the determination of k_1 for piperidine makes the interpretation of this plot rather uncertain. Nevertheless, it seems that the most likely straight line through morpholine and piperidine would have a small positive slope. Both benzylamine and pyrrolidine would show rate enhancements relative to this straight line. In fact, these two amines will show positive deviations to any straight line drawn through morpholine and piperidine.

The small negative Brönsted slope for $k_{-1}K_{-2}$ and the small positive one for k_1 can be interpreted through an early transition state for the nucleophilic reactions, which means a late transition state for the decomposition of the dithiocarbamates. There should be, therefore, little charge development on the sulfur and nitrogen atoms of the transition-state structure. The same conclusion was reached by Jencks and co-workers for the acid decomposition of carbamates and mono- and dithiocarbamates of basic aliphatic amines.⁵

The large nucleophilic rate enhancement (k_1) of the reaction with pyrrolidine relative to the other reactions means that the transition state for this reaction must be even closer to reactants than the corresponding state for the reactions with the other amines, according to the Hammond postulate.²¹ Both the transition state and the cationic adduct 1 of Scheme I for the reactions of pyrrolidine must be stabilized relative to the corresponding structures in the reactions of the other amines, whereas this relative stabilization does not take place in the reactants.

In order to account for the slow decomposition of tetramethylenedithiocarbamate compared to the other adducts, it is also necessary to assume that the former compound is much more stable than the dithiocarbamates of morpholine, benzylamine, and piperidine. Furthermore, the relative stabilization of product 2 of Scheme I for the reactions of pyrrolidine must be larger than for intermediate 1, since K_2 (= k_2/k_{-2}) is much larger for the pyrrolidino than for the other amino derivatives (see Results). The value of k_2 should not vary significantly with the nature of the amine, since this step involves the donation of a proton from the ammonium moity of intermediate 1 to the corresponding conjugate amine. Therefore, the value of k_{-2} must be much smaller for tetramethylenedi-

(21) Hammond, G. S. J. Am. Chem. Soc. 1955, 77, 334.

thiocarbamate than for the other amino derivatives. This means that the unshared electron pair on the nitrogen atom of product 2 must be strongly delocalized into the dithiocarbonyl moiety of the pyrrolidino compound compared to the other dithiocarbamates, hence the relatively higher difficulty of its protonation by the pyrrolidinium ion.

The great stability of tetramethylenedithiocarbamate toward protonation and, therefore, toward decomposition is evidenced by its slower rate of solvolysis compared to the piperidine analogue. This must be due to the greater ability of the pyrrolidino moiety compared to the piperidino one to conjugate toward the dithiocarbonyl group of the molecule. The above also occurs when replacing the dithiocarbonyl moiety by an aromatic ring. Bunnett and co-workers found that in the reactions of piperidine and pyrrolidine with 2,4-dinitro-1-naphthyl ethyl and 2,4-dinitrophenyl phenyl ethers, pyrrolidine shows an outstanding higher reactivity.^{16,17} This was attributed to the greater ability of the pyrrolidino moieties of 3 and 4 com-



pared to the piperidino one to expel the phenoxy and ethoxy groups, respectively. In other words, it seems that for the products of these reactions, the contribution of canonical forms of coplanar geometry for the amino moiety such as 5 are much more important for the pyrrolidino than for the piperidino derivatives.

Although dithiocarbamates are different from aromatic amines, nevertheless, we think that structures similar to 5 have much greater contribution in tetramethylenedithiocarbamate than in the piperidino analogue. This results in a greater difficulty of protonation on the amino moiety of the former.

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Registry No. Carbon disulfide, 75-15-0; morpholine, 110-91-8; benzylamine, 100-46-9; pyrrolidine, 123-75-1.

A Procedure for Gas-Phase Dehalogenation of Organic Dihalides with Alkali Metal Vapors Using Microwave and/or Ultrasound Excitation and Matrix Isolation of Products

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Gas-phase dehalogenation of organic dihalides with alkali metal vapors in excess argon is promoted by microwave and/or ultrasound excitation. The products were deposited on a cold window along with excess solid argon. The use of the method is demonstrated on three α, ω -diiodoalkanes. The procedure is useful for the preparation of small amounts of highly strained olefins and ring compounds from their dihalo precursors.

Biradicals and biradical-like species are believed to play a pivotal role in various thermal processes and in very many photochemical processes encountered in organic chemistry. $^{2-4}$ In spite of their generally acknowledged

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importance, they undoubtedly are the least well characterized among organic reaction intermediates. It is thus hardly surprising that their direct observation and study, both by fast time-resolved methods and by matrix isolation techniques, commands considerable attention.

