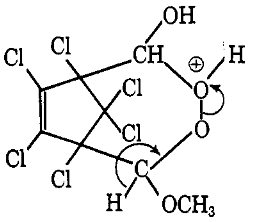


VII

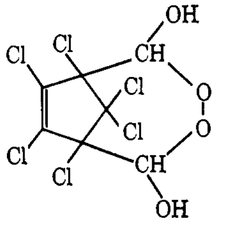


VIII

The conversion of V to VIII was found to occur in the presence of formic acid alone but not with refluxing carbon tetrachloride. By analogy to the work of Bailey and co-workers,[15] this rearrangement is probably due to protonic acid catalysis, possibly *via* IX.



IX



X

When I was ozonized in 90% formic acid, a white crystalline material was obtained which was determined to be 1,6,7,8,9,9-hexachloro-2,5-dihydroxy-3,4-dioxabicyclo[4.2.1]-7-nonene (X) by the infrared spectrum (which showed hydroxyl bands but no carbonyl band), elemental analysis, molecular weight determination, and polarogram. The half-wave potential of −1.05 v in the polarogram agrees well with V and VI[15] (Table I). The starch–iodide test was positive, and the lead tetraacetate test was weakly positive but only at higher temperatures. Treatment of X in formic acid with 50% hydrogen peroxide gave no reaction. Similar results were obtained when I was ozonized in (a) 50% aqueous formic acid followed by 50% hydrogen peroxide and dilute sulfuric acid; (b) water followed by hydrogen peroxide and sulfuric acid; and (c) an aqueous sodium hydroxide (2 mole equiv)–hydrogen peroxide (1.5 mole equiv) solution.[12]

It is interesting that 16 isomers of V and 8 isomers of X can be made with Stuart and Briegleb models. The conformations are so rigid that the peroxide oxygens may assume two different skewed positions for each of the optical and geometric isomers. Up to now we have been unable to determine which isomer(s) is present.

Oxidative ozonolysis of I in glacial acetic acid provided a 6% yield of an acid determined to be II by the infrared spectrum, elemental analysis, and acid number. As might be expected, II is a strong acid. The pK_a for the first dissociation step is 2.8, which is close to that of chloroacetic acid, pK_a = 2.85,[16] but which is considerably weaker than trichloroacetic

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[16] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 45th ed, The Chemical Rubber Co., Cleveland, Ohio, 1964, pp D-77, 78.

acid, pK_a = 0.70.[16] We were unable to esterify II by acid catalysis in alcoholic benzene, probably because of steric hindrance around the carboxyl groups owing to the presence of nearby bulky chlorine atoms. However, the dimethyl ester was synthesized by treatment of II with diazomethane.[17] If the difficulty in acid-catalyzed esterification were due to steric hindrance, it might be expected that acid hydrolysis of the dimethyl ester would also be difficult. This was found to be the case when attempted acid-catalyzed hydrolysis of the ester in aqueous acetone was unsuccessful.

Higher yields (about 30%) of II were finally obtained by treating V or X with 70% nitric acid. Other attempts to synthesize II by different routes, such as the treatment of I with potassium permanganate or concentrated nitric acid, failed.

Experimental Section[18]

General Ozonations.—Unless otherwise indicated, all ozonations were run by passing a stream of 2–5 wt % ozone in oxygen through a solution containing I at 20° at a rate of 56–72 mg of ozone/min; 1–1.25 moles of ozone was added per mole of reactant. The ozone was generated from a dry grade oxygen (minimum purity of 99.5%) by a Model T-23 ozonator manufactured by the Welsbach Corp., Philadelphia, Pa.

Ozonation of I in Carbon Tetrachloride.—A solution of 20 g (0.067 mole) of I in 125 ml of carbon tetrachloride was ozonized as above but at 0°. After stripping the solvent *in vacuo*, 20.6 g of a white solid remained which was recrystallized three times from a chloroform–hexane solvent couple to give III, mp 89–90.5°. The infrared spectrum (CCl_4) possesses peaks at 3500 (broad), 2950, 2925 (sh), 2860, 1780, 1750, 1610, and 1240 cm^{-1}, strong overlapping absorption in the 1200–925-cm^{-1} region, and a broad peak at 850 cm^{-1}. The nmr spectrum (CCl_4) shows one proton at 9.41 ppm, one at 4.97 ppm, and roughly five others in a multiplex between 6.5 and 3.3 ppm. The product was stable for only 1 day at 25° but for several months at −25°. Formation of the trimer III requires $^1/_3$ mole of water/mole of diene. The water most likely comes from storing the starting material under water prior to ozonation.[18,19]

Anal. Calcd for $C_{21}H_8Cl_{18}O_{10}$: C, 23.83; H, 0.76; Cl, 60.29; mol wt, 1058; active oxygen, 4.54. Found: C, 23.92; H, 0.74; Cl, 60.11; mol wt, 1044, 1089 (benzene); active oxygen,[20] 5.1.

