

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.

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

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

$$\text{mole fraction of methyl iodide (relative to cyclopenten-4-ol)} = \frac{2.6 \times 1.85}{2.6 \times 1.85 + 13.1} = 0.2686$$

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

$$\text{mole fraction of methylene iodide (relative to cyclopenten-4-ol)} = \frac{7.6 \times 0.612}{7.6 \times 0.612 + 13.1} = 0.262$$

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

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.]

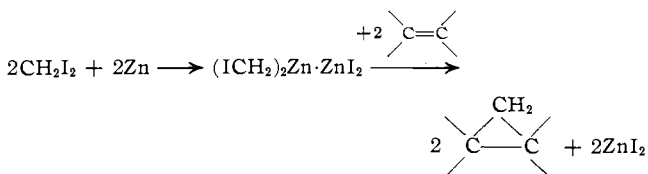
Cyclopropane Synthesis from Methylene Iodide, Zinc-Copper Couple, and Olefins. III. The Methylene-Transfer Reaction

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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).

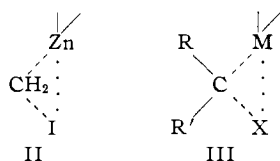
(2) Paper II: E. P. Blanchard and H. E. Simmons, *ibid.*, **86**, 1337 (1964).

(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).

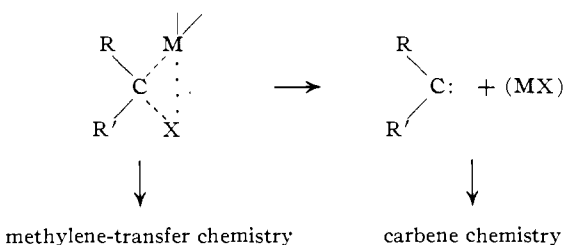
can be confidently expected between the extremes of addition by free carbenes and methylene-transfer reagents.

Recently, evidence was presented by Jones, Grasley, and Brey^{6b} that 2,2-diphenylcyclopropylidene, generated thermally from the diazo compound, adds stereospecifically to olefins giving spiropentanes, apparently does not insert at carbon-hydrogen bonds, and undergoes concurrent isomerization to 1,1-diphenylallene. Relative rates of addition to olefins revealed a sizable steric effect, similar to that observed with I. It is thus clear that steric effects can be large even when a free divalent species undergoes additions, and criteria concerning stereospecificity and carbon-hydrogen insertions may not be unequivocal in inferring the nature of such intermediates.

Bis(iodomethyl)zinc-zinc iodide (I) bears considerable resemblance to intermediates suspected in many halomethane reactions. It was shown^{1,2} that I contains units of the partial structure II, the coordination of the iodine atom with the metal producing a very re-



active methylene group. It is now suggested that this essential feature characterizes a class of organometallics III (M = metal and X = halogen or other stable anion). The lifetime of III with respect to dissociation to a free carbene will determine the characteristic chemistry observed. When R, M, and X in III combine



to produce a molecule capable of transferring RR'C to an olefin, several mechanisms can still be anticipated depending on the precise structural features.

We might expect two general types, either an essentially concerted process resembling carbene addition or a multistep addition. Previous studies^{1,2} and evidence presented below suggest that I reacts in the former manner.

The criterion of stereospecificity in olefin additions for inferring the electronic state of free carbenes is still not firmly established, and it seems to the authors that a general principle will remain elusive. The proposed one-step addition of free singlet carbenes in which two (C-C) bonds are formed is generally presumed to be stereospecific. Although spin conservation is not involved, the cyclopropane once formed must dissipate ca. 80 kcal./mole of thermal energy. Collisional deactivation in solution would have to be very efficient for these reactions always to show stereospecificity. In fact, one might anticipate that two-step additions would give intermediates more readily capable of reaching thermal equilibrium before rotation about

single bonds. The added complication of spin conservation in such triplet additions cannot be quantitatively assessed at present for solution systems containing sizable molecules and may well not be very stringent. At any rate, the presence of a third body in the transition state of one-step methylene transfer reactions, e.g., zinc iodide in I, should greatly aid dissipation of the excess vibrational energy of the newly formed cyclopropane. In addition, many such transition states contain halogen and other heavy atoms which should relax any potential problems concerning spin.

The occurrence of the formal structure III is not alone sufficient to ensure unusual reactivity. Iodomethylmercuric iodide (ICH₂HgI,⁶ III, R = R' = H, M = Hg, X = I) and iodomethylmagnesium iodide or methylene bis-(magnesium iodide)⁷ (III, R = R' = H, M = Mg, X = I) are stable molecules and do not react with olefins under moderate temperature conditions.¹ Many known organometallic intermediates, however, are encompassed by structure III and in particular react with olefins to give cyclopropanes. In no case has the intermediacy of free carbenes been proved, and some of the following reactions almost certainly are methylene-transfer types.

The reactions of certain diazo compounds with olefins to give cyclopropanes in the presence of copper or copper salts⁸ probably do not involve a free divalent carbon species but rather are transfer reactions to the double bond from an energy-rich complex of the carbene or methylene with the metal or salt.² The reaction of diazo compounds with nickel carbonyl⁹ has also been suggested to proceed through an intermediate which is formally a complex of this type.

Certain stable molecules in which the divalent carbon fragment is bound to the carrier by strong, covalent bonds behave similarly. The ylids, trimethylammoniummethylid, (CH₃)₃N⁺-C⁻H₂,¹⁰ and alkylidetriphenylphosphines, (C₆H₅)₃P=CHR,¹¹ react with unactivated olefins to give the corresponding cyclopropane, trimethylamine, and triphenylphosphine, respectively. Trifluoromethyltrimethyltin, CF₃Sn(CH₃)₃,^{12a} (CF₃)₃PF₂,^{12b} and trichloromethyltrichlorosilane, CCl₃SiCl₃,¹³ are similar examples of this class, which have been postulated to expel dihalocarbenes at moderate temperatures, although this suggestion has not yet been confirmed.

Reactions of halomethanes with strong base¹⁴ generate intermediates which are widely supposed to be free carbenes because of their exothermic addition to double bonds, although insertion at C-H bonds is infrequent.¹⁵ The former criterion, regardless of

(6) J. Sakurai, *J. Chem. Soc.*, **37**, 658 (1880).

(7) G. Emschwiller, *Compt. rend.*, **183**, 665 (1926); also see D. Y. Chang and C. L. Teng, *Trans. Sci. Soc., China*, **7**, 243 (1932); and D. A. Fidler, J. R. Jones, S. L. Clark, and H. Stange, *J. Am. Chem. Soc.*, **77**, 6634 (1955).

(8) (a) P. Yates, *ibid.*, **74**, 5376 (1952); (b) W. von E. Doering and I. H. Knox, *ibid.*, **78**, 4947 (1956); (c) P. S. Skell and R. M. Etter, *Chem. Ind. (London)*, 624 (1958).

(9) C. Rüchardt and G. N. Schrauzer, *Ber.*, **93**, 1840 (1960).

(10) V. Franzen and G. Wittig, *Angew. Chem.*, **72**, 417 (1960).

