

ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION NO. 925 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Cyclopropane Synthesis from Methylene Iodide, Zinc-Copper Couple, and Olefins. II.¹
Nature of the Intermediate

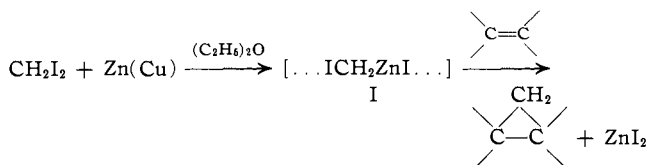
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RECEIVED OCTOBER 30, 1963

Methylene iodide and zinc-copper couple in ether solvents give a stable organozinc intermediate, probably $(\text{ICH}_2)_2\text{Zn}\cdot\text{ZnI}_2$, as the major product. This intermediate reacts in a kinetically bimolecular process with olefins to give a cyclopropane and zinc iodide. The reagent slowly attacks ether by α -proton abstraction to give methyl iodide. This interpretation accounts for the by-products now identified in cyclopropane synthesis: ethyl isopropyl ether, methyl ethyl ether, propylene, methyl iodide, and ethoxide ion. Competition studies with a variety of olefins were carried out, and the methylene-transfer process has been shown to have electrical requirements similar to carbenes, although a large steric effect was noted.

In paper I,^{1,2} a general synthesis of cyclopropanes by the reaction of an olefin with the reagent prepared from methylene iodide and zinc-copper couple was described. This paper and the following one³ give the results of some further studies that delineate the role of the organozinc intermediate and suggest optimum synthesis conditions.

The Cyclopropane-Forming Reaction.—It was previously found that methylene iodide reacted with zinc-copper couple in diethyl ether to give a solution that contained a stable organozinc intermediate (I)⁴ which reacted with iodine to regenerate methylene iodide,⁵ was hydrolyzed by water to methyl iodide,^{1,5} and reacted with olefins to give cyclopropanes.^{1,2} The

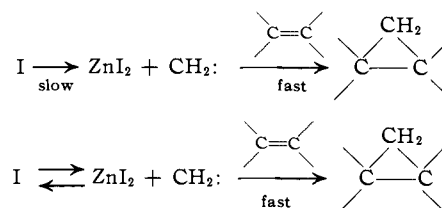


stoichiometry of the reaction of methylene iodide and zinc-copper couple in ether solution and the chemical behavior of the resulting intermediate^{1,5} indicated that 1 mole of zinc had combined with 1 mole of methylene iodide to form a stable, but reactive, organozinc intermediate. The reaction could be carried out in other oxygen-containing solvents, but diethyl ether was by far the most effective. It was shown that copper in the zinc couple plays no role in cyclopropane formation but merely serves to activate the zinc metal surface for reaction with methylene iodide. The presence of copper in zinc is a well-known experimental necessity for preparing organozinc iodides from primary aliphatic iodides.

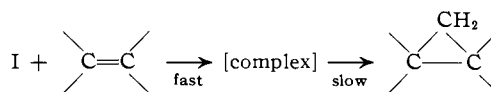
It was suggested previously¹ that multiple-step carbanion or free-radical addition mechanisms were unlikely in view of the rigorous stereospecificity of the cyclopropane synthesis. It also seemed likely that

addition of the methylene group to an olefin did not involve free methylene⁶ or carbene,⁷ since a filtered solution of the product from the reaction of methylene iodide and zinc-copper couple remained active in cyclopropane formation after storage for several hours at 0°.¹

Direct evidence has now been obtained that the organozinc intermediate I reacts in a bimolecular process with an olefin in the methylene-transfer step.^{8a,b} It was conceivable that cyclopropane formation occurs *via* free carbene or methylene after slow decomposition of I to CH_2 : and ZnI_2 , or by CH_2 : that is in equilibrium with I. If this were so, the rate of cyclopropane formation would be kinetically independent of the concentration of olefin under the assumption that CH_2 : "must be classed as the most indiscriminate reagent known in organic chemistry,"⁶ and that presumably the absolute rate of reaction with olefin in both cyclopropane formation and the carbon-hydrogen insertion reaction is very high. Another mechanism kinetically



independent of olefin concentration would involve the rapid, irreversible formation of a complex of I and olefin followed by slow conversion of the complex to products.



A solution of I in diethyl ether was prepared by allowing the mildly exothermic reaction of methylene iodide

(6) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

(7) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

(8) (a) The term "methylene-transfer step" is employed in this paper to distinguish the stereospecific transfer of a methylene group to a double bond in a process whose transition state requires a third body regardless of the exact mechanism, as opposed to the formal addition reactions of free divalent carbon species. (b) In this work, quantitative measurements of absolute properties have been frustrated, since it has not been possible to obtain solutions of I of accurately known concentration free from zinc iodide and other decomposition products. It has been possible, however, to perform experiments to obtain relative kinetic data.

(1) For the first paper in this series, see H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(2) A preliminary communication appeared by H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958).

(3) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, **86**, 1347 (1964).

(4) The intermediate responsible for cyclopropane formation will be referred to as "iodomethylzinc iodide" [$\dots\text{ICH}_2\text{ZnI}\dots$] (I),^{1,2} since this partial structure can be recognized with certainty. The structure of I is discussed more fully below.

(5) G. Emschwiller, *Compt. rend.*, **188**, 1555 (1929).

TABLE I
 RELATIVE REACTIVITIES OF OLEFINS

Olefin	"ICH ₂ ZnI"	(CH ₂) ₂ C=C=C ¹¹	CHCl ¹²	CCl ₂ ⁹	CBr ₂ ¹⁰	CHCO ₂ C ₂ H ₅ ¹³	$\begin{array}{c} \text{(C}_6\text{H}_6)_2 \\ \diagdown \quad \diagup \\ \text{C} \\ \diagup \quad \diagdown \\ \text{C} \text{---} \text{CH}_2^{14} \end{array}$
3,3-Dimethyl-1-butene	0.14						
1-Pentene			0.38	0.137			0.18 ^a
1-Hexene	0.36	0.25		0.186	0.167	0.9	
1-Heptene	0.39						
<i>trans</i> -2-Butene			0.75				0.34
<i>trans</i> -2-Pentene				2.14			
<i>trans</i> -3-Hexene	0.42						
1,2-Dimethylcyclohexene	0.58						
<i>cis</i> -2-Butene			1.52				0.93
<i>cis</i> -2-Pentene				1.62			
<i>cis</i> -3-Hexene	0.83						
Cyclohexene	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2,3-Dimethyl-2-butene	1.29	17.8	4.68	53.7	6.92	1.6	0.33
2-Methyl-2-butene	2.18	4.7	2.97	23.4	7.41	1.6	
2-Methyl-1-butene	2.53	5.0		5.50			
Isobutylene			1.67	7.94	3.72		0.81

^a Value for 1-butene.

and zinc-copper couple to proceed until the concentration of I was near the maximum (see below). The reaction was quenched by cooling to 0°, and a clear, colorless solution containing I was obtained after filtration. The concentration of I was estimated to be *ca.* 1.5 *M*. The solution was divided into two portions and cyclohexene was added at 0°. Solution A was 0.90 *M* and solution B was 3.33 *M* in cyclohexene, initially. The rate of norcarane formation was followed by removing aliquots which were hydrolyzed with ammonium chloride solution and the organic layer then analyzed by g.p.c. A simple plot of norcarane concentration *vs.* time (Fig. 1) over the first

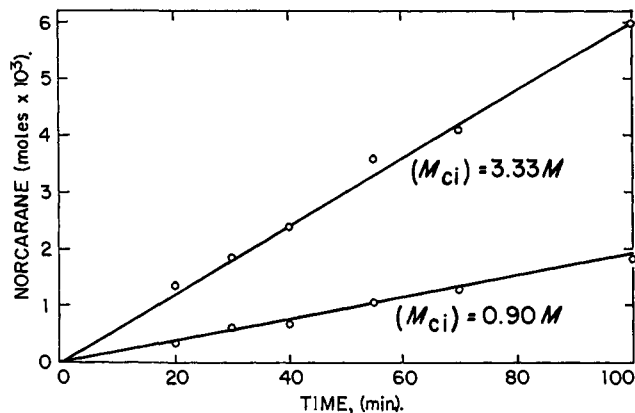


Fig. 1.—Moles of norcarane *vs.* time where M_{Ci} represents the moles of cyclohexene present initially in each case.