Ozonation of I in Pentane.—Ozonation of I (9.8 g, 0.033 mole) in pentane as before, except at −78°, provided a white precipitate. No visible change was observed as the mixture warmed to room temperature. The product (III, 10.7 g.) was found to be the same as that found above by the infrared spectrum, melting point, and mixture melting point.

Ozonation of I in Methanol.[19]—A solution of 20 g (0.067 mole) of I in 75 ml of methanol was ozonized by the general method but at 0°. Evaporation of the solvent *in vacuo* provided an off-white, viscous liquid which gave 17.3 g of a solid after washing several times with hexane. The solid was recrystallized from carbon tetrachloride to give a white crystalline material (V), mp 132.5–133°. The infrared spectrum (halocarbon mull) shows peaks at 3485, 2970, 2935, 2840, 1600, 1445, 1400, 1335, 1250 cm^{-1}, and numerous bands in the fingerprint region, including 888, 860, 835, and 825 cm^{-1}.

Anal. Calcd for $C_8H_6Cl_6O_4$: C, 25.36; H, 1.59; Cl, 56.15; mol wt, 378. Found: C, 25.38; H, 1.61; Cl, 56.46; mol wt, 408 ($CHCl_3$).

Some of the crude V (5 g) obtained above was placed in a solution consisting of 50 ml of 90% formic acid and 6 ml of 50% hydrogen peroxide and the mixture was stirred at 40–50° for 2 hr. At one point during this period an exotherm pushed the temperature temporarily to 70–75°. On cooling, a bright yellow oil was obtained which, when quick frozen in a Dry Ice–acetone bath and brought back to room temperature twice, gave 2.5 g of a solid (VIII). Recrystallization from an acetone–hexane solvent couple gave white crystals, mp 98–100°. The infrared spectrum (halocarbon mull) shows peaks at 3545, 3440, 3250, 3080 (broad), 2940 (w), 2710 (w), 1730 1600, and 1430 cm^{-1}. When the sample was dried *in vacuo* over phosphorus pentoxide, a new white crystalline compound (VII) resulted, mp 70–71°. The infrared spectrum (halocarbon mull) shows peaks at 2945, 2850 (w), 1745 (with shoulders on both sides), 1600, and 1425 cm^{-1}. The nmr spectrum (acetone-d_6) shows single peaks at 3.93 and at 9.5 ppm in an approximate area ratio of 3:1, respectively.

Anal. Calcd for $C_8H_4Cl_6O_3$: C, 26.60; H, 1.12; Cl, 58.95. Found: C, 26.50; H, 1.25; Cl, 58.09.

Treatment of V with Solvent and Heat.—Heating V with 50% formic acid on a stream bath for 1 hr provided the same results as treatment of V with 90% formic acid and hydrogen peroxide. When carbon tetrachloride was used as a solvent, only V was recovered.

Ozonation of I in 90% Formic Acid.—A solution of 20 g (0.067 mole) of I in 120 ml of 90% formic acid was ozonized by the general method. To this mixture were added 18 ml of 50% hydrogen peroxide and then a stream of ozone–oxygen at an ozone flow rate of 34 mg/min for 2 hr. Cooling the reaction mixture in a 2-propanol–Dry Ice bath gave an oily solid which was filtered, washed several times with water, and dried *in vacuo*. A yellow powdery solid (14.3 g) resulted, which gave white crystals (X) on recrystallization from a carbon tetrachloride–ethyl acetate solvent couple. Drying *in vacuo* over phosphorus pentoxide at 65° to constant weight resulted in a melting point of 138–139°. The infrared spectrum (halocarbon mull) shows peaks at 3590, 3495, 3400, 3040 (broad), 2880, 2780, 1620, 1360, 1260, 1170, 1155, 1125, 905, 820, 790, and 700 cm^{-1}.

Anal. Calcd for $C_7H_4Cl_6O_4$: C, 23.05; H, 1.10; Cl, 58.31; mol wt, 364. Found: C, 23.46; H, 1.01; Cl, 58.14; mol wt, 365 (ethanol).