One of the most direct approaches to the generation of a biradical from a precursor is the introduction of a single radical center, repeated twice. Gas-phase dehalogenation with alkali metal atoms is a time-honored method for the introduction of a radical center into an organic substrate,⁵

$$RX \xrightarrow{+M} R$$

and similar reaction on dihalides has been used on a semiquantitative scale to produce isolable amounts of products of further reactions of a biradical:⁶

$$XRX \xrightarrow{M} [\cdot R \cdot] \rightarrow products$$

A few years ago, we decided to investigate the use of such gas-phase dehalogenation of organic dihalides by metal atoms in argon carrier gas, followed by trapping of the products in a matrix of excess solid argon. Our aim is the production and direct study of highly reactive, and particularly, biradical-like species and of the products of their further transformation. We have found that useful quantities of reactive intermediates, some of them novel, can indeed be produced in this fashion and have reported our findings in a series of communications: o-xylylene,⁷ p-xylylene,⁷ benzocyclobutadiene,⁷ adamantene,⁸⁻¹⁰ [3.2.1] propellane, ^{10,11} [2.2.1] propellane, ^{10,11} and [2.1.1]propellane.^{10,12} Over the years, the design of our apparatus has developed and we have accumulated experience relative to the scope and limitations of the procedure. The purpose of the present article is (i) to provide a detailed description of the experimental setup, (ii) to describe the results obtained with three α, ω -diiodoalkanes by the way of illustration, and (iii) to describe briefly the negative results obtained with the three diiodobenzenes, which



Figure 1. Gas-phase dehalogenation apparatus with microwave excitation (A).

provide an indication of the limitations of the presently used procedure. Up to the present, we have made no attempt to perform kinetic or other quantitative measurements and have been viewing the procedure simply as another organic preparative method, albeit a somewhat unusual one. Some mechanistic speculation is provided in the Discussion in order to show that the observed trends in product nature and yields can be rationalized in terms of known processes.

Experimental Section

The cryostat was an Air Products CSA-202 unit equipped with a CsI deposition window (IR) or a sapphire deposition rod (ESR) and CsI windows in the vacuum shroud. Microwave irradiation during reaction was carried out by using a Kiva MPG-2 or a Kiva MPG-3 microwave generator (Opthos Instrument Co.) or a Microtron-200 microwave generator (Electro-medical Supplies) coupled to a tunable microwave cavity with a removable end cap (Electro-medical Supplies). Ultrasound mixing experiments utilized a Branson B-220 ultrasonic cleaning bath. Infrared spectra were measured on a Nicolet Model 6000 FT-IR spectrometer with a resolution of 0.5 cm^{-1} . Electron spin resonance spectra were measured on a Varian V-4502 spectrometer. Gas chromatographic-mass spectral analyses of collected product mixtures were carried out on a Varian MAT-112 spectrometer. GC separations were accomplished by using both a 6 ft \times $^{1}/_{8}$ in. i.d. glass column packed with *n*-octane/Porasil, 800-110 mesh, and a 12 ft \times $^{1}/_{8}$ in. i.d. glass column of 100-120 mesh Porapak-Q in a Varian Model 1400 gas chromatograph equipped with a slit separator.

Quantitative GC analysis utilized a Hewlett-Packard Model 700FID gas chromatograph equipped with a linear temperature programmer. Peak areas were calculated from the analogue integration trace of a Laboratory Data Control Model 320 recorder equipped with an electronic integrator. Separations were effected on a 2 m \times ¹/₈ in. stainless steel column packed with 0.19% picric acid on a 80-100 mesh Carbopack-C.

Two designs of the dehalogenation apparatus were developed, one for less reactive dihalides, which relied on electronic excitation of the metal atoms to enhance their reactivity, and one for more reactive dihalides. Both were fabricated from borosilicate glass.

A. Microwave Excitation Apparatus. As shown in Figure 1, the body of the reaction cell is constituted by a $^{3}/_{4}$ -in. diameter 6-in. long tube wrapped with nichrome resistance heating wire, covered with a layer of asbestos, except for a narrow viewing strip, and provided with a built-in thermocouple. This permits adequate temperature control of the cell walls. A temperature at which the metal used has a pressure of about 10⁻³ torr was found adequate to prevent metal condensation.

The left face of the reaction tube, which faced the cold window attached to the end of a closed-cycle helium refrigerator (not shown), was slightly constricted. The tube was connected to the vacuum shroud surrounding the cold window (not shown) with an O-ring compression fitting.