10–15% reaction clearly shows that the rate of cyclopropane formation is dependent on olefin concentration. Analysis of the data over >95% reaction by the usual bimolecular equation gave $k_A = 6.5 \pm 0.5 \times 10^{-3} M^{-1} \text{ sec.}^{-1}$ and $k_B = 6.0 \pm 0.3 \times 10^{-3} M^{-1} \text{ sec.}^{-1}$. In light of the above discussion these findings cannot be reconciled with the intermediacy of free methylene or carbene. Although the rate of norcarane formation would be expected to increase with increasing olefin concentration even if $\text{CH}_2\cdot$ were involved, it would be highly fortuitous to observe identical *specific second-order constants* in the cases studied. Further-

more, in view of the high *yield* of norcarane obtained in both experiments, it seems unlikely that the higher *rate* of formation of norcarane in one of these simply reflects more efficient trapping of some highly reactive intermediate such as $\text{CH}_2\cdot$.

A bimolecular process is in accord with the original postulation of a methylene-transfer mechanism,¹ although no conclusions can be drawn concerning a one- or two-stage addition. Additional support for a methylene-transfer mechanism is found in the large steric requirements of these reactions as determined by competition studies.

Competition Studies.—The ability of I to discriminate between variously substituted olefins by methylene transfer was confirmed by studying the reaction with mixtures of olefins. Competition studies are usually carried out by allowing pairs of olefins in large excess to compete for a deficiency of the reagent. The relative rate ratios are then simply determined from the known mole fractions of the olefins and the measured mole fractions of products. In the present case, experimental difficulties were encountered in initiating the reactions in media containing high concentrations of hydrocarbons. The relative rates were obtained by allowing an ether solution of a mixture of two olefins, each *ca.* 2.5 *M*, to compete for the reagent generated *in situ*, whose maximum concentration in the absence of cyclopropane formation would have been *ca.* 1 *M*. The relative rates were therefore calculated from the equation

$$k/k_C = \ln [O/O_0] / \ln [C/C_0]$$

(9) W. von E. Doering and W. A. Henderson, *J. Am. Chem. Soc.*, **80**, 5274 (1958).

(10) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

(11) H. D. Hartzler, *ibid.*, **83**, 4997 (1961).

(12) (a) G. L. Closs and G. M. Schwartz, *ibid.*, **82**, 5729 (1960); (b) G. L. Closs and L. E. Closs, *ibid.*, **85**, 99 (1963). These authors have warned of hasty conclusions concerning the intermediacy of carbenes in cases in which α -halolithium compounds are generated.

(13) P. S. Skell and R. M. Etter, *Chem. Ind. (London)*, 624 (1958). The addition of carbethoxycarbene, generated by photolysis or by copper-catalyzed decomposition of ethyl diazoacetate, to olefins was shown to occur stereospecifically. The relative rates in Table I refer to competition studies carried out in the copper sulfate-catalyzed reaction.

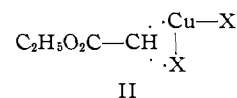
(14) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).

where O_0 and C_0 refer to the initial concentrations of an olefin and cyclohexene (the standard), and O and C are final concentrations. The results are shown in Table I along with results from other systems for comparison. Since the state of aggregation and thus the chemical reactivity of organometallic species may be a function of concentration (see below), it was also determined that k/k_C was not a sensitive function of concentration. 1-Hexene and cyclohexene were allowed to compete for I under the same conditions in solutions containing 0.30, 0.45, 0.60, and 0.75 mole of diethyl ether. The values of k/k_C observed were 0.356, 0.333, 0.363, and 0.360, respectively, demonstrating the insensitivity of k/k_C to concentration changes.

It is clear from Table I that the intermediate behaves as an electrophile toward olefinic bonds in the manner of dichlorocarbene⁹ and dibromocarbene¹⁰; that is, the reactivity of the olefin increases with increased substitution of the double bond with alkyl groups. This general behavior is obviously followed by I; however, some significant exceptions are observed. 2-Methyl-1-butene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene are more reactive than cyclohexene with both I and, *e.g.*, CCl_2 ; however, the order of reactivity for these three olefins is exactly reversed. The most obvious explanation lies in the postulation of sizable steric requirements in the transition state for methylene transfer from I. Another interpretation could account for the behavior of the three "fastest" olefins. In each case there is *gem*-dialkyl substitution and the reactivity increases as the electrical asymmetry of the olefin increases. This would be in accord with a transition state possessing considerable carbonium ion character and further with one that is itself unsymmetrical. The transition state for a one-step methylene-transfer reaction is supposed to resemble that of electrophilic addition and, moreover, is inherently unsymmetrical if based on any of the reasonable structures of I postulated below. At the present time, the relative importance of steric and electrical effects cannot be assessed with certainty, but the high stereoselectivity of certain additions to olefins⁸ has tentatively caused us to favor the steric explanation.

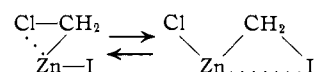
The spread in reactivity, which reflects the ability of the reagents to discriminate, from 1-hexene to 2-methyl-2-butene (where steric effects become obviously important), with I, $(\text{CH}_3)_2\text{C}=\text{C}=\text{C}$,¹¹ CHCl ,^{12a} CCl_2 ,⁹ CBr_2 ,¹⁰ and $\text{CHCO}_2\text{C}_2\text{H}_5$ ¹³ is 6.1, 18, 7.8, 126, 44, and 1.8, respectively. In all these reactions a *formally* divalent carbon species adds to an olefinic bond to form a cyclopropane under mild conditions, and all of the additions have been shown, furthermore, to occur stereospecifically. Unfortunately, these relative rate data alone are insufficient to give a meaningful measure of discriminatory ability even if the mechanisms of the various addition reactions were closely similar. Each case in Table I, except " ICH_2ZnI ," has been characterized in the literature as involving a carbene, but it is seen that " ICH_2ZnI ," CHCl , and $\text{CHCO}_2\text{C}_2\text{H}_5$ show much less ability to discriminate. The role of copper or its salts in modifying the reactivity of carbenes when generated from diazo compounds is well known¹⁵ and probably involves a complex of the car-

bene with the copper surface or with a copper salt, *e.g.*



The two species (I and II) in Table I that almost certainly do not react as free carbenes have low reactivity spreads. 2,2-Diphenylcyclopropylidene,¹⁴ generated thermally (spontaneously) from the diazo compound, reacts with *cis*- and *trans*-2-butene stereospecifically to give spiropentanes, and 1,1-diphenylallene is formed in a concurrent reaction during these olefin additions. The data in Table I shows this species is basically an electrophile, but a strong reversal in reactivity with highly substituted olefins, similar to that of " ICH_2ZnI ," is evident. In this case the authors have attributed the reversal to steric effects during addition by the free carbene. The "freeness" of carbenes will be discussed in a subsequent publication, but it is interesting that although chlorocarbene^{12b} has been implied to be free when generated from methylene chloride and an alkylolithium, it too shows a small reactivity spread compared to dichlorocarbene and dibromocarbene.

Nature of the Halogen.—It is important to know whether the kind of halogen atom influences the chemical behavior of I. It was previously shown¹ that the reagent prepared from chloriodomethane reacted with cyclohexene to give norcarane under the usual reaction conditions. In this case the organozinc reagent first formed presumably contains the unit $[\dots\text{Cl}-\text{CH}_2-\text{Zn}-]$ rather than $[\dots\text{I}-\text{CH}_2-\text{Zn}-]$. In this work it has been found that solutions of reagent obtained after filtration of the reaction product of chloriodomethane and zinc-copper couple gave predominantly methyl iodide on aqueous hydrolysis. Only traces of methyl chloride were detected. It is concluded that an equilibrium of the type



must be rapidly established and lies far to the right.

In order to secure additional information on whether the nature of the carbon-bound halogen is important for methylene transfer to an olefin, chloromethylzinc chloride and bromomethylzinc bromide⁴ were synthesized employing the observation of Wittig and Schwarzenbach¹⁶ that diazomethane reacts with zinc iodide in ether solution to give iodomethylzinc iodide and nitrogen.

When a solution of diazomethane was added to solutions of zinc chloride or zinc bromide in ether at 0° , the color was discharged immediately. Aliquots of these solutions gave methyl chloride and methyl bromide, respectively, on aqueous hydrolysis, indicating the desired organozinc compounds had been formed. Both solutions were treated with cyclohexene, and the sole reaction product in each case was identified as norcarane by g.p.c. It is apparent that the nature of the halogen atoms in XCH_2ZnY is not critical in determining whether methylene transfer to a double bond occurs.

Chemistry of the Intermediate.—The previously noted¹ slow decomposition of I to ethylene has been

(15) (a) P. Yates, *J. Am. Chem. Soc.*, **74**, 5376 (1952); (b) W. von E. Doering and L. H. Knox, *ibid.*, **78**, 4947 (1956).