(11) H. J. Bestmann and F. Serg, *Angew. Chem. Intern. Ed. Engl.*, **1**, 116 (1962).

(12) (a) H. C. Clark and C. J. Willis, *J. Am. Chem. Soc.*, **82**, 1888 (1960); (b) W. Mahler, *ibid.*, **84**, 4600 (1962).

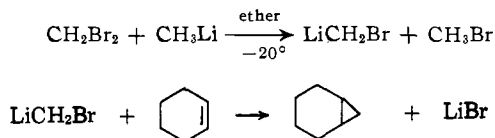
(13) W. I. Bevan, R. N. Haszeldine, and J. C. Young, *Chem. Ind. (London)*, 789 (1961).

(14) J. Hine and A. M. Dowell, Jr., *J. Am. Chem. Soc.*, **76**, 2688 (1954).

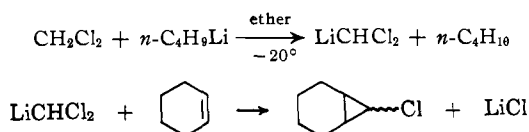
(15) E. K. Fields, *ibid.*, **84**, 1744 (1962); J. C. Anderson and C. B. Reese, *Chem. Ind. (London)*, 575 (1963); D. Seyferth and J. M. Burlitch, *J. Am. Chem. Soc.*, **85**, 2667 (1963).

stereospecificity, now seems insufficient, while the latter is more in accord with a reaction expected of divalent carbon.

Miller and Kim¹⁶ found that methylene bromide and methyl lithium undergo halogen-metal exchange at -20° in ether in the presence of cyclohexene to give norcarane. It was suggested that the intermediate bromomethyl lithium (III, $R = R' = H$, $M = Li$, $X = Br$) may have given free carbene. On the other hand,



methylene chloride and *n*-butyllithium under similar conditions gave a mixture of the isomeric 7-chlorobicyclo[4.1.0]heptanes.¹⁷ Hydrogen-metal exchange occurred in this case to produce dichloromethyl lithium (III, $R = H$, $R' = Cl$, $M = Li$, $X = Cl$), and similar alkyl derivatives $\text{Li}^+\text{RCHCl}^-$ derived from it¹⁸ were



postulated to have a finite lifetime based on their demonstrable intermediacy in other systems.¹⁹ Closs¹⁸ has presented evidence that free alkylcarbenes derived from $\text{Li}^+\text{RCHCl}^-$ are the species involved in the carbon-hydrogen insertion reactions observed in these systems. It is still unclear whether cyclopropane formation occurs *via* the free carbene or dichloromethyl lithium. Closs and Closs²⁰ have shown that the intermediate generated from diphenyldibromomethane and methyl lithium adds stereospecifically to olefins, while that generated by photolysis of diphenyldiazomethane does not.²¹ They have suggested that the former addition occurs *via* III ($R = R' = \text{C}_6\text{H}_5$, $M = Li$, $X = Br$) in a transition state reminiscent of a $\text{S}_\text{N}2$ displacement,^{22a} *i.e.*, a one-step methylene transfer. Perhaps the most striking demonstration of the nonequivalence of such similarly related intermediates was given by Closs and Coyle,^{22b} who were able to prepare chlorodiazomethane. Photolysis and thermolysis of the diazo compound in *cis*- and *trans*-2-butene gave stereospecific addition with low steric discrimination compared to the intermediate generated from methylene chloride,¹⁷ while similar decompositions in pentane gave the three possible carbon-hydrogen insertion products.

Type III structures can be written in a completely analogous fashion for the intermediates in the reactions of haloforms,²³ trihaloacetic esters,²⁴ and perhalo ketones²⁵ with bases and of tetrahalomethanes with

(16) W. T. Miller, Jr., and C. S. Y. Kim, *J. Am. Chem. Soc.*, **81**, 5008 (1959).

(17) G. L. Closs and L. E. Closs, *ibid.*, **81**, 4996 (1959).

(18) G. L. Closs, *ibid.*, **84**, 809 (1962).

(19) C. R. Hauser, W. R. Brasen, P. S. Skell, S. W. Kantor, and A. E. Brodhag, *ibid.*, **78**, 1653 (1956).

(20) G. L. Closs and L. E. Closs, *Angew. Chem. Intern. Ed. Engl.*, **1**, 334 (1962).

(21) P. S. Skell and R. M. Etter, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

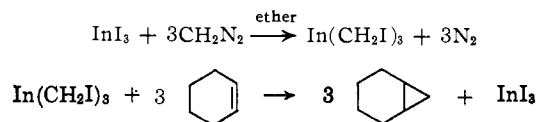
(22) (a) Also see G. L. Closs and L. E. Closs, *ibid.*, **85**, 99 (1963); (b) G. L. Closs and J. J. Coyle, *ibid.*, **84**, 4350 (1962).

(23) J. Hine, *ibid.*, **72**, 2438 (1950).

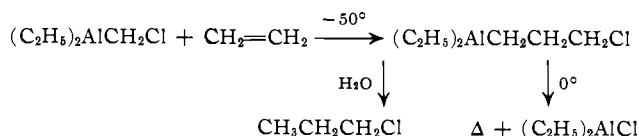
(24) W. E. Parham and E. E. Schweizer, *J. Org. Chem.*, **24**, 1733 (1959).

alkyllithium reagents,¹⁶ all of which have been suggested to involve dihalocarbenes.

Schwarzenbach²⁶ has found that the intermediate formed in the reaction of indium iodide and diazomethane transfers its methylene group to cyclohexene. This reaction is presumably very similar to that in-

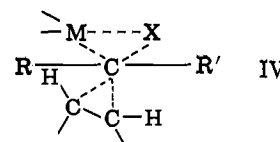


volving I. Even when the organometallic itself is involved in the transition state for cyclopropane formation, a variety of mechanisms can be envisaged for this methylene-transfer step. It is conceivable that addition of I to olefins occurs in a stepwise fashion that would still be compatible with the kinetics of the reaction.² Hoberg²⁷ has shown that diethylaluminum chloride and diazomethane form diethylchloromethylaluminum which is stable at -50° but reacts with cyclohexene at -10° to give norcarane. Although reaction of chloromethyldiethylaluminum with ethylene has been shown to proceed by an addition across the double bond, the suggestion²⁸ that reactions of I with olefins occurs similarly could not be substantiated in our work.



The reagent prepared from chloriodomethane and zinc-copper couple in ether was allowed to react with *cis*-3-hexene at 0° for 4 hr. Hydrolysis of an aliquot with ammonium chloride solution gave only 1,2-dichloroethane,² chloriodomethane, methyl iodide,² and *cis*-1,2-diethylcyclopropane¹ (0.6%). Gas phase chromatographic and mass spectral analyses revealed no $\text{C}_7\text{H}_{16}\text{Cl}$ or $\text{C}_7\text{H}_{16}\text{I}$ compounds which would have been formed by analogy with Hoberg's observation that his intermediate addition compound could be hydrolyzed to propyl chloride.