At the right end of the reaction tube shown in Figure 1, an argon inlet was attached. This was represented by an 11-mm diameter $3^{1}/_{2}$ -in. long tubing, which passed through a commercial microwave

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Figure 2. Gas-phase dehalogenation apparatus with ultrasound excitation (B).

cavity. Discharge in the argon, ignited with a Tesla coil, generated ions and metastables in the stream of gas, resulting in an intense violet afterglow. Near the right end of the reaction tube this gas stream mixed with the vapors of the alkali metal, effusing from a side arm heated with a separately controlled resistance wire and thermocouple. In this zone, the color of the discharge changed to that characteristic of the alkali metal (yellow for sodium, etc.), as the excitation was transferred to the metal atoms. The yellow discharge persisted through the whole volume of the reaction tube and often reached inside the vacuum shroud. The advantage of the spatial separation of the microwave discharge and the metal oven was in a much increased stability of both the discharge and the metal evaporation rate relative to earlier designs⁷ when the metal vapor was passed through the microwave cavity.

The dihalide vapor was allowed to diffuse into the reaction zone from yet another side arm located about 1 in. downstream from the metal vapor inlet. The side arm was equipped with a stopcock, and the rate of effusion was controlled by a constant-temperature bath in which the dihalide sample container was immersed (not shown).

The rate of argon flow was controlled by a leak value on the argon inlet and by the choice of pressure on the vacuum line from which the argon was fed into the cell. The latter was held constant within $\pm 0.5\%$ by a suitable setting of the pressure regulator at the attached argon supply cylinder. The pressure inside the reaction cell was not measured but was just sufficient to sustain a stable microwave discharge (about 1 torr).

With this apparatus, it was possible to carry out microwaveenhanced reactions of four to 8 h duration without any adjustment of the microwave cavity after the initial ignition was accomplished and the discharge was stabilized. Each new ampule of metal was initialized by heating it quickly in position, with argon flowing, to 450-500 °C to burst any crust of oxidized material that had formed while loading the metal, encased in a glass tube, into the furnace. As soon as movement was detected in the metal or when metal began to deposit on the sample window, the furnace temperature was quickly lowered to the value chosen for the deposition and the reaction was started. When this procedure was used, the vaporization rate of the metal was fairly reproducible from one experiment to the next. The same ampule of metal could be used for many reactions, until the metal was used up or some other circumstance required opening the cell to the atmosphere.

B. Ultrasound Excitation Apparatus. A second design which proved useful is shown in Figure 2. The reaction cell itself is quite similar to that described under A, except that it is longer $(7^3/_4 \text{ in.})$ and the dihalide inlet side arm is missing. Instead, the dihalide vapor is premixed with excess argon before the latter enters the hot reaction zone and mixes with the metal vapor. This precludes the use of microwave discharge on the argon stream since it is generally undesirable to pass the organic vapor through the discharge. If desired, it should be readily possible to modify the design by adding yet another side arm through which microwave discharged argon would be introduced, but we did not try to do this.

The inlet system for the argon-dihalide mixture is shown on the left. The argon stream is divided in two, and valves in each



branch are used to regulate their relative magnitudes. One stream is led over the dihalide sample, held in a constant-temperature bath. Both are recombined in a container immersed in an ultrasound cleaning bath. The ultrasound not only helps the gases to mix but also propagates through the walls of the whole assembly and apparently helps to keep the metal surface clean since much lower metal furnace temperatures can now be used (~40 °C lower). The sample vial is attached through an O-ring connector since a ground joint tends to heat up, lose grease, and lock under the effect of the ultrasound.

An example of reaction conditions typically used are those for complete conversion of 1,4-diiodobutane to products: argon flow, 0.2–0.4 mmol/min; manifold pressure, 635 torr; cold window temperature, 25–32 K; reaction zone temperature, 210–230 °C for sodium, 160–180 °C for potassium; metal furnace temperature, 330–360 °C without and 270–300 °C with sonication for sodium and 270–300 °C without and 210–240 °C with sonication for potassium.

It was found empirically that the argon matrix quality was superior when ultrasound was used, and we have been using ultrasonication of deposition cells routinely even in depositions that require no metal vapor.

Results

Dehalogenation of α, ω -**Diiodoalkanes.** The present version of the apparatus has been used successfully for the generation and first direct observation of matrix-isolated adamantene from 1,2-diiodoadamantane and 1,2-dibromoadamantane⁸⁻¹⁰ and for the generation of new propellanes with three-membered rings from 1,3-diiodides.¹⁰⁻¹² We have also carried out a series of dehalogenation experiments in cell B (ultrasound) on three dihalides, which were expected to yield already known products but which represented precursors for biradicals that are of considerable intrinsic interest. These were 1,3-diiodopropane (1a), 1,4-diiodobutane (2a), and 1,5-diiodopentane (3a), potential precursors for the trimethylene (1b), tetramethylene (2b), and pentamethylene (3b) biradicals (Chart I).