(16) G. Wittig and K. Schwarzenbach, *Angew. Chem.*, **71**, 652 (1959).

found to be only one of several side reactions which occur. A study of these side reactions has provided further information on the structure and reactivity of I.

Methylene iodide (0.1 mole), zinc-copper couple (0.1 mole), cyclohexene (0.1 mole), and diethyl ether (0.3 mole) were allowed to react under the usual conditions, and the gaseous products were collected during reaction. These conditions have been found to be near optimum for cyclopropane formation.³ The mixture was hydrolyzed by cold, concentrated ammonium chloride solution, and a gas was evolved which was collected separately. The two gases, the ethereal solution, and the aqueous wash were examined to determine the major products of the reaction. With a given batch of zinc-copper couple, all of the reactions described in this paper were reproducible to a few per cent.

In a typical run, g.p.c. analysis of the gas evolved during reaction showed it to consist of ethylene (6.5%), propylene (0.9%), cyclopropane (0.1%), and methane (0.8%).¹⁷ The gas evolved after hydrolysis was methane (0.6%).

The presence of ethanol in the aqueous ammonium chloride solution was established by g.p.c., although an accurate yield could not be determined.

Gas phase chromatographic analysis of the ethereal solution showed norcarane was formed in 63.8% yield, and unreacted olefin was accounted for quantitatively. No other products derived from cyclohexene were detected. The following products were identified by their g.p.c. retention times and subsequent isolation: methyl iodide (7.0%), ethyl isopropyl ether (~0.5%), and methyl ethyl ether (~0.5%). The total material balance was approximately 90%, based on methylene iodide consumed.

Three reaction paths of the organozinc intermediate(s) could thus be distinguished: methylene transfer to give norcarane, conversion to ethylene, and reaction with the solvent to form products such as methyl iodide and ethyl isopropyl ether.

The reaction with solvent is perhaps simplest to rationalize. Since the reagents were pure and the apparatus was scrupulously purged of water vapor, methyl iodide was not merely an incidental product. The finding of ethyl isopropyl ether among the products is reminiscent of the well-known insertion reaction of methylene. Photolysis of diazomethane in ether solution gives ethyl isopropyl ether and *n*-propyl ether.¹⁸ Both products are believed to be formed in the usual insertion reaction, although the possibility of an ylid intermediate has been considered.¹⁹ The mixture from the reaction of cyclohexene, methylene iodide, and zinc-copper couple contained no trace of ethyl *n*-propyl ether as shown by the retention time of an authentic sample.

It was further found that when hydrolysis was carried out with deuterium oxide, the gaseous product after hydrolysis was essentially pure monodeuteriomethane,

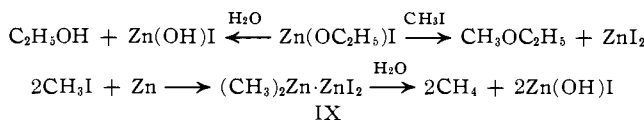
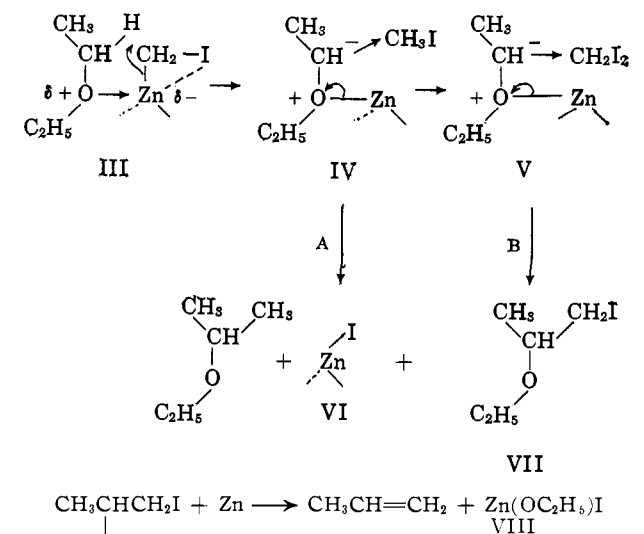
(17) Throughout this paper yields are given as the percentage of methylene iodide converted to the indicated product. In this manner the fate of the single carbon atom of methylene iodide can be traced and is made the basis for comparisons.

(18) H. Meerwein, H. Rathjen, and H. Werner, *Ber.*, **75**, 1610 (1942).

(19) R. Huisgen, *Angew. Chem.*, **67**, 439 (1955); however, see W. von E. Doering, L. H. Knox, and M. Jones, *J. Org. Chem.*, **24**, 136 (1959); and V. Franzen and L. Fikentscher, *Ann.*, **617**, 1 (1958).

and no deuterium was incorporated into the recovered diethyl ether as determined by mass spectroscopic analysis.

A mechanism can be written formally involving an ylid which accounts for the formation of ethyl isopropyl ether and at the same time predicts the other products. Norcarane, ethylene, and cyclopropane will be discussed separately below.



We assume the partial structure III showing the solvation of the organozinc intermediate with ether. The occurrence of the unit ($\dots\text{I}-\text{CH}_2-\text{Zn}-$) was established previously by hydrolysis studies. The charge separation shown in III is real, since the less polar dimethylzinc, whose dipole moment is 0 in heptane, possesses a moment of 1.82 D. in dioxane²⁰ which has been ascribed to discrete charge-separated solvates such as III. The increased acidity of the α -protons of the ether molecule promotes cleavage of the carbon-zinc bond, possibly in a five-membered ring transition state III, to give the ylid and a molecule of methyl iodide (IV). The molecule of methyl iodide still in the primary cage IV may alkylate the nearby carbanion in process A to give ethyl isopropyl ether and the neutral zinc fragment VI (ZnI_2 or ICH_2ZnI). Similar alkylation by methylene iodide (process B) gives the same fragment VI and 2-ethoxy-1-iodopropane (VII). The conversion of β -haloethers such as VII to olefins by zinc is a well-known preparative method.²¹ In the present system, VII gives propylene and zinc ethoxy iodide (VIII). Methylation of the alcoholate VIII by methyl iodide gives methyl ethyl ether, and terminal hydrolysis gives ethanol. In the presence of the activated couple surface, methyl iodide gives "methylzinc iodide" or the dimer IX, which is stable in this system and gives methane on terminal hydrolysis. The material balance is in qualitative agreement with that predicted, but experimental uncertainties make exact comparisons impossible. Thus, a single scheme easily

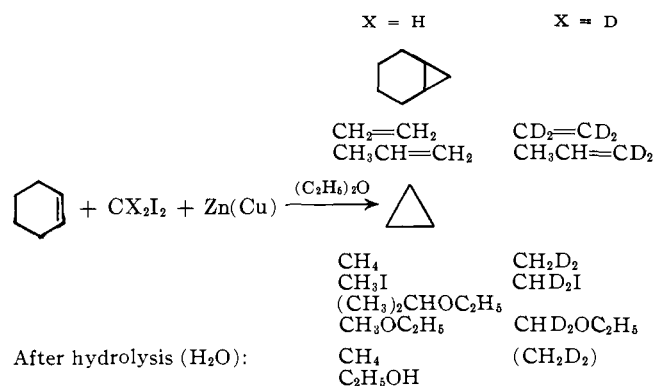
(20) W. Strohmeier and K. Nützel, *Z. Elektrochem.*, **62**, 188 (1958).

(21) C. G. Schmitt and C. E. Boord, *J. Am. Chem. Soc.*, **54**, 751 (1932); M. L. Sherrill and G. F. Walter, *ibid.*, **58**, 742 (1936).

accounts for all of the observed products from attack of the reagent on the solvent ether.

Isotopic labeling of methylene iodide should lead to products, the distribution of whose label can be predicted by the mechanism outlined. Dideuteriomethylene iodide has not been described previously²² and was prepared by exchange of methylene iodide in $C_2H_5OD-D_2O-CH_3ONa$ containing sodium iodide to suppress carbene hydrolysis. After two exchanges, deuteriomethylene iodide was obtained in 49% overall yield. Mass spectroscopic analysis showed the product to contain 81.7% CD_2I_2 , 16.5% $CHDI_2$, and 1.8% CH_2I_2 . Material of this composition was sufficient to establish the mechanistic points.

The reaction with cyclohexene in ether was repeated under identical conditions with dideuteriomethylene iodide. Where feasible, the minor products were isolated by g.p.c., and their infrared and mass spectra were examined.



Mass spectroscopic analysis of the ethylene formed revealed that no more than 1.5% could have arisen from the diethyl ether. Methyl iodide, methane, and methyl ethyl ether were dideuterated as shown. The infrared spectrum of the propylene showed it to be >95% 1,1-dideuteriopropylene.²³ These results are in complete accord with the proposed mechanism.