There is no evidence that coordination of the metal atom in III with the π -electrons of the olefin is involved in the methylene-transfer reactions of I,²⁹ and the transition state of the transfer has been postulated to resemble IV.^{1,20,30} Such a one-step mechanism is in accord with the above observation, and relative reactivity² and stereoselectivity studies with I have given experimental evidence of the steric effects implied by this structure. For example, the balance of



(25) P. K. Kadaba and J. O. Edwards, *ibid.*, **25**, 1431 (1960); F. W. Grant and W. B. Cassie, *ibid.*, **25**, 1433 (1960).

(26) K. Schwarzenbach, Thesis, Heidelberg and Zurich, 1961.

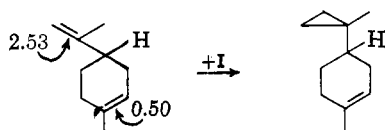
(27) H. Hoberg, *Angew. Chem.*, **73**, 114 (1961); *Ann.*, **656**, 1 (1962).

(28) H. Hoberg, *ibid.*, **656**, 15 (1962).

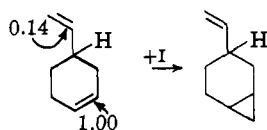
(29) The infrared spectra of olefins in methylmagnesium iodide and methylzinc iodide show no perturbation of the double-bond stretching frequencies.

(30) L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961, p. 538.

electrical and steric effects affords an explanation for the apparent anomaly that *d*-limonene is attacked by I preferentially at the vinyl double bond,¹ while 4-



vinylcyclohexene is attacked at the ring double bond.³¹

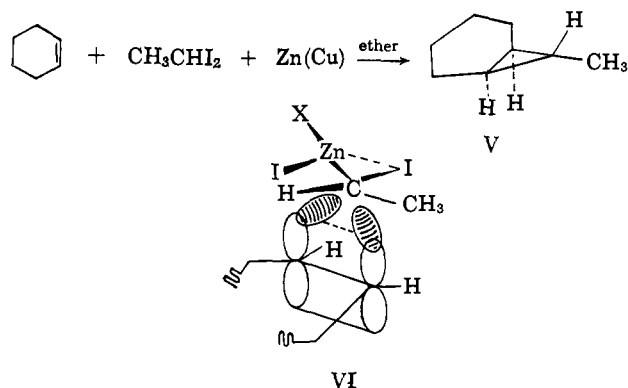


The approximate relative reactivity ratios (cyclohexene = 1.00) for the different types of double bonds are shown in the equations.

To assess the influence of substituents in I, ethylidene and isopropylidene iodide were treated with zinc-copper couple in ether containing cyclohexene. Ethylidene iodide reacted vigorously to give 3.6% of an adduct, C₈H₁₄, which was isolated by distillation and purified by g.p.c. The remainder of the ethylidene iodide was converted to ethylene. Transfer of the ethylidene group from III (R = CH₃, R' = H, M = Zn, X = I) can give rise to two isomers³²; however, only a single saturated hydrocarbon was detected in the fractions boiling higher than cyclohexene. The product was shown to be identical with a sample of authentic *exo*-7-methylbicyclo[4.1.0]heptane (V)^{33, 34} by comparison of their infrared spectra.

The *exo* isomer was formed to the virtual exclusion of the *endo* isomer, which would have been detected in amounts of 0.5% by the g.p.c. techniques. This stereoselectivity appears to be a consequence solely of the large steric requirements imposed in the transition state for transfer of the [CH₃-C-H] group.

If model IV is accepted for the transition state for transfer, the carbon atom approaches the π -bond so



(31) S. D. Koch, R. M. Kliss, D. V. Lopickes, and R. J. Wineman, *J. Org. Chem.*, **26**, 3122 (1961).

(32) D. W. Setser and B. S. Rabinovitch, *ibid.*, **26**, 2985 (1961), reported that the addition of ethylidene iodide to ethylene in a closed system gave methylcyclopropane in 25% yield accompanied by much ethylene formation.

(33) The stereochemistry of bicyclo[4.1.0]heptanes substituted in the 7-position will be designated *exo/endo*. An *endo* substituent in the 7-position will signify the substituent lies "over" the cyclohexane ring, and an *exo* substituent lies "away from" this ring (e.g., V).

(34) Private communication from Professor A. C. Cope. Authentic *exo*-7-methylbicyclo[4.1.0]heptane was synthesized by the lithium aluminum hydride reduction of the crystalline tosylate of *exo*-7-hydroxymethyl[4.1.0]heptane.

that maximum overlap of the forming orbitals (shaded) is achieved (VI). We suppose that the forming zinc iodide fragment has receded considerably in the transition state, so that (I_C-C) and (Zn-C) bond breaking have proceeded to a greater extent than (C-C) bond forming. Such a transition state would then resemble the addition of a carbene to a π -bond. As the zinc iodide fragment falls away, the angle CH₃-C-H undergoes inversion. This representation of the transition state predicts that the reagent prepared from a substituted methylene iodide (R \neq R') should experience asymmetry of approach to the double bond. If the double bond is part of a ring, e.g., cyclohexene, we would expect the smaller of the groups to lie over the ring on the grounds of nonbonded steric repulsions. This group must be sandwiched between the ring atoms and the ligand X.³⁵

The addition to cyclohexene of chlorocarbene, generated from methylene chloride and *n*-butyllithium, gave a 2:1 mixture of *endo*- and *exo*-7-chlorobicyclo[4.1.0]heptanes, respectively.^{17, 36} The radii for nonbonded repulsive interaction (van der Waals) of the methyl group and the chlorine atom are 2.0 and 1.8 Å., respectively³⁷; thus, transfer of [CH₃-C-H] and [Cl-C-H] groups to the double bond of cyclohexene should experience similar steric repulsions in the corresponding transition states. Nonbonded repulsions would also be of similar magnitude in the corresponding isomeric products. The formation of *both* isomeric 7-chlorobicyclo[4.1.0]heptanes is in accord with the view¹⁸ that chlorocarbene generated in this system is essentially free and contrasts strongly with the ethylidene/zinc-copper couple results. The reason for the predominance of the *endo* isomer in monochlorocarbene additions is still unclear.³⁶

Isopropylidene iodide reacted vigorously with zinc-copper couple in ether solution containing cyclohexene. When the reactants were mixed in one operation, a high yield of propylene was obtained, no cyclopropane formation could be detected, and a low yield of tetramethylethylene was isolated. When this reaction was repeated, adding isopropylidene iodide dropwise to maintain reflux in the manner of Grignard formation, again no cyclopropane was detected, and tetramethylethylene (45%) and propylene (40%) were obtained. These results are similar to those of Applequist and Babad³⁸ who observed the formation of propylene and tetramethylethylene from the reaction of 2-diazopropane and zinc iodide in ether. It is not known if the organozinc intermediate in this case is the same as that formed from isopropylidene iodide and zinc-copper couple, but neither formed cyclopropanes with olefins.

As the hydrogen atoms in II are successively replaced by methyl groups, the rate of addition to double bonds is strongly depressed for steric reasons, and the competing decomposition to ethylene and propylene becomes important. It may be that "opened" ionic structures, such as VII, become important with pro-

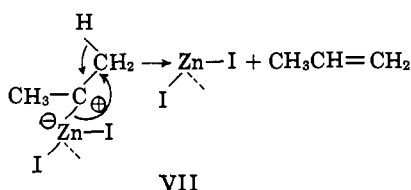
(35) Accurate scale atomic models show that the *endo* isomer, in which the methyl group lies over the ring, is subject to severe internal nonbonded hydrogen repulsions in the transition state corresponding to VI.