A similar ozonation without the oxidation step gave similar results.

Ozonation of I in Aqueous Solvents.—In each of the following systems ozonation of I gave X: (a) 50% aqueous formic acid followed by 50% hydrogen peroxide and dilute sulfuric acid; (b) water followed by 50% hydrogen peroxide and dilute sulfuric acid; and (c) aqueous sodium hydroxide (2 mole equiv) plus 1.5 mole equiv of 50% hydrogen peroxide.[12]

Ozonolysis of I in Glacial Acetic Acid.[19]—A solution of 36 g (0.12 mole) of I in 130 ml of glacial acetic acid was ozonized by the general method. To this mixture were added 20 ml of 50% hydrogen peroxide and 20 ml of 1 *M* sulfuric acid; the resulting mixture was allowed to stir overnight. An oil separated from the aqueous layer which was then decanted. The aqueous layer was extracted four times with 50–75 ml portions of ether after which the extracts were combined and dried over anhydrous magnesium sulfate. Evaporation of the ether gave a solid residue which was recrystallized several times from an ethyl acetate–hexane solvent couple to give 2.6 g (6%) of a white powdery solid (II), mp 258–259° dec. The infrared spectrum (halocarbon mull) shows peaks at 3100, 3000 (broad), 2870 (broad), 2650, 2520, 1730, 1620, and 1410 cm^{-1}. The pK_a = 2.8.

Anal. Calcd for $C_7H_2Cl_6O_4$: C, 23.17; H, 0.56; Cl, 58.63; acid no., 309. Found: C, 23.59; H, 0.54; Cl, 59.00; acid no., 303.8.

Treatment of the oily layer, which had been dissolved in ether, with a saturated sodium bicarbonate solution resulted in both the

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[17] Th. J. DeBoer and H. J. Backer, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 250.

[18] The 1,2,3,4,7,7-hexachlorobicyclo[2.2.1]hepta-2,5-diene, generously supplied by the Shell Chemical Co. and Velsicol Chemical Corp., was redistilled (98% by glpc) and stored under water prior to use. All melting points are corrected. The elemental analyses were performed by either Huffman Laboratories, Inc., Wheatridge, Colo., or Weiler and Strauss Microanalytical Laboratories, Oxford, England. The molecular weight determinations were made on a Mecrolab vapor pressure osmometer at several concentrations in the solvents indicated in each case. The infrared spectra were obtained on a Perkin-Elmer 237B grating spectrophotometer and the nmr spectra on a Varian A-60 spectrometer with tetramethylsilane as an internal standard.

[19] At the suggestion of a referee these reactions were rerun with dry solvents and with starting material that had been stored under dry nitrogen instead of water after distillation. In the case of the ozonation of I in carbon tetrachloride, the product was the same as before by infrared and nmr spectra, melting point, and molecular weight determination, indicating that the water for termination of the trimer must, at least in this case, come from the solvents during work-up. In the cases of ozonation of I in methanol and ozonolysis in glacial acetic acid, the products were identical with those obtained before by comparison of their melting points, mixture melting points, and infrared spectra.

[20] D. H. Wheeler, *Oil Soap*, **9**, 89 (1932).

ethereal layer and the extracts turning dark. The extracts were acidified with hydrochloric acid and extracted with ether, and the ether extracts were dried. Evaporation of the ether layers gave a small amount of a residue which did not contain any II.

Dimethyl Ester of II.—To 25 ml of an ethereal solution of about 0.2 g of diazomethane[17] was added dropwise a solution of 0.42 g (0.0016 mole) of II in 10 ml of ether. After being stirred at room temperature for 3 days, the mixture was filtered and evaporated *in vacuo* to give a tan solid which, after recrystallization in carbon tetrachloride, gave 0.2 g of white crystals, mp 138–139°. Vapor phase chromatography on a fluorosilicone column showed one component which is believed to be the *cis* isomer. The infrared spectrum (halocarbon mull) shows expected sharp peaks at 2955, 1755, 1595, and 1435 cm^{-1}.

Anal. Calcd for $C_9H_6Cl_6O_4$: C, 27.66; H, 1.55; Cl, 54.42. Found: C, 27.37; H, 1.41; Cl, 54.14.