Traces of cyclopropane observed in most reactions presumably arise from addition of the reagent to ethylene generated *in situ*, since it is known that this reaction is remarkably facile.¹ When methylene iodide and zinc-copper couple were allowed to react in ether in the absence of olefin, approximately 85% of the methylene iodide was converted to ethylene. The mechanism of ethylene formation and its relation to the methylene-transfer reaction are considered below.

Nature of the Intermediate.—Because of experimental difficulties⁸ it has not been possible to isolate or determine the molecular weight of I, but other studies have given some clues to its structure. In ether solvents, as described above, the three main reactions undergone by I are the methylene-transfer reaction to olefins, formation of ethylene, and reduction to methyl iodide by the solvent. Attempts have been made to assess the relation between these reactions to deduce information on the state and structure of I in solution.

The influence of reaction conditions on the ratio of norcarane and ethylene formation was studied briefly.

(22) Monodeuteriomethylene iodide, prepared by reduction of deuterioiodoform, has been described by D. W. Setser and B. S. Rabinovitch, *J. Org. Chem.*, **26**, 2985 (1961).

(23) The authors wish to thank Prof. R. C. Lord for helpful discussions of the spectra.

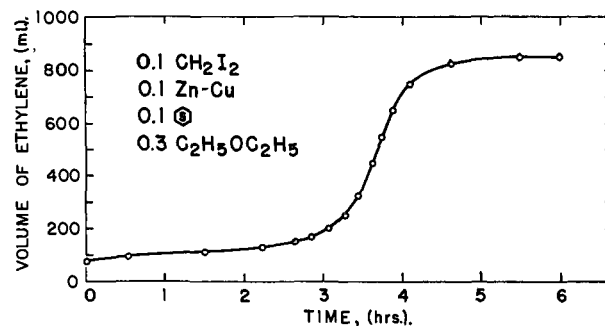


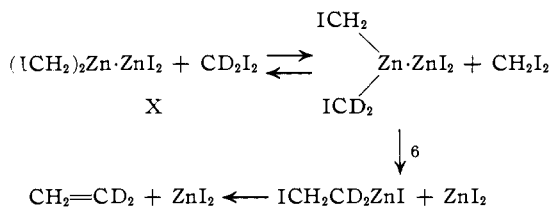
Fig. 2.—The rate of ethylene formation in a typical reaction in which cyclohexane was substituted for the reacting olefin.

Although the over-all reaction is reproducible for synthetic purposes, only crude kinetic information can be gained by studying systems in which I is formed *in situ*, since the reaction must be followed from a point after an uncertain induction period. The rate of the various processes occurring are dependent on the rate at which methylene iodide reacts heterogeneously with the zinc surface. Under the usual conditions it was noted that when the reagent was formed rapidly there were small, but measurable, differences in product distribution compared to runs in which the reagent formed (uncontrollably) at a slower rate. The rate of reaction of methylene iodide with zinc could be accelerated by the prior addition of zinc iodide (a reaction product) which apparently functions to scavenge the metal surface of oxide. This finding was utilized to aid reproducibility to some extent, but the effect was still not sufficiently important so that the desired studies could be made.

When compound I was generated under optimum synthesis conditions³ in ether containing cyclohexane in place of an olefin (to maintain approximately the same medium as in synthesis), the rate of ethylene formation for a typical run was followed and is shown in Fig. 2. Such plots were quite reproducible with a given sample of zinc-copper couple, and only minor variations were observed between batches of couple. Methylene iodide was converted to ethylene in 80% yield along with the other products discussed above. The rate of ethylene formation only becomes rapid after 3 hr. The induction period can be shortened slightly by the prior addition of zinc iodide.

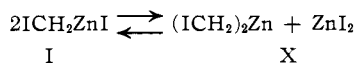
When cyclohexane was replaced by cyclohexene, and ethylene and norcarane formation were followed *simultaneously*, the results are shown in Fig. 3. The induction period (the point at which both rates became rapid) was decreased to 1.5 hr., because norcarane formation immediately releases zinc iodide into the reacting system. Ethylene formation is rather slow compared to the methylene-transfer reaction, and in blank runs (Fig. 2) a considerable concentration of I builds up before ethylene formation becomes rapid.

Ethylene formation ceased some 3–4 hr. before norcarane formation, which suggests that two different organozinc intermediates may be involved: one that primarily acts as a methylene-transfer reagent and one that predominantly reacts to give ethylene. Alternatively, it is more likely that ethylene is produced in a reaction of the active methylene-transfer reagent with methylene iodide. This bimolecular reaction would be expected to be important only when the concentrations of both I and methylene iodide are large, *i.e.*, in the



Few data on the structure and configuration of organozinc compounds are available in the literature. Molecular zinc iodide in the gas phase is linear,²⁵ and the same geometry was found for dimethylzinc on the basis of its Raman spectrum.²⁶ Dialkylzincs and especially alkylzinc halides are strongly solvated in basic solvents such as ethers,²⁷ and zinc usually is four-coordinate and tetrahedral.²⁸ The $\text{Zn}(\text{NH}_3)_4^{+2}$ ion is tetrahedral in aqueous ammonia, and the much rarer six-coordinate complexes $\text{Zn}(\text{NH}_3)_6^{+2}$ and $\text{Zn}(\text{H}_2\text{O})_6^{+2}$ are presumed to be octahedra.^{29,30} Organozinc compounds are tetrahedral in ether solvents^{20,27} but may be capable at most of weak, unsymmetrical octahedral coordination.

The structure of the intermediate responsible for the methylene-transfer reaction is probably not a simple, monomeric species such as iodomethylzinc iodide (I) or bis-(iodomethyl)-zinc (X); however, the chemical reactions of organozinc (and other Group II metals) compounds can be interpreted in terms of these simple structures.³¹



Equilibria of the Schlenk type ($\text{I} \rightleftharpoons \text{X}$) have been reported to be unimportant with other Group II metals: magnesium,³² beryllium,³³ cadmium.³⁴ It is not clear whether Schlenk equilibria may be important with organozinc compounds, but there are indications that they may be.³⁵ Recently, the rapid exchange of

(25) O. Hassel and L. C. Stromme, *Z. physik. Chem.*, **38**, 466 (1938).

(26) F. Fehér, W. Kolb, and L. L. Leverenz, *Z. Naturforsch.*, **2a**, 454 (1947).

(27) E. G. Rochow, D. T. Hurd, and R. N. Lewis, "The Chemistry of Organometallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 103.

(28) See F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 82. The zinc tetrachloride anion has been shown conclusively by its Raman spectrum to be tetrahedral in aqueous solution by L. A. Woodward and A. A. Nord, *J. Chem. Soc.*, 3721 (1956). X-Ray studies have shown that $\text{ZnCl}_2 \cdot 2\text{NH}_3$ and $\text{ZnBr}_2 \cdot 2\text{NH}_3$ are tetrahedral with the nitrogen orbitals directed toward the zinc atom (C. H. MacGillavry and J. M. Bijvoet, *Z. Krist.*, **94**, 249 (1936)).

(29) L. E. Orgel, "Transition-Metal Chemistry," Methuen and Co., Ltd., London, 1960, pp. 76, 83.

(30) See F. Basolo and R. G. Pearson, ref. 28, p. 83.

(31) Group II organometallics in systems containing the corresponding metal halide probably exist as low polymers with the salts acting as a coordinate bridge (private communication from Prof. R. E. Dessy). This must particularly be so in the rather concentrated solutions in which most studies in this paper were carried out.

(32) R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.*, **80**, 5824 (1958). See, however, E. C. Ashby and W. E. Becker, *ibid.*, **85**, 118 (1963), who have presented evidence that, although Grignard reagents are dimeric in diethyl ether, they are monomeric in tetrahydrofuran. The latter authors conclude that the existence of the Schlenk equilibrium is highly solvent dependent and that halide ion bridges occur in dimeric ethylmagnesium chloride in diethyl ether.

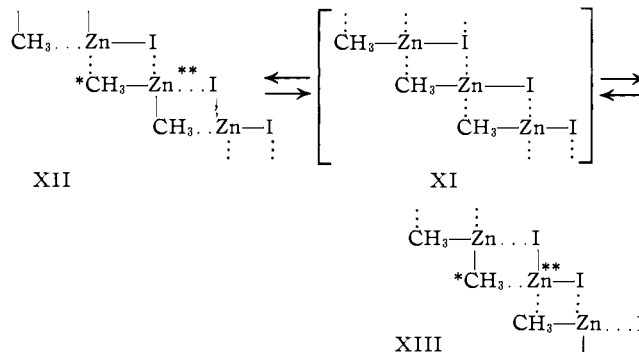
(33) R. E. Dessy, *ibid.*, **82**, 1580 (1960).