(36) G. L. Closs, R. A. Moss, and J. J. Coyle, *J. Am. Chem. Soc.*, **84**, 4985 (1962).

(37) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 189.

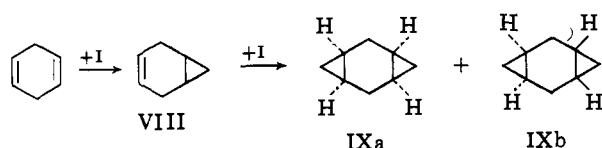
(38) D. E. Applequist and H. Babad, *J. Org. Chem.*, **27**, 288 (1962).

gressive methyl substitution so that rearrangement by hydride migration is favorable. The coupling



reaction to give tetramethylethylene may be similar to that observed with methylene iodide.²

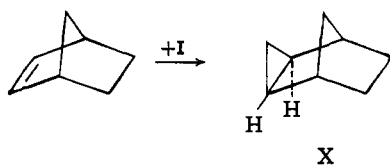
Steric Considerations.—The addition of I to some cyclic and bicyclic olefins has provided further insight into the steric requirements of the cyclopropane-forming reaction. Reagent I added stepwise to 1,4-cyclohexadiene to give bicyclo[4.1.0]hept-3-ene (VIII) and a mixture of the *endo* and *exo* isomers of tricyclo[5.1.0.-(0^{3,5})]octane (IXa,b) in the ratio 3.3:1. The isomers could be purified by g.p.c.; however, the isomer formed



in lesser amount was isolated only in a quantity sufficient for spectral characterization. Both hydrocarbons are saturated, contain cyclopropane rings, and have almost identical mass spectral cracking patterns. The major ion formed from VIII, IXa, and IXb was $C_7H_7^+$, presumably tropylium ion.³⁹ The absolute configurations have not been unequivocally assigned to IXa,b, although on steric grounds it seems likely that the isomer formed in larger amount is *trans*-IXb.⁴⁰

A remarkable example of highly stereoselective addition of I to a cyclic olefin was recently reported by Boikess and Winstein.⁴¹ *cis-cis-cis*-1,4,7-Cyclononatriene reacted with an excess of I to afford 80–90% of *cis*-tetracyclo[9.1.0.0^{3,5}.0^{7,9}]dodecane.

Bicyclo[2.2.1]heptene and I gave a single monoadduct X,¹ whose structure was assigned on the basis of steric considerations⁴² and was in accord with the n.m.r. and infrared spectral data. None of the *endo* isomer was detected.



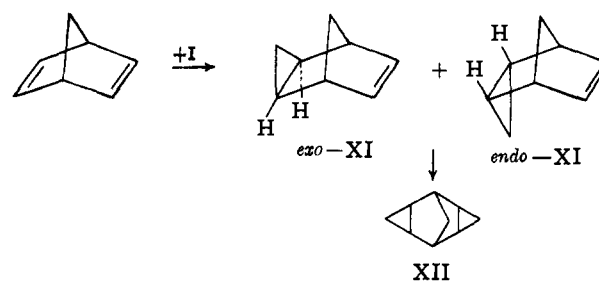
The addition of I to bicyclo[2.2.1]heptadiene gave a mixture of both isomers, *exo*-XI and *endo*-XI, in the ratio 5.7:1. Further treatment of the mixture XI with I gave the diadduct XII whose isomers were not separated.

(39) Cf. P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

(40) Prof. S. Winstein has informed the authors that the addition of dibromocarbene to 1,4-cyclohexadiene followed by reduction gave a hydrocarbon identical with the isomer we obtained in larger amount. The serious steric repulsions expected in the tetrabromo derivative corresponding to IXa are in accord with the above assignment.

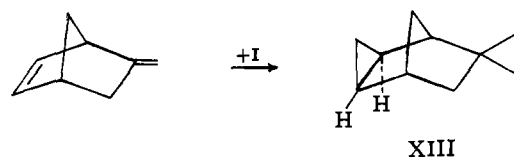
(41) R. S. Boikess and S. Winstein, *J. Am. Chem. Soc.*, **85**, 343 (1963).

(42) The epoxidation of bicyclo[2.2.1]heptene by monoperoxyphthalic acid has been reported to give only the *exo*-epoxide by H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954).



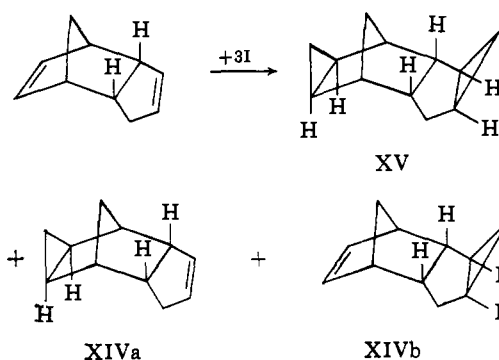
endo-XI was identical with a sample of the authentic hydrocarbon prepared by the Diels–Alder reaction of cyclopentadiene and cyclopropene.⁴³ The formation of *endo*-XI may be due to the well-known complexing ability of bicyclo[2.2.1]heptadiene on the electron-rich underside of the molecule, which in this case helps to orient the approach of the organozinc intermediate I. Similar results were reported previously.³¹

5-Methylenebicyclo[2.2.1]hept-2-ene, the Diels–Alder adduct of cyclopentadiene and allene,⁴⁴ reacted with 2 moles of I to give a single diadduct XIII. The infrared and proton n.m.r. spectra of XIII reveal that no skeletal rearrangement occurred during the addition.



More information on the stereoselectivity was provided by the reaction of excess I with *endo*- and *exo*-dicyclopentadiene. *exo*-Dicyclopentadiene was prepared according to Bartlett and Goldstein⁴⁵ by the hydroiodination of the *endo* isomer followed by dehydroiodination with alcoholic potassium hydroxide. This procedure gave a mixture of 75% *exo*- and 25% *endo*-dicyclopentadiene, and pure *exo* isomer could only be obtained by preparative g.p.c.

endo-Dicyclopentadiene was treated with 3 moles of methylene iodide and an equivalent amount of zinc-copper couple in refluxing ether. Fractionation of the product followed by g.p.c. yielded two isomeric monoolefins, $C_{11}H_{14}$ (XIVa, 12%, and XIVb, 11%), and a single saturated hydrocarbon, $C_{12}H_{16}$ (XV, 63%). The starting material was shown to be stable to the reaction conditions by isolation of 5% of unchanged *endo* isomer, no *exo* isomer being detected. Isomer

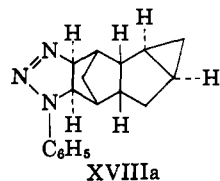


(43) K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

(44) D. S. Matteson, J. J. Drysdale, and W. H. Sharkey, *ibid.*, **82**, 2853 (1960).