The products of the reactions of these diiodides were trapped in excess argon on a cesium iodide window and characterized by FT IR spectroscopy. Control experiments showed that all of the detected and identified products were stable to the reaction conditions. After warm-up of the excess metal-containing matrix and trapping of the volatiles in a trap cooled by liquid nitrogen, the products were further characterized by quantitative gas chromatography combined with mass spectral identification. In this step, methane would not have been trapped, but there was little if any evidence for its presence from the IR spectra. The trapping of ethylene required considerable care and its relative abundance may be underestimated. In the cases of 1a and 3a, where there was little evidence



Figure 3. IR spectrum (transmittance) of argon-matrix-isolated products from the reaction of 1,3-diiodopropane with sodium vapor. The spectrum at the bottom was obtained with a larger metal vapor pressure; metal oven temperature is given; C = cy-clopropane, P = propene.

for its presence from IR, no special attempt was made to trap it. There was no evidence in any of the spectra for ethane or acetylene, which would have been difficult to trap as well. With these limitations in mind, the results can be summarized as follows.

Conditions for complete conversion to dehalogenated products were first established by optimizing argon pressure and flow, diiodide cell temperature, reaction cell temperature and length, and cold window temperature. Then a series of experiments was run in which only the metal furnace temperature and thus the concentration of the metal atoms in the vapor was varied, from the lowtemperature extreme at which there was almost no conversion of the starting material to an arbitrarily chosen upper limit at which the metal concentration was much higher than necessary for complete conversion of the starting material. Within this range, there was a clear change in the ratio of the major products resulting from 1a and from 2a as the concentration of sodium was changed. On the other hand, variation of potassium concentration had essentially no effect, the results being always much like those observed with high concentrations of sodium.

Next to the monoiodoalkane and to the unreacted starting diiodide, the first species that appears in the IR spectra as the sodium atom concentration is gradually raised is the same as the major product observed at all concentrations: cyclopropane (4) from 1,3-diiodopropane (1a), ethylene (5) from 1,4-diiodobutane (2a), and comparable quantities of cyclopentane, 1-pentene, and npentane from 3a. As the sodium concentration is increased, the spectra of the starting diiodide and of the monoiodide are no longer observed and rising proportions of propene (6) appear in the reaction of 1a (Figure 3), while

1(CH2)41 + NA 320C







Figure 4. IR spectrum (absorbance) of argon-matrix-isolated products from the reaction of 1,4-diiodobutane with sodium vapor. The spectrum on top was obtained with a larger metal vapor pressure; metal oven temperature is given; B = butadiene, E = ethylene.

Table I. Product Composition from Dehalogenation of α, ω -Diiodoalkanes with Sodium Vapor^a

	percent of total		
	$I(CH_2)_3I$	$I(CH_2)_4I$	$I(CH_2)_5I$
	1a	2a	3a
ethylene	<1 b	79	<1°
cyclopropane	67	< 0.1	8
propene	32	<1	5
cyclobutane		3	<1
1-butene		1	<1
cis-2-butene		2	<1
trans-2-butene		2	<1
<i>n</i> -butane		11	< 0.1
1,3-butadiene		1	<1
cyclopentane			20
1-pentene			29
<i>n</i> -pentane			33
unidentified		<1	3

^a Estimated by cold trapping followed by gas chromatography. ^b No particular effort was made to trap ethylene. It was barely detectable by IR. ^c No particular effort was made to trap ethylene. In IR spectra it appeared as a minor product in amounts roughly comparable to those of cyclopropane.

the proportion of ethylene (5) rises further in the reaction of **2a** (Figure 4).

The proportions of the major products in the high sodium concentration limit, as obtained by trapping and gas chromatography, within the limitations noted above, are listed in Table I.

Electron spin resonance detection revealed the presence of alkali metal atoms and their aggregates and of small amounts of organic paramagnetic products whose structure has not been elucidated. Their concentration was apparently insufficient to produce any IR bands of observable intensity.

Dehalogenation of Diiodobenzenes. Attempts to generate the three isomeric benzynes by using the present version of the apparatus yielded only trace amounts at best and revealed clearly the limitations of the current instrument and possibly of the method itself. They shall be described at least briefly since they suggest a way toward further progress. Most experiments were performed with o-diiodobenzene, since the spectrum of o-benzyne is known¹³ and its formation would be readily detected.