(34) A. B. Garrett, A. Sweet, W. L. Marshall, D. Riley, and A. Touma, *Record Chem. Progr.*, 155 (1952).

(35) Preliminary equilibrium constant measurements³⁴ have suggested that such equilibria are not important in the diethylzinc-zinc bromide system in heptane, but a private communication from Prof. R. E. Dessy based on unpublished observations indicates that this is not so in diethyl ether.

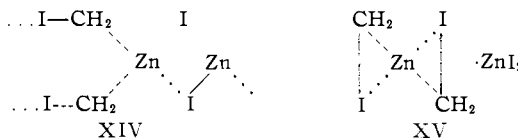
methyl groups in mixtures of dimethylzinc and dimethylcadmium in ether by way of bridged methyl structures has been demonstrated,³⁶ and it seems very likely that similar bridging occurs in systems containing halogen atoms, e.g., RZnI and $\text{R}_2\text{Zn} \cdot \text{ZnI}_2$.

The mechanism of the heterogeneous reaction of an alkyl iodide, e.g., methyl iodide, with zinc-copper couple in ether, solution is unknown, but it is reasonable to presume that the first-formed solution species is an alkylzinc iodide which rapidly "stacks" in the manner of XI. It is proposed that the collapse of XI to the chemically identical XII or XIII occurs simply by



favorable electron reorganization. The existence of a Schlenk equilibrium,³⁵ in effect, requires the conversion $\text{XII} \rightleftharpoons \text{XIII}$, i.e., carbon* and zinc** strongly bound in XII and weakly bound in XIII. It is not known if XI (CH_3ZnI -type) is an intermediate, as assumed in the classical Schlenk equilibrium, or a transition state for the possible interconversion of XII and XIII ($(\text{CH}_3)_2\text{Zn} \cdot \text{ZnI}_2$ -type).

The structure of the organozinc intermediate obtained from methylene iodide is complicated by the presence of an α -iodine atom in the alkyl group. In the simplest terms, we might regard the polymeric structure XIV or the monomeric structure XV as reasonable representations of the cyclopropane-forming reagent. The extent and type of coordination is a function of solvent and probably of concentration. Ether solvation can occur at the ends of short polymers and weakly at octahedral positions. If (I_C-Zn) interaction is important, it can be inferred that the carbon atoms in XIV and XV will have enhanced electrophilic character³⁷



in accord with observation.³⁸

Evidence that solutions of the reagent contained an intermediate possessing units of the $(\text{ICH}_2)_2\text{Zn} \cdot \text{ZnI}_2$ -type was gained by the following experiments.

(1) Methylene iodide (0.1 mole), cyclopentene (0.1 mole), cyclopentanol (0.1 mole), zinc-copper couple (0.1 mole), and ether (0.3 mole) were allowed to react under the usual conditions. Quantitative determination of the products revealed bicyclo[3.1.0]hexane (0.0013 mole), methyl iodide (0.0448 mole), methane

(36) C. R. McCoy and A. L. Allred, *J. Am. Chem. Soc.*, **84**, 912 (1962).

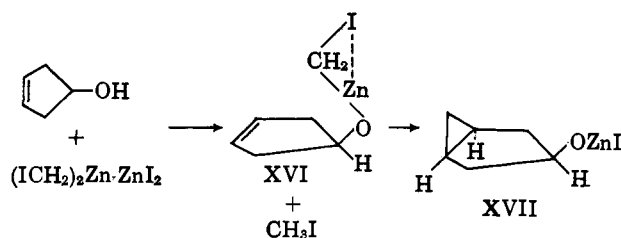
(37) This is expected, simply, on the basis of Walsh's rules: A. D. Walsh in "The Labile Molecule," Gurney and Jackson, London, 1947, p. 18.

(38) Scale molecular models indicate that polymers such as XIV possess methylene groups that are accessible to approach by an olefinic double bond.

(0.0266 mole), and unreacted methylene iodide (0.0258 mole). This experiment clearly shows that the intermolecular reaction of the organozinc compound responsible for cyclopropane formation with an olefin cannot compete effectively with intermolecular hydrolysis by an aliphatic alcohol.

(2) When methylene iodide (0.1 mole), zinc-copper couple (0.1 mole), and cyclopenten-4-ol³⁹ (0.1 mole) were allowed to react in ether (0.3 mole), methane (0.0149 mole) was evolved during the reaction.⁴⁰ Methylene iodide (0.0236 mole) was recovered, and *cis*-3-bicyclo[3.1.0]hexanol⁴¹ (0.0334 mole) and methyl iodide (0.0245 mole) were isolated from the hydrolyzed mixture (no gas was evolved on hydrolysis). No *trans*-bicyclohexanol was detected in accord with the results of Winstein and Sonnenberg.⁴¹

It has been previously suggested that oxygen-containing functions coordinate the reagent, increase the rate, and control the stereochemistry of the addition to a double bond.^{1,41} If the reagent has structure XIV or XV rather than a structure containing only one carbon-zinc bond (ICH₂ZnI-type), it would be expected that cleavage of the reagent by the acidic hydroxyl group would give a salt XVI and methyl iodide. Intramolecular methylene transfer would then yield *cis*-3-bicyclo-



[3.1.0]hexanol after hydrolysis of XVII. The high stereoselectivity observed in the addition to this and other hydroxyl-containing olefins⁴² can only be accounted for by prior complex formation or reaction of the reagent with the hydroxyl groups. If the reagent contains on the average two carbon-zinc bonds, we would expect to obtain equivalent amounts of *cis*-3-bicyclo[3.1.0]hexanol and methyl iodide as products, and this is indeed so. Based on the equal amounts of reactants employed, it is striking that a 33% yield of the cyclopropane was formed at all considering the very rapid cleavage of Group II organometallics with active hydrogen compounds. If the reagent contained units largely of the ICH₂ZnI-type, its destruction to give methyl iodide would have predominated as in the reaction with cyclopentene and cyclopentanol where no intramolecular transfer is possible.

Experimental

Gas partition chromatography has been used extensively to determine product compositions. Two systems were employed:

(39) S. Winstein, E. L. Allred, and J. Sonnenberg, *J. Am. Chem. Soc.*, **81**, 5833 (1959); E. L. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).

(40) Hydrolysis of an unfiltered solution of I in ether with water gave methane as a principal product. A solution filtered prior to hydrolysis gave principally methyl iodide. This suggests that methyl iodide is rapidly reduced by active zinc-copper couple in an amphiprotic solvent. Hence, the number of moles of zinc necessary to account for the above products is 0.0877.

(41) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

(42) For other examples, see A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4843 (1962), and subsequent papers in this series. A study of the stereochemistry of the formation of cyclopropyl carbinols by this method has been carried out by W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

(A) a Perkin-Elmer apparatus equipped with capillary columns (squalane or polyglycol) with hydrogen flame detector; and (B) a Perkin-Elmer vapor chromatograph utilizing columns prepared from commercially available liquid substrates on crushed firebrick support, the components being detected by a thermal conductivity cell. In all⁴³ cases, the peak areas of the various components are related to the mole fraction by analysis of known synthetic mixtures and calculation of correctional factors. Typical determinations will be found in this Experimental section.

The zinc-copper couple was prepared by the method of Shank and Shechter.⁴⁴ In those experiments where the percentage of copper in the couple was varied, this percentage was based on the amount of zinc metal and copper sulfate used. Methylene iodide (Matheson Coleman and Bell) was distilled and the portion with b.p. 65° (15 mm.) used. Cyclohexene was passed over a short column of activity 1 alumina just prior to use. The commercially available hydrocarbons were all at least 99% pure as evidenced by g.p.c. and were used without further purification.

The gas collections reported were effected by displacement of brine in a calibrated, pressure-equalized system.