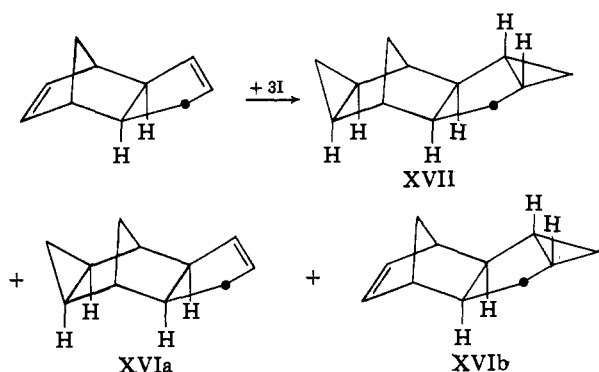
(45) P. D. Bartlett and I. S. Goldstein, *ibid.*, **69**, 2553 (1947).

XIVa showed olefin absorption at 6.19μ in the infrared, characteristic of the cyclopentene double bond,⁴⁶ while XIVb had the typical absorption at 6.36μ characteristic of the strained bicycloheptene system.⁴⁷ Isomer XIVb reacted with phenyl azide in pentane solution in a few hours to give a crystalline adduct XVIIIa, whose spectrum was in accord with the assigned structure,⁴⁸ while XIVa did not react with this



reagent in 1 week. Compound XV showed no olefin absorption in the infrared and did not react with potassium permanganate in acetone or with bromine in carbon tetrachloride. The infrared spectra of XIVa, XIVb, and XV in the 9.8μ region also provided strong evidence for the structural assignments (see below). By further treatment with I, both XIVa and XIVb gave XV.

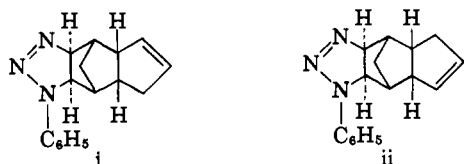
exo-Dicyclopentadiene was converted to a mixture of cyclopropyl hydrocarbons under conditions identical with those employed with the *endo* isomer. The *exo* isomer was also shown to be stable under the reaction conditions by the isolation of approximately 10% of the starting material uncontaminated by *endo* isomer. From the reaction mixture there were isolated two isomeric monoolefins, $C_{11}H_{14}$ (XVIa, 14%,



(46) ($C=C$) stretching in cyclopentene is reported at 6.20μ by R. C. Lord (unpublished observations); see R. N. Jones and C. Sandorfy in "Chemical Application of Spectroscopy," W. West, Ed., Interscience Publishers, Inc., New York, N. Y., 1958, p. 371.

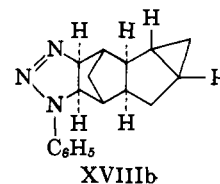
(47) *endo*- and *exo*-dicyclopentadiene show bands at 6.38 and 6.37μ , respectively, that we have ascribed to the strained bicycloheptene double bond. See Table I for further comparisons. Also see P. von R. Schleyer, *J. Am. Chem. Soc.*, **80**, 1700 (1958), and H. E. Simmons, *ibid.*, **83**, 1657 (1961).

(48) Adducts XVIIIa and XVIIIb (see later) were isolated as sharply melting, crystalline solids. The triazole ring is presumably of *exo* configuration since only the *exo* isomer has been found in additions of phenyl azide to dicyclopentadienes. For example, *endo*-dicyclopentadiene gave i (or ii) as an apparently pure crystalline adduct (K. Alder and G. Stein, *Ann.*, **504**, 216 (1933)). In this system the double bonds appear to introduce only rarely, if at all, sufficient asymmetry to allow separation of isomers, such as i and ii. The same seems to be true if a cyclopropane ring is fused at the point of the double bonds in i and ii.



and XVIb, 2.5%) and a saturated hydrocarbon $C_{12}H_{16}$ (XVII 52%).

Compound XVIa showed olefin absorption at 6.15μ (cyclopentene ring)⁴⁶ and did not react with phenyl azide in pentane in 1 week, while compound XVIb showed olefin absorption at 6.34μ (bicycloheptene ring)⁴⁷ and reacted with phenyl azide in pentane in a few hours to give a crystalline adduct XVIIIb. The hydrocarbon XVII did not react with potassium



permanganate in acetone or with bromine in carbon tetrachloride, and both XVIa and XVIb gave XVII on further treatment with I.

Strong support was lent to the gross skeletal structures of XIVa,b, XV, XVIa,b, and XVII by consideration of the infrared spectra in the regions characteristic of the carbon-carbon double bond and the cyclopropane ring. Much controversy has arisen in the literature concerning the usefulness of the 9.8μ region in the infrared for inferring the presence of the cyclopropane ring.⁴⁹ Derfer, Pickett, and Boord⁵⁰ have claimed that the presence of absorption around 9.8μ is diagnostic of a deformation of the three-membered carbon ring, while Blomquist and Longone⁵¹ have expressed doubt in the validity of positive assignments in this region. Of the many compounds prepared earlier¹ and in this work, all showed absorption in the 9.8μ region, which was frequently of value in determining the environment of the cyclopropane ring. In all structures containing the 2,3-*exo*-cyclopropane ring fused to the bicyclo[2.2.1]heptane nucleus, a medium to strong absorption was found in the narrow range 9.68 – 9.74μ . The controversial band normally occurs from 9.60 – 9.95μ , depending on the type and degree of substitution of the cyclopropane. When the cyclopropane ring is fused to the cyclopentane ring, as in XIVb and XVIb, the three-membered ring deformation absorption occurred at 9.78 – 9.81μ (bicyclo[3.1.0]hexane¹ has a single strong band at 9.81μ). The diadducts XV and XVII showed two bands in this region, each exactly reflecting the environments of the two cyclopropane rings. For example, XIVa and b had bands at 9.74 and 9.81μ , respectively, and the corresponding diadduct XV showed bands at 9.74 and 9.81μ . A similar correlation was observed in the products from *exo*-dicyclopentadiene (XVIa,b, XVII). All these correlations are given in Table I and strongly support the structural assignments.

Both *endo*- and *exo*-dicyclopentadiene on treatment with an excess of I can give four isomeric diadducts, all eight of which are stereoisomers. It is striking that each diolefin gave only a single, different diadduct (XV and XVII). Four stereoisomeric monoadducts might also be expected from each diolefin,

(49) The preparation of several new cyclopropane derivatives in our study of the olefin/methylene iodide/zinc-copper couple system has provided much new spectral data which will be reported elsewhere.

(50) J. M. Derfer, E. E. Pickett, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 2482 (1949).