In cell A complete conversion of o-diiodobenzene was achieved with excited sodium and potassium, but the IR spectra showed only weak bands for the three most intense o-benzyne peaks, 469, 736, and 849 cm⁻¹, and occasionally some evidence of peaks near 1040, 1450, 1605, and 1625 cm⁻¹, which presumably correspond to the reported obenzyne bands at 1038, 1451, 1607, and 1627 cm^{-1} . There was no evidence for biphenylene¹⁴ or triphenylene¹³ under any conditions, even when matrices that appeared to contain traces of o-benzvne were warmed up (all matrices contained excess metal atoms). The major product was benzene, with its strongest IR band at 675 cm⁻¹, and a minor product was iodobenzene, not only with excited sodium and potassium but also with excited zinc and magnesium which yielded no trace of o-benzyne IR bands.

The reactions of p-diiodobenzene proceeded with similar ease as those of o-diiodobenzene, while those of m-diiodobenzene were slightly more facile. In all three cases, it was possible to obtain good conversion with ultrasound without microwave excitation. These starting materials also produced benzene as the major matrix-isolated product, iodobenzene as a minor product, and only traces of other species, which could not be identified.

The reaction of o-dibromobenzene and m-dibromobenzene with sodium yielded similar results. The reaction of iodobenzene yielded benzene.

At no time was evidence for the presence of the phenyl radical observed in the IR spectra¹⁵ or ESR spectra that were also taken. A series of reactions was run with mdiiodobenzene and metal in which the argon carrier gas was doped up to 10% with either D_2O or C_6D_6 . The products, as before, were ordinary benzene and traces of ordinary iodobenzene, with no evidence of the mono- or dideuterated compounds. Almost no D_2O was observed in the matrix; apparently, even large amounts in the carrier gas stream are effectively removed by the alkali metal.

m-Diiodobenzene-4,5,6- d_3 was synthesized by the procedure of ref 16. The IR spectra obtained from its reaction with sodium were not interpreted completely due to the large number of product peaks. The strongest peaks corresponded well to the published¹⁷ bands of benzene- d_5 and of the three isomers of benzene- d_4 . There was no evidence of the presence of substantial amounts of benzene-1,2,3-d₃.^{17,18}

Discussion

The products of the gas-phase dehalogenation of four previously investigated dihalides7-12 as well as those investigated presently can be rationalized by invoking a

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(1)



$$- \frac{1}{2} - \frac{1}{2} - \frac{1}{2}$$
(2.1)

$$- \underbrace{X + M}_{-MX} + \underbrace{M}_{-MX}$$
(3.1)

$$\frac{+M_{\bullet}}{-MX} \square + \square \qquad (3.3)$$

$$\begin{array}{c} \leftarrow & X \stackrel{+R-H}{-R} & \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ -RH & \hline \\ \hline \\ \hline \\ \hline \\ \\ \end{array} \begin{array}{c} + R \cdot \\ \hline \\ \\ -RH & \hline \\ \end{array} \begin{array}{c} (4.1) \\ (4.2) \\ \hline \\ \end{array}$$

sequence of reaction steps most of which are already well documented. Since we have performed no kinetic measurements, the mechanistic discussion will be necessarily qualitative but it will still serve our present purpose, i.e., a delineation of the factors that govern the applicability of the method for the production of small amounts of biradicals and related products.

The mechanism of the gas-phase dehalogenation of monohalides is well understood.⁵ These reactions can be viewed as S_R^2 replacements on the halogen atom in which an alkyl group is displaced by a metal atom. The alkali halide product, and certainly already the transition state, are highly polar, with considerable negative charge on the halogen atom. There is no indication that organometallic products are formed in these gas-phase reactions, and we have seen no evidence for them in our IR spectra. The IR frequencies were the same in sodium and potassium reactions, and all peaks of any significant intensity could be assigned to known metal-free materials.

The first step in the reaction sequence can therefore be assumed to be the removal of one of the two halogen atoms from the dihalide, forming a singly halogenated radical We leave open the question of Hal-R· (Scheme I). whether some of the haloradicals exist in a cyclic form.

Since, at most, traces of the haloradicals are present among the trapped products, they clearly undergo rapid destruction. The three main likely paths are listed in Scheme II. They are (i) unimolecular reactions, (ii) bimolecular reactions with a second alkali metal atom, and (iii) bimolecular hydrogen-transfer reactions.

(i) The first among these (2.1) is well known in the case of 2-haloalkyl radicals, as the reverse step of a radical addition to an olefin or to a conjugated polyene. In the

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case of 3-haloalkyl radicals it represents the reversal of a ring-opening halogen atom attack on cyclopropane. It might possibly occur even for *n*-haloalkanes with n > 3 but will be entropically less favorable.

Another possible fate of the haloradical is rearrangement (2.2), e.g., by a 1,3- or 1,4-hydrogen-atom transfer. A third possibility (2.3) is the loss of ethylene in an "unzipping" fragmentation reaction reminiscent of the depolymerization of polyethylene.