Kinetic Determination—Effect of Cyclohexene Concentration on the Rate of Formation of Norcarane.—In a 200-ml. round-bottom flask equipped with magnetic stirrer, heating mantle, condenser, and gas collection apparatus was charged zinc-copper couple (13.45 g., 0.2 mole), ether (62 ml.), methylene iodide (53.6 g., 0.2 mole), and a crystal of iodine. The mixture was stirred and heated to reflux. After 53 min. the rate of gas evolution was 17 ml./min. and totaled 235 ml. The reaction flask was chilled in ice-water under a positive nitrogen pressure. The cold mixture was filtered under helium pressure through a previously dried funnel. The clear, pale yellow filtrate was transferred by means of pipets to two flame-dried, 100-ml., two-necked, reaction flasks cooled with ice-water baths. Each flask was charged with 30 ml. of the filtrate, and then cyclohexene was added by a syringe through a serum cap in the side arm of the flask. The time was measured with a stop watch, zero time being taken as the time when the cyclohexene was injected. Vessel 1 was charged with cyclohexene (3.1 ml., 2.43 g., 0.03 mole) and vessel 2 with cyclohexene (15.0 ml., 12.15 g., 0.15 mole). Samples (0.5 ml.) of the solution were removed with a syringe and quenched in 1.5 ml. of saturated aqueous ammonium chloride solution. The ether phase was analyzed by g.p.c., and the moles of norcarane calculated by the equation

$$M_n = \frac{PA_n F}{PA_n F + PA_c} M_{c_1}$$

where M_n = moles of norcarane, M_{c_1} = moles of cyclohexene initially present, PA_n = peak area of norcarane, PA_c = peak area of cyclohexene, and F = a fraction (0.857) experimentally determined from known mixtures of norcarane and cyclohexene by the formula

$$\frac{PA_n F}{(PA_n F + PA_c)} = \frac{M_n}{(M_n + M_c)}$$

From the M_n in run 2 at $t = 1500$ min., we estimate the moles of reagent (M_R) present initially in each case to be ca. 0.045. Utilizing the general second-order rate equation, where C_R is the initial concentration of reagent, C_C the initial concentration of cyclohexene, and C_N the concentration of norcarane, the values given in Table IV were found. The average k of run 1 was $0.65 \pm 0.05 \times 10^{-3} M^{-1} \text{ sec.}^{-1}$ and of run 2, $0.60 \pm 0.03 \times 10^{-3} M^{-1} \text{ sec.}^{-1}$.

$$-k = \frac{2.303}{t(C_C - C_R)} \log \frac{C_R(C_C - C_N)}{C_C(C_R - C_N)}$$

Competition Studies.—All competition studies were carried out in the same manner, typified by the following procedure. A 100-ml. round-bottom flask with side arm equipped with con-

(43) In the competition studies, the peak areas of the hydrocarbons were related to the mole fraction by a correctional factor based on the number of carbon atoms present in the molecule. In two cases checked experimentally (cyclohexene vs. norcarane and 1-heptene vs. *n*-amylcyclopropane), this correctional factor was well within the experimental error.

(44) R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

TABLE IV
RATE OF REACTION OF CYCLOHEXENE AND I IN DIETHYL ETHER
AT 0°

Time, min.	C _N , mole/l. ^a (no. 1)	k ₂ × 10 ³ , M ⁻¹ sec. ⁻¹	C _N , mole/l. ^a (no. 2)	k ₂ × 10 ³ , M ⁻¹ sec. ⁻¹
20	0.0109	0.604	0.0302	0.635
30	.0193	.719	.0416	.585
40	.0212	.601	.0533	.572
55	.0324	.673	.0802	.639
70	.0391	.640	.0193	.576
100	.0555	.647	.133	.612
	.691		.744	

^a C_N = concentration of norcarane.

denser and nitrogen inlet was flamed while being swept with a slow stream of nitrogen. The flask was allowed to cool and then charged with zinc-copper couple (6.73 g., 0.1 mole), a mixture of cyclohexene (8.2 g., 0.1 mole) and 1-heptene (9.8 g., 0.1 mole), methylene iodide (26.8 g., 0.1 mole), and ether (31 ml.). A crystal of iodine was added, and the system was swept with nitrogen. An ice-water-cooled condenser was used. The mixture was stirred at reflux for 20 hr. under nitrogen. At this point the flask was cooled in ice-water, and 25 ml. of cold aqueous ammonium chloride solution added with stirring. After 5 min., the upper layer was decanted and analyzed by g.p.c.

The composition of the product mixture was determined as

$$M_n = \frac{PA_n \times 0.857}{PA_n \times 0.857 + PA_c} \times 0.1$$

where 0.857 = 6/7 = number of carbon atoms in cyclohexene/number of carbon atoms in norcarane.

$$M_c = 0.1 - M_n$$

$$M_{cco} = \frac{PA_{cco} \times \frac{7}{C_{cco}} \times M_n}{PA_n}$$

$$M_{cco} = 0.1 - M_{cco}^{45}$$

The relative reactivity⁴⁶ is equal to

$$\frac{k}{k_c} = \frac{\ln \frac{M_{cco}}{0.1}}{\ln \frac{M_c}{0.1}}$$

where M_n = moles of norcarane, PA_n = peak area of norcarane, PA_c = peak area of cyclohexene, M_{cco} = moles of cyclopropane formed from competing olefin, PA_{cco} = peak area of cyclopropane formed from competing olefin, C_{cco} = number of carbon atoms in the cyclopropane formed from the competing olefin, M_c = moles of competing olefin remaining, and M_c = moles of cyclohexene remaining.

A typical experiment employing 1-heptene gave the values $PA_n = 146.64$, $PA_c = 163.2$, $PA_{cco} = 79.44$, from which $k/k_c = 0.404$. A duplicate run gave $k/k_c = 0.381$ (average 0.393).

Effect of Ether Concentration on Competition between 1-Hexene and Cyclohexene.—The reactions were carried out as described for the competition studies above using 0.1 mole of each reagent except that the ether concentration was varied as shown below. Calculations of relative reactivities were carried out as described above.

Vol. ether, ml.	31.0	46.5	62.0	77.5
k/k _c	0.36	0.33	0.36	0.36

(45) The amount of competing olefin remaining was not calculated from the peak area of this olefin, since in most cases this was a very sharp, narrow peak in which it was difficult to measure the peak width at peak half-height accurately.

(46) This relationship is used, rather than simply comparing the yields of the two cyclopropanes, to correct for changes in the relative concentrations of the two olefins as the reaction proceeds.

Hydrolysis of a Filtered Solution of the Reagent Generated from ClCH₂I and Zinc-Copper Couple.—Zinc-copper couple (6.73 g., 0.1 mole) and chloriodomethane (17.65 g., 0.1 mole) in diethyl ether (31 ml.) were heated under reflux with stirring for 2.67 hr., at which time the ethylene evolved equaled 200 ml. and it was being formed at a rate of 5 ml./min. The reaction mixture was chilled in ice-water under nitrogen, and the mixture filtered through a dry filter. Hydrolysis of the filtrate with water (25 ml.) and analysis of the ether phase revealed 0.014 mole of methyl iodide in addition to traces of methyl chloride.

Reaction of Diazomethane with Zinc Bromide.—A solution of 2.7 g. (0.064 mole) of diazomethane in 250 ml. of ether⁴⁷ was dried over potassium hydroxide pellets and then poured slowly into a cold (0°) solution of 15 g. (0.066 mole) of anhydrous zinc bromide in 100 ml. of dry ether. The yellow color of the diazomethane was discharged immediately, and nitrogen was evolved. A 10-ml. aliquot of the resulting homogeneous solution was hydrolyzed with dilute sulfuric acid. The gaseous hydrolysis products were collected in a Dry Ice trap and analyzed by g.p.c. Methyl bromide was the main hydrolysis product; it was formed in low yield and was identified by comparison of its retention time with that of an authentic sample.

The remainder of the bromomethylzinc bromide solution was heated under reflux for 15 hr. with 10 g. of cyclohexene. The solution was then washed with water and dried over magnesium sulfate. After removal of the ether, examination of the residue by g.p.c. showed only three peaks corresponding to ether, recovered cyclohexene, and norcarane, which were identified by comparison of their retention times with those of pure samples. The yield of norcarane based on diazomethane was 5%.

Reaction of Diazomethane with Zinc Chloride.—In an experiment carried out identically with that described for the reaction of diazomethane with zinc bromide, diazomethane (2.7 g., 0.064 mole), anhydrous zinc chloride (10 g., 0.073 mole), and dry ether (250 ml.) were employed. Hydrolysis of a 10-ml. aliquot of the reaction mixture gave a low yield of methyl chloride which was identified by g.p.c. The remaining ether solution was heated under reflux with 10 g. of cyclohexene and afforded a 3% yield (based on diazomethane) of norcarane, as determined by g.p.c.