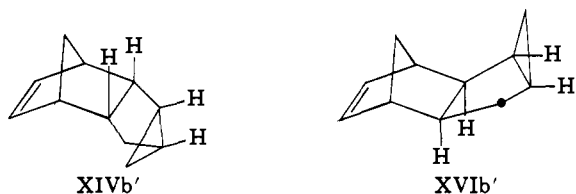
(51) A. T. Blomquist and D. T. Longone, *ibid.*, **81**, 2012 (1959).

but the isolation of only two monoadducts (XIVa,b and XVIa,b) from each is demanded by the observation that a single diadduct was formed from each diolefin. The stereochemistry of the cyclopropane rings in the two monoadducts in each series was shown chemically to be the same as in the corresponding diadducts, and this is supported by the data in Table I. Since

TABLE I
INFRARED SPECTRAL DATA

Compound	Infrared absorption, μ	
	(C=C) stretch	Deformation, Δ
X	..	9.68 (s)
<i>exo</i> -XI	6.28 (w) + 6.41 (w)	9.70 (s)
XII	..	9.66 (s) + 9.72 (s)
XIVa	6.06 (w) + 6.19 (w)	9.74 (s)
XIVb	6.08 (w) + 6.36 (w)	9.81 (s)
XV	..	9.74 (s) + 9.81 (s)
XVIIIa	..	9.80 (w)
XVIa	6.10 (w) + 6.15 (w)	9.72 (s)
XVIb	6.19 (w) + 6.34 (w)	9.78 (s)
XVII	..	9.72 (s) + 9.78 (s)
XVIIIb	..	9.80 (w)
<i>endo</i> -Dicyclopentadiene	6.12 (w) + 6.21 (w) + 6.38 (w)	..
<i>exo</i> -Dicyclopentadiene	6.10 (w) + 6.20 (w) + 6.37 (w)	..
Bicyclo[3.1.0]hexane	..	9.81 (s)

the *exo* configuration is expected for the cyclopropane ring fused to the bicyclo[2.2.1]heptane system in X, *exo*-XI, and XIII, monoadducts XIVa and XVIa presumably are of the same configuration. The uncertainty of the configuration of the cyclopropane fused to the cyclopentane ring in XIVb and XVIb was resolved by inspection of accurate scale atomic models. When models of the isomeric monoadducts XIVb' and XVIb' (which were *not* isolated) and of the transition states for the methylene transfer leading to these isomers were examined, it was apparent that excessive nonbonded steric repulsion was present. In fact, the transition states for approach of I are so



cluttered, no adequate representation can be approximated.

The above discussion emphasizes the strong steric requirements that are placed on transition states in the transfer of the methylene group from I to olefinic double bonds. This stereoselectivity is remarkable in view of the high yield observed under mild conditions for such strained hydrocarbons as XV and XVII.

Synthesis of Cyclopropanes.—In this section some comments are made on the scope of and synthetic procedures for this reaction which have been utilized in paper II and in this work. It has been found that optimum yields for the conversion of olefins to the corresponding cyclopropanes are realized by employing the olefin, methylene iodide, zinc-copper couple,⁵²

(52) A procedure for the preparation of zinc-copper couple that functions well in the cyclopropane synthesis has been reported by R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

and diethyl ether in the mole ratio 1:1:1:3, respectively.⁵³ In this manner cyclohexene gives norcarane in 65% yield (by g.p.c.), of which 60% of the pure product can be isolated by simple distillation. The use of relatively concentrated solutions ensures rapid formation of the intermediate and minimizes by-products.² Cyclopropane formation has been demonstrated in tetrahydrofuran, ethylene glycol dimethyl ether (glyme), ethyl acetate, and other solvents, but the use of diethyl ether gave yields twice as large as any other solvent.

A modification of the usual procedure has been found valuable when the starting olefinic compound or the resulting cyclopropane is unstable to Lewis acids, such as zinc iodide.⁵⁴ The modification employs diethyl ether containing 1 equivalent of glyme as solvent. Zinc iodide is removed rapidly and quantitatively from reaction solution as the crystalline, insoluble 1:1 glyme complex.

Most of the usual substituents do not interfere with the addition reaction if they are separated by at least one methylene group from the double bond. In general, negative groups on the double bond lead to lower yields, while electron donors (*e.g.*, vinyl ethers) give high yields of cyclopropanes. Some recent examples demonstrate the scope and special applications of the synthesis.

Mono-, di-, tri-, and tetrasubstituted olefinic hydrocarbons give the corresponding cyclopropane, uncontaminated by isomeric products, in yields of 45–70%. Setser and Rabinovitch⁵⁵ have prepared dideuterated methylcyclopropanes from monodeuteriomethylene iodide and *cis*- and *trans*-1-*d*-propene. The synthesis of *cis*- and *trans*-dideuteriocyclopropane was similarly accomplished from *cis*- and *trans*-1,2-dideuterioethylene, respectively. Ullman and Fanshawe⁵⁶ have added I to an allene, methyl 3,4-pentadienoate, to give a monoadduct, methyl 2-methylenecyclopropylacetate, and a diadduct, methyl spiro-pentylacetate. Castellucci and Griffin⁵⁶ have extended the reaction to an acetylene by achieving the first total synthesis of the naturally occurring *cyclopropene*, sterculic acid, by addition of I to stearolic acid.

An aspect of the reaction of considerable importance theoretically and practically was the finding of high stereoselectivity in the addition of the reagent to cyclic olefinic alcohols. Winstein, Sonnenberg, and DeVries^{57a} reported that I added in high yield to cyclopenten-4-ol to give exclusively *endo*-3-hydroxybicyclo[3.1.0]hexane, and Corey and Dawson^{57b} have proved the stereochemistry of the addition. The olefinic acetate gave a lower yield of a mixture of *endo*- and *exo*-acetates. The influence of oxygen functions on the steric course of addition was pointed out initially

(53) Also see R. D. Smith and H. E. Simmons, *Org. Syn.*, **41**, 72 (1961).

(54) Private communications from Professors W. G. Dauben and W. R. Moore have indicated that certain cyclopropanes prepared by the methylene iodide/zinc-copper couple method do not survive the presence of zinc iodide unless special precautions are taken. The sensitivity of the cyclopropane ring to attack by Lewis acids is well known; *e.g.*, bicyclo[3.1.0]hexane (nor-thujane) is rapidly attacked by aqueous mercuric acetate to give 1-acetoxymercurimethyl-2-hydroxycyclopentane (R. Y. Levina, V. N. Kostin, and T. K. Ustynuk, *J. Gen. Chem. USSR*, **30**, 383 (1960)).

(55) E. F. Ullman and W. J. Fanshawe, *J. Am. Chem. Soc.*, **83**, 2379 (1961).

(56) N. T. Castellucci and C. E. Griffin, *ibid.*, **82**, 4107 (1960).

(57) (a) S. Winstein, J. Sonnenberg, and L. DeVries, *ibid.*, **81**, 6524 (1959); S. Winstein and J. Sonnenberg, *ibid.*, **83**, 3235 (1961); (b) E. J. Corey and R. L. Dawson, *ibid.*, **85**, 1782 (1963).

for cyclohepten-2-yl acetate and certain anisole derivatives.^{1,58} Dauben and Berezin have studied these additions in detail and developed useful synthetic procedures.⁵⁹ In reactions of olefinic alcohols with I, transfer of the methylene group occurs intramolecularly *via* an intermediate zincate,^{2,59} so that addition is only possible from the side of the double bond nearest the oxygen atom. Vinyl esters have also been employed; *e.g.*, 1-methylcyclopropanol was obtained from isopropenyl acetate.⁶⁰

Experimental⁶¹

Reagents were purified as previously described.¹ Infrared spectra were determined on a Perkin-Elmer Model 21 double beam infrared spectrometer equipped with NaCl optics (2–15 μ) (liquids, neat; solids, potassium bromide wafers).