(ii) The second possibility is the repetition of the bimolecular metal-atom dehalogenation step, with formation of a free biradical in a singlet or triplet state (3.1), which can either survive or react further as shown in Scheme III, with formation of a new bond (3.2) as was the case in (2.1), or with fragmentation (3.3) as was the case in (2.3). If the radical is a 1-halo radical, perhaps formed by an intramolecular rearrangement of type 2.2, reaction 3.1 will proceed via a carbene, which will then undergo a rapid 1,2-hydrogen shift so that the end product is the same olefin as would result from a 2-halo radical in step 3.2.

(iii) The third possibility is hydrogen abstraction, either by the halo radical (4.1) or from the halo radical (4.2). In the former case, the reaction partner may be a closed-shell molecule, most likely a species with an easily abstractable hydrogen of an allylic or benzylic type, or at least one in a geminal position to a halogen. It may also be another radical, in which case the reaction is of the radical disproportionation type. Abstraction from the halo radical can be caused by any of a number of radicals or biradicals present.

For our purposes, halo-radical reactions of the type 2.1, 3.1, and 3.2 are generally desirable, the others are undesirable. The competition among the unimolecular processes 2.1, 2.2, and 2.3 can be directed toward 2.1 by choosing iodine as the halogen since the breaking of the weak C-I bond will require the least activation energy. This is also the best choice for reactions 1, 3.1, and 3.2, since the reactivity of alkyl halides decreases strongly in the order I > Br > Cl.⁵

The competition between 3.1 and 3.2 on the one hand and 3.3 on the other will be difficult to influence. However, the dehalogenation-with-fragmentation reaction 3.3 was only included for completeness and is unlikely to be a general cause for concern.

The serious potential troublemakers are the intermolecular hydrogen-transfer reactions 4.1 and 4.2, which direct the reactants irreversibly into a blind alley characterized by the processes listed in Scheme IV. They can be suppressed relative to processes 2.1–3.3 by using a high concentration of a reactive metal and low concentration of the starting dihalide in the vapor. The most reactive metal probably is cesium but it is unpleasant to work with. At times, also its very low ionization potential could lead to complications due to electron-transfer reactions in the solid as mentioned below. Thus, we have settled on potassium as the best choice for most purposes. The use of very high concentrations of the metal in the vapor brings its own problems, since too high an excess of metal in the matrix



$$\xrightarrow{+RH}_{-R}$$
(7.1)

$$\begin{array}{c} & +R \\ \hline -RH \end{array}$$
 (7.2)

+<u>M·</u> -MX (8.2)

interferes with spectroscopic measurements. The promoting effect of electronic excitation introduced by the microwave discharge can be ascribed to the lower ionization potential and larger size of the excited alkali metal atom. It is possible that some free electrons are also present in the reaction zone under these conditions.

The lower limit on the concentration of the starting dihalide is imposed by the need to obtain spectroscopically observable quantities of the products within a matrix of 1-2 mm thickness, since thicker matrices tend to be of poor optical quality. It is the local concentration in the mixing zone that matters, and good mixing of the dihalide vapor with excess carrier gas and subsequent good mixing with the metal vapor saturated gas are essential. We believe that the salutary role of ultrasound is due to the improved mixing. Another effect of the ultrasound, renewal of the molten metal surface, has already been mentioned.

The critical nature of the mixing step is also clear from the results of the doping experiments: the presence of even a substantial amount of C_6D_6 , not to mention D_2O , produced no deuterium-transfer products but only hydrogen-transfer products from o-diiodobenzene. It is apparently the boundary region between the gas pockets of the dihalide and the surrounding metal-containing gas where reaction 1 proceeds at a nearly diffusion-controlled rate, producing a metal atom depleted region at the interface and allowing the halo radical products to diffuse toward the hydrogen donors inside the pocket. We believe that even with ultrasound mixing, the reaction does not proceed in a truly homogeneous manner. Conceivably, the use of a less reactive halogen such as bromine instead of iodine would permit better mixing and might be beneficial in some cases.

The rates of reactions 4.1 and 4.2 depend on structure in a predictable fashion. Benzylic or allylic hydrogens in a starting dihalide will be the most easily abstractable, those in a saturated aliphatic dihalide less so, and those in an aromatic or vinylic dihalide will be hard to abstract. On the other hand, the monohalo radicals from benzylic or allylic dihalides will be very poor abstractors and those from the aromatic or vinylic dihalides the very best ones. In the compounds investigated here, the two trends are opposed and undoubtedly compensate to some degree.

We have made the following observations as a function of the structure of the dihalide.