Dideuteriomethylene Iodide.—To a solution of sodium iodide (45 g., 0.3 mole) in deuterioethanol (210 ml.) and deuterium oxide (64 g., 3.2 moles) was added sodium metal (7 g., 0.3 g.-atom) in small pieces. Methylene iodide (80 g., 0.3 mole) was added, and the two-phase system stirred at room temperature for 7 days. The lower phase was separated, dried over sodium sulfate, filtered, and distilled to give 65.5 g. (82%) of partially deuterated methylene iodide, b.p. 65° (15 mm.). This product was added to a solution of sodium iodide (45 g., 0.3 mole) in deuterioethanol (130 ml.) and deuterium oxide (64 g., 3.2 moles), and sodium methoxide (18 g., 0.33 mole) was added with stirring. The two-phase system was stirred at room temperature for 2 days and then at reflux for 4 days. The mixture was cooled and worked up as described above to give 39.9 g. (49%) of dideuteriomethylene iodide. Mass spectra analysis revealed a maximum of 1.8% CH₂I₂ and 16.5% CHDI₂, the remainder being CD₂I₂. The exchange can easily be followed by infrared spectroscopy. It was observed that bands at 3000, 1105, and 725 cm.⁻¹, associated with methylene iodide, disappear as exchange proceeds. Bands at 2215, 2180, 1075, and 780 cm.⁻¹, due to CHDI₂, appear and subsequently disappear. Finally, bands at 2290 and 835 cm.⁻¹, due to CD₂I₂, dominate the spectrum.

Products from the Reaction of Dideuteriomethylene Iodide.—The following experiment including techniques for product analysis is typical of all similar reactions reported in Table III.

Zinc-copper couple (6.73 g., 0.1 mole), dideuteriomethylene iodide (27.0 g., 0.1 mole), and cyclohexene (8.2 g., 0.1 mole) in diethyl ether (31 ml.) were allowed to react in the usual manner. After 21 hr. at reflux, 225 ml. of gas had been evolved. The flask was cooled, and the system swept with nitrogen until the total volume equaled 500 ml. Hydrolysis of the organic phase with 25 ml. of saturated ammonium chloride solution resulted in the evolution of 43 ml. of gas. The system was swept with 140 ml. of nitrogen.

Analysis. A. Organic Phase.—The ether solution was shown by g.p.c. to have the composition: norcarane, 0.0638; cyclohexene, 0.0362; methyl iodide, 0.0070; methyl ethyl ether, ~0.0005; ethyl isopropyl ether, ~0.0005 mole. The solution was

(47) T. J. DeBoer and H. J. Backer, *Org. Syn.*, **36**, 16(1956).

separated by g.p.c. and the components analyzed by mass spectroscopy which revealed the methyl ethyl ether⁴⁸ and the methyl iodide to be predominantly deuterated.

B. Gas Evolved during Reaction.—Analysis of this gas by g.p.c. and calculation of mole % gave the results

	% of sample	Mole formed
Methane	3.6	0.0008
Ethylene	29.0	.0065
Cyclopropane	0.3	.0001
Propylene	4.0	.0009

Mass spectral analysis of this gas mixture gave the results: C₃H₄D₂, 1.5%; C₃H₃D, 1.5%; C₂D₄, 20%; C₂D₃H, 6%; C₂DH₃ and C₂H₄, <1.5%; CH₂D₂, 5.6%.

C. Gas Evolved during Hydrolysis.—Analysis of this gas by g.p.c. and calculation of mole % gave the results

	% of sample	Mole
Methane ^a	6.8	0.00055
Ethylene	2.0	.00022
Propylene	0.4	.00003

^a In a similar experiment in which methylene iodide, zinc-copper couple, and cyclohexane in ether were allowed to react for 20 hr., hydrolysis with deuterium oxide gave monodeuteriomethane.

Identification of Ethyl Isopropyl Ether.—Although this ether could be detected by g.p.c. in all experiments carried out with diethyl ether as solvent, a reaction in the absence of olefin was carried out to enhance the yield of this product and thus simplify isolation.

A reaction between zinc-copper couple (6.73 g., 0.1 mole) and methylene iodide (26.8 g., 0.1 mole) in diethyl ether (31 ml.) was carried out in the usual manner. The reaction mixture was hydrolyzed with ammonium chloride solution (25 ml.), and the ether layer separated. The ethyl isopropyl ether was identified in the ether phase both from its retention time on g.p.c. and from comparison of its mass spectrum with that of an authentic sample. Examination of the gas chromatogram failed to reveal any component with the retention time displayed by *n*-propyl ethyl ether.

Rate of Formation of Norcarane and Ethylene in a Typical Experiment.—The reaction was carried out in the usual manner with 6.73 g. (0.1 mole) of zinc-copper couple, 26.8 g. (0.1 mole) of methylene iodide, and 8.2 g. (0.1 mole) of cyclohexene in 31 ml. of ether. Samples (*ca.* 0.1 ml.) were withdrawn at various times and quenched in 1 ml. of saturated aqueous ammonium chloride solution. The organic phase was analyzed by g.p.c., and amounts of norcarane estimated from the peak areas as previously described.

Time, min.	Ethylene, ml.	Norcarane, mole	Time, min.	Ethylene, ml.	Norcarane, mole
72	25	0.0061	148.5	200	0.0511
94	50	.0121	165	215	.0555
107	75	.0206	210	225	.0584
116	100	.0245	270	225	.0634
127	125	.0313	330	225	.0647
130.5	150	.0374	1680	225	.0680
138	175	.0442			

Rate of Ethylene Formation in the Absence of a Reacting Olefin.—In a dry 100-ml. flask was charged 6.73 (0.1 mole) of zinc-copper couple, 26.8 g. (0.1 mole) of methylene iodide, 8.4 g. (0.1 mole) of cyclohexane, and 31 ml. of ether. A small crystal of iodine was added, and the mixture was heated at reflux with stirring. The zero time was taken when reflux began and the initial sweep volume settled (see Table V).

Effect of Olefin Reactivity on the Product Composition. A.—In a 100-ml., round-bottom flask equipped with stirrer, condenser, and gas collection apparatus was charged zinc-copper couple (7.05 g., 0.105 mole), ether (31 ml.), and iodine (1.27 g., 0.005 mole). The mixture was stirred until the iodine color disappeared. At this point, methylene iodide (26.8 g., 0.1 mole) and 3,3-dimethyl-1-butene (8.4 g., 0.1 mole) were added. The mixture was stirred at reflux for 17 hr. during which time 362

TABLE V

Time, min.	Vol. of gas evolved, ml.	Time, min.	Vol. of gas evolved, ml.
0	0	215.5	350
72	30	223	450
134	55	231	550
178	110	241.5	650
192	150	252.5	700
201	200	277.5	750
207	250	330	775
211.5	300		

ml. of gas was evolved. Hydrolysis of the reaction mixture with 25 ml. of concentrated ammonium chloride solution resulted in the evolution of 240 ml. of gas. Analysis of the liquid phase revealed a 38.5% yield of *t*-butylcyclopropane.

B.—In the same manner described above, a solution of zinc iodide (0.005 mole) in ether (31 ml.) and zinc-copper couple (6.73 g., 0.1 mole) was prepared and treated with 2-methyl-1-butene (8.4 g., 0.12 mole) and methylene iodide (26.8 g., 0.1 mole). The mixture was stirred at reflux for 16.5 hr. during which time 115 ml. of gas was evolved. Hydrolysis with 25 ml. of concentrated aqueous ammonium chloride solution resulted in the evolution of 10 ml. of gas. Analysis of the liquid phase revealed a 79.5% yield of 1-methyl-1-ethylcyclopropane.

C.—In a 100-ml., round-bottom flask equipped with condenser, stirrer, and gas collection apparatus was charged zinc-copper couple (6.73 g., 0.1 mole), methylene iodide (26.8 g., 0.1 mole), ether (31 ml.), cyclohexene (8.2 g., 0.1 mole), and zinc iodide (3.2 g., 0.01 mole). The mixture was heated at reflux with stirring for 21.5 hr. during which time 188 ml. of gas was evolved. Analysis of the liquid phase revealed a 59.5% yield of norcarane.

Competition between Cyclopentanol and Cyclopentene.—In a flame-dried, nitrogen-purged, 100-ml. flask equipped with stirrer, condenser, and gas collection apparatus was charged zinc-copper couple (6.73 g., 0.1 mole), methylene iodide (26.8 g., 0.1 mole), cyclopentanol (8.6 g., 0.1 mole), cyclopentene (6.8 g., 0.1 mole), and ether (31 ml.). The mixture was stirred and heated at reflux for 66.5 hr. The system was cooled in ice-water and swept with nitrogen until the volume of gas collected equaled 1100 ml. The ether phase was treated with 50 ml. of concentrated aqueous ammonium chloride solution, separated, and dried over magnesium sulfate.