Attempted Identification of an Organometallic-Olefin Adduct.—Zinc-copper couple (19.25 g., 0.286 mole) and chloriodomethane (51.43 g., 0.286 mole) in ether (100 ml.) were stirred at reflux for 3 hr. During this time 415 ml. of gas was evolved, and at the end evolution was at the rate of 5 ml. per minute. The reaction mixture was chilled in an ice water bath and filtered under nitrogen pressure through a dry fritted disk. The clear filtrate was treated with *cis*-3-hexene (12.0 g., 0.143 mole), and the mixture stirred at 0° for 4 hr. During this time 0.25-ml. aliquots were withdrawn at 30-min. intervals and hydrolyzed with 1 ml. of ammonium chloride solution, and the ether phase was analyzed by g.p.c. which revealed no component of longer retention time than chloriodomethane (b.p. 109°). At 4 hr., the yield of *cis*-1,2-diethylcyclopropane was 0.6%. The mixture was then heated at reflux for 64 hr., cooled, and treated with 25 ml. of ammonium chloride solution. Analysis of the ether phase by g.p.c. and subsequent mass spectral analysis revealed 1,2-dichloroethane, chloriodomethane, methyl iodide, *cis*-1,2-diethylcyclopropane (47.5% based on *cis*-3-hexene) but no C₇H₁₅Cl or C₇H₁₅I compounds from hydrolysis of an organometallic-olefin adduct.

Reaction of Cyclohexene with Ethylidene Iodide and Zinc-Copper Couple.—A mixture of cyclohexene (20.0 g., 0.24 mole), ethylidene iodide⁶² (28.2 g., 0.10 mole), zinc-copper couple (10.9 g., 0.15 g.-atom of zinc), iodine (crystal), and anhydrous ether (100 ml.) was stirred and heated at gentle reflux under anhydrous conditions. A vigorous reaction began shortly, and the evolved gases were collected in a liquid nitrogen-cooled trap. By infrared spectral and g.p.c. studies, the liquid collected in the trap was shown to be largely ethylene. After the reaction subsided, the mixture was heated under reflux for 12 hr. and was then worked up in the usual manner.¹ Cyclohexene (18 g.), b.p. 83°, was recovered by distillation through a semimicro spinning-band column.⁶³ A single, high-boiling fraction, b.p. 83–130° (2.1 g.), was collected and was analyzed by g.p.c. (2 m., 25% dimethyl sulfolane on 40–60 mesh Columpak, 62°, helium flow rate 100 ml./min.). The mixture contained 54% cyclohexene and 46% of a saturated hydrocarbon, which was purified by preparative g.p.c. to give 0.96 g. (3.6%) of *exo*-7-methylbicyclo[4.1.0]heptane (V), b.p. *ca.* 130° (microdetermination), *n*_D²⁰ 1.4528. The infrared spectrum was identical with that of an authentic sample prepared by Cope⁶⁴; g.p.c. of the crude distillate of material boiling higher than cyclohexene gave several minor components present in amounts <0.5%, but none were identified as the corresponding *endo* isomer.

Anal. Calcd. for C₈H₁₄: C, 87.19; H, 12.81. Found: C, 87.38; H, 12.97.

Reaction of Isopropylidene Iodide with Zinc-Copper Couple.—The reaction with isopropylidene iodide was carried out in the manner described for ethylidene iodide. The reaction became exothermic after a brief induction period and required moderation by external cooling. The gas evolved was shown to be largely propylene contaminated with diethyl ether and traces of propyne. Distillation gave 10% tetramethylethylene, and

cyclohexene was recovered unchanged. No evidence for the formation of 7,7-dimethylbicyclo[4.1.0]heptane was obtained by examining the minor peaks of the gas phase chromatogram.

The reaction was repeated under the same conditions except that the isopropylidene iodide was added dropwise to maintain gentle reflux, the temperature not exceeding 35°. Only a negligible amount of gaseous propylene was evolved during the addition, and distillation of the reaction mixture gave tetramethylethylene in 45% yield.

Reaction of 1,4-Cyclohexadiene with Methylene Iodide and Zinc-Copper Couple.—Distilled 1,4-cyclohexadiene (16.0 g., 0.200 mole), methylene iodide (107.2 g., 0.400 mole), zinc-copper couple (36.3 g., 0.50 g.-atom of zinc), and ether (200 ml.) were heated under reflux for 8 hr. under the usual conditions.¹ After work-up, the crude product was distilled through a semimicro spinning-band column⁶³ to give 6.7 g. of pure VIII; g.p.c. analysis of all of the distillation cuts showed the total yield of VIII was 10.4 g. (55%). An analytical sample of pure bicyclo[4.1.0]hept-3-ene had b.p. 57° (100 mm.), *n*_D²⁵ 1.4739. The physical constants and infrared spectrum agreed with those of a sample of VIII prepared by Winstein by another method.⁴⁰ In this experiment, considerable methylene iodide and zinc-copper couple were recovered, indicating incomplete reaction. This presumably accounts for the failure to detect any of the bis-adduct which is described in the next experiment.

Anal. Calcd. for C₇H₁₀: C, 89.29; H, 10.71. Found: C, 88.86; H, 10.58.

Reaction of Bicyclo[4.1.0]hept-3-ene with Methylene Iodide and Zinc-Copper Couple.—Bicyclo[4.1.0]hept-3-ene (5.53 g., 0.059 mole), methylene iodide (39.7 g., 0.148 mole), zinc-copper couple (12.0 g., 0.164 g.-atom of zinc), and ether (50 ml.) were heated under reflux for 26 hr. under the usual conditions.¹ After work-up, distillation gave approximately 4 g. of a crude product, b.p. 73–80° (100 mm.), which was shown by g.p.c. to consist of two components besides recovered starting material. The yields of IXb and IXa were 2.3 (36%) and 0.7 g. (11%), respectively. Pure *trans*-tricyclo[5.1.0¹.7^{3,5}]octane (IXb) was obtained by preparative g.p.c. The physical constants and infrared spectrum agreed with those of a sample of IXb prepared by Winstein by another method.⁴⁰ Isomer IXa was not obtained in sufficient quantity for analysis.

Anal. Calcd. for C₈H₁₂: C, 88.80; H, 11.20. Found: C, 89.03; H, 11.33.

On a g.p.c. column (20% tris-cyanoethyl glyceryl ether on Columpak, 2 m., 101°, He flow rate 55 ml./min.) the retention times of IXb and IXa were 4.20 and 4.75 min., respectively. No columns were found that allowed better separation on a macro scale. Micro samples of IXa could be obtained in a state of good purity employing analytical g.p.c. columns; IXa was characterized by mass spectrographic analysis. The cracking patterns of IXa and IXb were extremely similar. Both showed a parent peak for C₈H₁₂⁺ and in addition a strong peak for C₇H₇⁺, tropylium ion, a product not unexpected on the basis of the assigned structures. The determinations were carried out on a Consolidated Electrodynamics Corp. Model CEC 21-103-C mass spectrograph (ionization chamber temperature (250°), ionization current (10.5 ma.), ionization voltage (70 v.), and magnet current (0.253 amp.)).