(i) Aliphatic 1,2-dihalides and their benzologues such as o-xylylene dibromide yielded only the expected olefins.⁷⁻¹⁰ Even when the olefin was the very highly strained adamantene, only traces of radical products were detectable.⁸⁻¹⁰

(ii) Aliphatic 1,3-dihalides gave cyclopropanes.¹⁰⁻¹² In the one case (1,3-diiodopropane) in which the corresponding olefin was easily accessible energetically (propene), it, too, was formed in considerable quantities (Table I). Its quantity increased with metal atom concentration. As the strain energy involved in forming the three-membered ring increased in the order [3.2.1]propellane, [2.1.1]propellane, [2.2.1]propellane, the competing hydrogen-transfer reactions became more serious.¹⁰⁻¹² For [2.2.1]propellane, they were not removed completely even by the use of ultrasound, although they were suppressed considerably.

(iii) The one aliphatic 1,4-dihalide investigated, 1,4-diiodobutane, produced primarily ethylene (Table I). Its amount increased with metal atom concentration and reactivity.

(iv) The one aliphatic 1,5-dihalide investigated, 1,5-diiodopentane, produced comparable amounts of cyclopentane, 1-pentene, and *n*-pentane.

(v) Aromatic 1,2-, 1,3-, and 1,4-dihalides yielded the hydrogen-transfer product benzene as the only major volatile product, and only traces of the benzynes at best. The fate of the hydrogen-donor molecules is not known. It is probably significant that small amounts of visible polymer coating gradually build up on the reaction vessel walls; this is much more noticeable with aromatic than with aliphatic dihalides. The presence of such coatings had no detectable effect on the spectra observed in subsequent runs.

An empirical generalization then is that the method produces useful amounts of desired products from dihalides whose halogens are attached to saturated carbons but not from those whose halogens are attached to aromatic carbons, and this could guide future attempts to use the procedure for the preparation of new biradicals or, more likely, their further transformation products. The mechanistic considerations outlined above permit a somewhat more detailed proposal even in the absence of kinetic data: it seems that those dihalides whose initial halo radical product would be expected to be particularly prone to unimolecular loss of a halogen atom (2.1) give the cleanest reaction to the desired product. These are the aliphatic 1,2-dihalides and vinylogous dihalides, above case i, and 1,3-dihalides, above case ii. The trend in the latter is particularly suggestive: as the strain in the product propellane grows, so should that in the transition state leading to it, and hydrogen-transfer reactions should compete better, as they are observed to do.

Thus, we propose that a low free energy of activation for step 2.1 is extremely important for success in the gas-phase dehalogenation approach to "biradical" products, at least as presently practiced and that in these successful cases the reactants never actually reach the stage of a free biradical. We believe that 2.1 is operative even when endothermic by a fair amount, since the entropy change is favorable, the reactions are performed at fairly high temperatures and are irreversible since the halogen atoms will be scavenged by the excess alkali metal present.

In the case of the aromatic dihalides tested, above case v, the free energy of activation for 2.1 is expected to be much higher, so that 2.1 is too slow to compete successfully. In the case of aliphatic 1,4 and 1,5-dihalides, above cases iii and iv, the entropy of activation for 2.1 must be far less favorable than in the case of 1,2- or 1,3-dihalides; the transition state for cyclobutane formation from the 1,4dihalide moreover undoubtedly suffers from ring strain. The formation of cyclopropane from 1,5-diiodopentane suggests that the fragmentation process 2.3 is competitive; such a process would also account for at least some of the observed ethylene formation from 1,4-diiodobutane. The production of 1-pentene from 1.5-diiodopentane can be assigned to an intervention of the rearrangement reaction 2.2: a 1,4- or a 1,5-hydrogen transfer in the 5-iodopentyl radical leads to the 1-iodopent-2-yl or 1-iodopent-1-yl radicals. The former will spontaneously lose an iodine atom (2.1), and the latter can react with a metal atom to yield a carbene. In both cases, the ultimate product is 1-pentene.

The other observed products, such as norbornane from 1,4-diiodonorbornane,⁸⁻¹⁰ the butenes, *n*-butane, and butadiene from 1,4-diiodobutane (Table I), and *n*-pentane from 1,5-diiodopentane, are easily envisaged as originating in the hydrogen-transfer reactions.