Analysis of the gas phase by mass spectroscopy revealed the presence of ethylene (1.3 mole %) and methane (54.3 mole %).

$$\text{ethylene} = (0.013 \times 1100)/22400 = 0.00064 \text{ mole}$$

$$\text{methane} = (0.543 \times 1100)/22400 = 0.0267 \text{ mole}$$

Analysis of the ether phase by g.p.c., application of experimentally determined area correctional factors, and calculations similar to those described gave the product analysis: cyclopentene, 0.0987 mole; bicyclo[3.1.0]hexane, 0.0013 mole; methyl iodide, 0.0448 mole; methylene iodide, 0.0258 mole.

Cyclopenten-4-ol was prepared in 15% yield from freshly prepared cyclopentadiene (315 g., 4.78 moles) and diborane (13.2 g., 0.477 mole) according to a published procedure.⁴¹ The alcohol had b.p. 67–68° (38 mm.), *n*_D²⁰ 1.4670–1.4680 (lit.⁴¹ b.p. 67–68° (36 mm.), *n*_D²⁰ 1.4673).

Reaction Products from Cyclopenten-4-ol.—In a flame-dried, 100-ml., round-bottom flask equipped with condenser, stirrer, and gas collection apparatus was charged zinc-copper couple (6.73 g., 0.1 mole), methylene iodide (26.8 g., 0.1 mole), ether (31 ml.), and cyclopenten-4-ol (8.4 g., 0.1 mole). The mixture was warmed to reflux whereupon an exothermic reaction occurred. An ice bath was used to moderate the reaction during the first 0.5 hr. External heat was provided to maintain reflux for 19 hr. The system was cooled in an ice bath and swept with nitrogen until the gas collected equaled 1000 ml. The ether phase was treated with 50 ml. of saturated aqueous ammonium chloride solution and separated. The aqueous phase was extracted with two 30-ml. portions of ether and the combined ether phases were dried over magnesium sulfate.

Mass spectral analysis of the gas phase revealed 1.2 mole % ethylene and 33.4 mole % methane.

	ml.	Mole	Mole of CH ₂ I ₂ consumed
Ethylene	12	0.00054	0.0011
Methane	334	0.0149	0.0149

(48) An authentic sample of methyl ethyl ether was prepared by the reaction of ethyl iodide with sodium methoxide in methanol, isolated by g.p.c., and its mass spectrum determined.

Analysis of the liquid phase revealed the peak areas

		F^a
Methyl iodide	2.6	1.85
Methylene iodide	7.6	0.612
Cyclopenten-4-ol	13.1	1.00
3-Hydroxybicyclo[3.1.0]hexane	6.9	0.954

^a F , experimentally determined area correctional factors relating peak area of component to peak area of cyclopenten-4-ol.

$$\text{cyclopenten-4-ol} = \frac{13.1}{13.1 + 6.9 \times 0.954} \times 0.1 = 0.0666 \text{ mole}$$

$$3\text{-hydroxybicyclo[3.1.0]hexane} = 0.1 - 0.0666 = 0.0334 \text{ mole}$$

mole fraction of methyl iodide (relative to cyclopenten-4-ol) =

$$\frac{2.6 \times 1.85}{2.6 \times 1.85 + 13.1} = 0.2686$$

$$\text{methyl iodide} = \frac{0.2686 \times 0.0666}{1 - 0.2686} = 0.0245 \text{ mole}$$

mole fraction of methylene iodide (relative to cyclopenten-4-ol) =

$$\frac{7.6 \times 0.612}{7.6 \times 0.612 + 13.1} = 0.262$$

$$\text{methylene iodide} = \frac{0.262 \times 0.0666}{1 - 0.262} = 0.0236 \text{ mole}$$

In the manner described above, a reaction was carried out using cyclopenten-4-ol (8.4 g., 0.1 mole), methylene iodide (53.6 g., 0.2 mole), zinc-copper couple (13.56 g., 0.2 mole), and ether (31 ml.). Analysis of the gas and liquid products as described gave the product composition: cyclopenten-4-ol, 0.0069 mole; 3-hydroxybicyclo[3.1.0]hexane, 0.0931 mole; methyl iodide, 0.0270 mole; methylene iodide, 0.0241 mole; methane, 0.0156 mole.

Hydrolysis of an Unfiltered Solution of I (X).—In a dry 100-ml., round-bottom flask equipped with magnetic stirrer, condenser, and gas collection apparatus were mixed zinc-copper couple (6.73 g., 0.1 mole), methylene iodide (26.8 g., 0.1 mole), and ether (31 ml.). A crystal of iodine was added and the mixture heated at reflux. When 205 ml. of gas had evolved (111 min., rate at end equaled 12.5 ml./min.), the flask was cooled in ice-water, and a fresh gas collection bottle attached. The cold mixture was treated with 5 ml. of deuterium oxide and a rapid exothermic reaction occurred evolving 380 ml. of gas. Analysis of the gas by mass spectroscopy revealed 52–60 mole % CH_2D_2 .

Reaction of Dideuteriomethylene Iodide with a Filtered Solution of I (X).—A reaction of zinc-copper couple (6.73 g., 0.1 mole) and methylene iodide (26.8 g., 0.1 mole) in ether (31 ml.) was carried out as described above until the gas evolution equaled 215 ml. The mixture then was cooled in ice-water and filtered under helium pressure through a dry sintered-glass filter. The filtrate was collected in a 100-ml. round-bottom flask, treated with 11.5 g. of dideuteriomethylene iodide, and heated at reflux. After 88 hr. at reflux, 80 ml. of gas had been evolved. Mass spectral analysis revealed 9–10% dideuterioethylene and 50–60% ethylene.

[CONTRIBUTION NO. 929 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

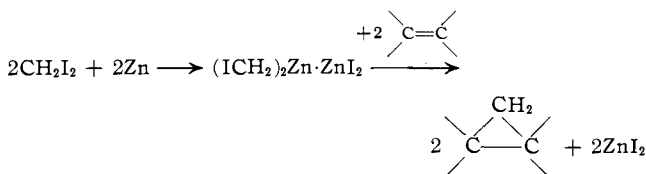
Cyclopropane Synthesis from Methylene Iodide, Zinc-Copper Couple, and Olefins. III. The Methylene-Transfer Reaction

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RECEIVED OCTOBER 30, 1963

The methylene-transfer reagent obtained from methylene iodide and zinc-copper couple, bis-(iodomethyl)-zinc-zinc iodide (I), is discussed in terms of the transition state involved in the transfer step with olefins. The "freeness" of carbenes, *i.e.*, the extent of their solvation by neutral species and metal salts, is considered in light of the present results. The conditions of cyclopropane synthesis are discussed, and several examples of stereoselective additions of I to olefins are given. *endo*-Dicyclopentadiene reacted with excess of I to give a mixture of a single diadduct and the two corresponding monoadducts; *exo*-dicyclopentadiene behaved similarly giving two different monoadducts and a different diadduct from those obtained from the *endo* isomer. Ethylidene iodide reacted with zinc-copper couple in the presence of cyclohexene to give ethylene and *exo*-7-methylbicyclo[4.1.0]heptane; none of the corresponding *endo* isomer was detected. 2,2-Diiodopropane reacted with zinc-copper couple to give propylene, and in the presence of cyclohexene no cyclopropane formation could be detected.

Evidence has been presented^{1,2} that methylene iodide and zinc-copper couple react in ether solution to give bis(iodomethyl)zinc-zinc iodide (I), although an unequivocal structure has not been established. The reaction of I with olefins to give cyclopropanes was shown to be a bimolecular process in which there is no



carbene or methylene intermediate, and such reactions were termed methylene-transfer reactions. This paper considers the methylene-transfer reaction in more detail.

Methylene-Transfer Reactions.—Divalent carbon species, methylenes³ and carbenes,⁴ are frequently proposed as intermediates in many reactions of olefins where cyclopropane formation or insertion into unactivated carbon-hydrogen bonds is observed. Most photochemical and many thermal reactions of diazo compounds with olefins which give cyclopropanes almost certainly involve a free divalent carbon molecule.⁵ In contrast, the addition of bis-(iodomethyl)-zinc-zinc iodide (I) to unactivated carbon-carbon double bonds and its formal insertion into diethyl ether have been shown not to involve methylene or carbene.² The intermediacy of free species in most other cyclopropane-forming reactions is open to question. The mode of addition of I to olefins is probably representative of some of these reactions, but a spectrum of mechanisms

(3) W. von E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

(4) P. S. Skellern and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

(1) Paper I: H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959); also see H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958).

(2) Paper II: E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

(5) (a) See review by R. Huisgen, *Angew. Chem.*, **67**, 439 (1955); (b) W. M. Jones, M. H. Grasley, and W. S. Brey, Jr., *J. Am. Chem. Soc.*, **85**, 2754 (1963).