Oxidation of V with Nitric Acid.—A mixture of 1.9 g (0.005 mole) of V and 15 ml of 70% nitric acid was heated on a steam bath, while being rapidly stirred, for 1 hr. When the mixture was allowed to cool slowly to room temperature without stirring, white crystals appeared which were filtered and washed with cold water. The filtrate was extracted several times with ether, and the combined ether extracts were washed with water before they were dried over anhydrous magnesium sulfate. Evaporation of the ether gave an off-white material which was washed with hot carbon tetrachloride to give, along with the white crystals, 0.55 g of II, as shown by the infrared spectrum, melting point, mixture melting point, and thin layer chromatography.

Oxidation of X with Nitric Acid.—In a similar fashion to the preceding experiment, oxidation of X with nitric acid gave II.

Acknowledgment.—The author is indebted to Dorothy J. Woessner and Arnold E. Bloomquist for excellent technical assistance and to Drs. Edward B. Dunning, Robert A. Grimm, and William E. Link for helpful discussions and suggestions. The author thanks the Archer Daniels Midland Company for permission to publish this work.

Carbonylation of Amines in the Presence of Palladium(II) Chloride. A New Route to Isocyanates

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Despite the availability of numerous methods for the preparation of isocyanates, the most widely used route to these important compounds is treatment of a primary amine or its salt with phosgene.[1] In this reaction, introduction of the carbonyl group proceeds stepwise, elimination of the first mole of HCl leading to formation of the carbamyl chloride from which the isocyanate is generated by elimination of a second mole of HCl.

It has now been found that a more direct preparation of isocyanates is effected by combining primary aliphatic or aromatic amines with carbon monoxide in the presence of $PdCl_2$. The reaction proceeds readily under rather mild conditions (Table I) and is accompanied by reduction of $PdCl_2$ to metal (eq. 1).

$$RNH_2 + CO + PdCl_2 \longrightarrow RNCO + Pd + 2HCl \quad (1)$$

TABLE I

CARBONYLATION OF AMINES IN THE PRESENCE OF $PdCl_2$

Amine	Pressure, atm.	Temp., °C.	Reaction time, hr.	Isocyanate yield, mole %
n-Butylamine	1.4	65	48	49.2
Aniline	1.4	80	96	53.4
Aniline	1.0	85	21	68.0
Toluene-2,4-diamine	1.0	85	2.5	9.2

While detailed information concerning the mechanism of this new and interesting reaction is lacking to date, several possible reaction paths can be eliminated from further consideration. For example, formation of formamides from amines and carbon monoxide in the presence of a number of transition metal salts and carbonyls has been reported.[2] One might, therefore, speculate that isocyanate formation in the present case is preceded by production of formamides followed by dehydrogenation, the latter step leading to reduction of $PdCl_2$ (eq. 2 and 3). Since reduction of

$$RNH_2 + CO \longrightarrow RNHCHO \quad (2)$$

$$RNHCHO + PdCl_2 \longrightarrow RNCO + Pd + 2HCl \quad (3)$$

$PdCl_2$ as well as the presence of isocyanates in the reaction mixtures was observed shortly after the combination of reagents, and the presence of formamides was not detected at any time, it was assumed that reaction 3, if it had occurred, was quite fast. However, contact of formanilide with $PdCl_2$, under conditions leading to fairly rapid formation of phenyl isocyanate from aniline and CO, resulted in no reduction of $PdCl_2$ or isocyanate production in 240 hr. It is clear, therefore, that reaction 3 does not occur and that production of isocyanates does not proceed through intermediate formation of formamides.

It is also clear that isocyanate formation is not due to *in situ* phosgene formation from $PdCl_2$ and CO. In the absence of amine, no reduction of $PdCl_2$ by CO was observed during extended periods of time at temperatures ranging from 40 to 200°.

The readily visible reduction of Pd(II) to metal which accompanies formation of isocyanates has also been noted in the previously reported vinylation in which olefins react with nucleophiles in the presence of $PdCl_2$.[3] The reaction is independent of the order in which amines or CO are added to $PdCl_2$ and, moreover, has been observed when amines are added to $(PdCOCl_2)_2$ or CO to $Pd(RNH_2)_2Cl_2$. Mechanistically then, it is possible that amines and carbon monoxide combine in a palladium complex containing both species and that decomposition of this material leads to isocyanate formation.

Experimental Section

Liquid reagents were freshly distilled and stored over molecular sieves. Solids were vacuum dried at 100°. Infrared and vapor phase chromatographic analyses are based on calibrations with authentic materials.

***n*-Butyl Isocyanate.**—A mixture of $PdCl_2$ (4.43 g., 25 mmoles) and Na_2HPO_4 (5.89 g., 41 mmoles) was evacuated at 95° for 16 hr. in a 250-ml. round-bottom flask connected to a manifold.

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