However, while almost all of the results can be rationalized on the basis of competition between processes 2.1-2.3 on the one hand and the hydrogen-transfer processes 4.1 and 4.2 on the other hand, the dependence of the product ratios on the metal concentration suggests that reactions 3.1–3.3 can be involved as well. We propose that the reaction of a second metal atom with the 3-iodopropyl radical leads to the formation of the trimethylene biradical (3.1), which then partitions between cyclopropane and propene. Similarly, we propose that the reaction of a second metal atom with the 4-iodobutyl radical, presumably primarily present in its extended trans form, yields either the tetramethylene biradical (3.1) or directly ethylene (3.3). The trans conformer of the tetramethylene biradical fragments to ethylene (5.2); the cis conformer may be responsible for some of the observed cyclobutane (5.1).¹⁹⁻²¹ Also some of the products from 1,5-diiodopentane may originate from a biradical. Certainly the pentamethylene biradical would be expected to partition between cyclopentane and 1-pentene,²² both observed as major reaction products. Its fragmentation to ethylene and the trimethylene biradical (5.3) is perhaps improbable under our reaction conditions, but we see no explanation of the production of propene in the dehalogenation of 1,5-diiodopentane that would be less improbable (the fragmentation of the 5-iodopentyl radical to ethylene and the 3-iodopropyl radical and the subsequent reaction of the latter with a metal atom is one such possibility). The fact that the percentage of ethylene observed in gas chromatographic analysis of trapped material is far smaller than the sum of cyclopropane and propene could well be due to incomplete ethylene retention in the cold trap. In IR spectra, the quantities of ethylene and cyclopropane present appear to be of the same order of magnitude.

In conclusion, the products observed in the gas-phase dehalogenation reactions of the dihalides can be understood in terms of reasonable mechanistic steps. We believe

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that the present version of the apparatus is suitable for those dihalides that yield the desired products after abstraction of the first halogen atom by spontaneous loss of the second halogen atom (2.1). Thus, suitable future target molecules are strained olefins and small-ring propellanes. For other targets, a better mixing system is needed.

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Registry No. 1a, 627-31-6; **2a**, 628-21-7; **3a**, 628-77-3; **4**, 75-19-4; **5**, 74-85-1; **6**, 115-07-1; **K**, 7440-09-7; Na, 7440-23-5; *n*-butane, 106-97-8; cyclopentane, 287-92-3; 1-pentene, 109-67-1; *n*-pentane, 109-66-0; *o*-diiodobenzene, 615-42-9; *o*-benzyne, 462-80-6; *p*-diiodobenzene, 624-38-4; *m*-diiodobenzene, 626-00-6; *o*-dibromobenzene, 583-53-9; *m*-dibromobenzene, 108-36-1; iodobenzene, 591-50-4.

Studies in Lipid Mimics. Synthesis and Carbon-13 Relaxation Time Measurements (T_1 Values) of Methyl Esters of ω -(2-Anthryl)alkanoic Acids

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The syntheses of methyl 12-(2-anthryl)dodecanoate, methyl 14-(2-anthryl)tetradecanoate, and methyl 17-(2-anthryl)heptadecanoate have been achieved. Both ¹H and ¹³C chemical shifts and T_1 values for carbons in the systems have been recorded. By using selected heteronuclear decoupling and performing heteronuclear correlated 2-dimensional (HETCOR-2-D) experiments, it was possible to assign protons to specific carbons in most cases.

Structure and functions of biological membranes continue to be major areas of interest.² Diagnostic evaluation of the two variables via the use of fluorescent probes³ has generated a lively stimulus to synthesize artificial lipid mimics. A preliminary report⁴ disclosed an approach to certain ϵ -(2- and 9-anthryl)alkanoic acids and a few esters. However, these esters have relatively short chains, and, since natural membranes have longer carbon chains, we report herein the preparations and NMR spectral properties of three members of 1. The strategy to obtain 1 is



outlined in Scheme I and involved intermediates 2-4. Phosphonium salt 2 was prepared starting from available





2-methylanthraquinone (5). With known procedures,⁵ the latter was converted to 2-(hydroxymethyl)anthracene (6) (45% overall). Treatment of the alcohol with triphenyl-phosphine dibromide in DMF at room temperature gave 7 (84%). Alkylation of phosphorus in triphenylphosphine with 7 in boiling benzene gave salt 2.

Since ω -oxo esters $3\mathbf{a}-\mathbf{c}$ were not available, methods to obtain these materials have been developed and are outlined in Scheme II [$^8 \rightarrow {}^9 \rightarrow {}^3\mathbf{a}$, $10 \rightarrow 11 \rightarrow 12 \rightarrow 3\mathbf{b}$, $13 \rightarrow 14 \rightarrow 3\mathbf{c}$]. In general, members of $3\mathbf{a}-\mathbf{c}$ were used shortly after preparation. Treatment of the anion of 2 with $3\mathbf{a}-\mathbf{c}$ were used shortly after preparation. Treatment of the anion of 2 with $3\mathbf{a}-\mathbf{c}$ gave the unsaturated esters $4-\mathbf{c}$, which could be hydrogenated in ethyl acetate over 10% Pd/C (without reduction of the 9,10-positions of the an

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