Reaction of Bicyclo[2.2.1]heptadiene with Methylene Iodide and Zinc-Copper Couple.—This reaction was carried out in the normal manner with zinc-copper couple (37.5 g., 0.54 g.-atom Zn, 6.85% Cu), bicyclo[2.2.1]heptadiene (4.6 g., 0.5 mole), and methylene iodide (134 g., 0.5 mole) in diethyl ether (155 ml.). After stirring at reflux for 19 hr., the slurry was treated with 200 ml. of cold aqueous ammonium chloride. The ether phase was separated and extracted with 150 ml. of aqueous ammonium chloride followed by 200 ml. of distilled water and finally 20 ml. of 5% sodium bicarbonate solution. The ether phase was dried over magnesium sulfate, filtered, and the ether distilled. The residue was distilled under high vacuum into a Dry Ice-acetone cooled receiver leaving 32 g. of polymeric material (direct fractionation of this reaction product on occasions led to violent decomposition in the distilling pot near the end of the fractionation). Fractionation of this distillate gave 9.9 g. (18.6%) of product, b.p. 125–130°, collected as three cuts. Each cut appeared homogeneous on various packed gas chromatography columns; however, analysis on a Perkin-Elmer Golay column U (squalane) revealed the composition shown in Table II.

The above 9.9 g. of product was added to 50 ml. of saturated silver nitrate solution to give a clear solution which deposited

(58) A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959).

(59) W. G. Dauben and G. H. Berezin, *ibid.*, **85**, 468 (1963).

(60) C. H. Depuy, L. R. Maloney, and K. L. Eilers, *J. Org. Chem.*, **26**, 3616 (1961).

(61) All boiling points are uncorrected and melting points are corrected.

(62) B.p. 66–67° (15 mm.); kindly supplied by Professor A. C. Cope.

(63) R. G. Nester, *Anal. Chem.*, **28**, 278 (1956).

TABLE II

Cut	B.p., °C.	<i>exo</i> -XI	<i>endo</i> -XI ^a	Unknown
1	125-128.5	73.2	15.3	11.5
2	128.5-129.0	73.3	18.0	8.7
3	129.0-130.0	72.5	22.2	5.3

^a The identity of the *endo* product is based on the appearance of resonances in the n.m.r. also present in the n.m.r. of pure *endo*-XI kindly provided by Prof. K. Wiberg.

colorless plates on standing. The mixture was cooled in an ice water bath, filtered, and the crystals air-dried for 3 min. on the filter. Addition of the crystals to 65 ml. of water followed by steam distillation, separation of the hydrocarbon phase, and distillation resulted in 3.47 g. of product, n_D^{25} 1.4875. Analysis by gas chromatography (Golay U) revealed this product to be 96.3% *exo*-XI.

The more volatile unknown product has not yet been identified.

Reaction of 5-Methylenebicyclo[2.2.1]hept-2-ene with Methylene Iodide and Zinc-Copper Couple.—Methylene iodide (80.4 g., 0.30 mole), zinc-copper couple (29.0 g., 0.40 g.-atom of zinc), 5-methylenebicyclo[2.2.1]hept-2-ene (10.6 g., 0.10 mole), and ether (100 ml.) were allowed to react under the usual conditions. After 24 hr. the reaction mixture was worked up as previously described, and distillation of the product through a semimicro spinning-band column⁶³ afforded 3.88 g. of a mixture, b.p. 105-60° (95-11 mm.). Material boiling lower than that collected was a complex mixture that probably contained the mono-adducts, which were not investigated. Analysis by g.p.c. (2 m., 20% tris-cyanoethyl glyceryl ether on 40-60 mesh Columpak, 100°, helium flow rate 30 ml./min.) of the fractions collected showed they contained 91% of a single product. Preparative g.p.c. gave 3.50 g. (26%) of pure spiro[cyclopropane-1,6-tricyclo[3.2.1.0^{2,4}]octane] (XIII), b.p. 174° (microdetermination), n_D^{25} 1.4894. The infrared spectrum of XIII has been discussed above and is in accord with the assigned structure.

Anal. Calcd. for C₁₀H₁₄: C, 89.50; H, 10.50. Found: C, 89.78; H, 10.58.

Reaction of *endo*-Dicyclopentadiene with Methylene Iodide and Zinc-Copper Couple.—Pure *endo*-dicyclopentadiene (b.p. 170°, m.p. 33.6°, n_D^{25} 1.5121, 13.2 g., 0.10 mole), methylene iodide (80.4 g., 0.30 mole), zinc-copper couple (29.0 g., 0.40 g.-atom of zinc), and ether (100 ml.) were allowed to react under the usual conditions. After 48 hr. the reaction mixture was decanted into a separatory funnel, and the solids were washed well with ether. The combined ether solution was shaken successively with cold 5% hydrochloric acid, 5% sodium carbonate solution, and water and was then dried over anhydrous magnesium sulfate. Fractionation through a semimicro spinning-band column⁶³ afforded the following fractions.

Frac- tion	B.p. (8.5 mm.), °C.	n_D^{25}	Wt., g.	Per cent		
				XIVa	XIVb	XV
1	62-68	1.5075	0.82	6	64	...
2	68-72	1.5111	0.47	20	58	...
3	72-76	1.5146	0.85	40	47	0.8
4	76-86	1.5185	1.16	57	23	17
5	85-95	1.5200	1.36	42	9	49
6	95	1.5216	3.92	2	0.3	98
7	95	1.5219	3.15	100
8	95	1.5217	1.97	99

The percentage composition of the fractions was determined by g.p.c. (2 m., 25% tris-cyanoethyl glyceryl ether on 40-60 mesh Columpak, 122°, helium flow rate 135 ml./min.). The distilled commercial *endo*-dicyclopentadiene used as starting material was shown to be of 99.5% purity on the same column. The retention times of XIVa, XIVb, and XV were 6.6, 4.1, and 11.6 min., respectively. The products were separated by preparative g.p.c. on a similar larger column.

Pure tetracyclo[5.3.1.0^{2,6}.0^{8,10}]undec-3-ene (XIVa) was isolated in 12% yield (1.79 g.), b.p. 214° (microdetermination), n_D^{25} 1.5224.

Anal. Calcd. for C₁₁H₁₄: C, 90.37; H, 9.63. Found: C, 90.67; H, 9.76.

Pure tetracyclo[6.2.1.0^{2,7}.0^{3,8}]undec-9-ene (XIVb) was isolated in 11% yield (1.60 g.), b.p. 198° (microdetermination), n_D^{25} 1.5089.

Anal. Calcd. for C₁₁H₁₄: C, 90.37; H, 9.63. Found: C, 90.49; H, 9.88.

Pure pentacyclo[6.3.1.0^{2,7}.0^{3,8}.0^{9,11}]dodecane (XV) was isolated in 62% yield (9.90 g.), b.p. 95° (8.5 mm.), n_D^{25} 1.5219. The infrared spectra of the products were discussed above.

Anal. Calcd. for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 90.18; H, 10.04.

In separate experiments, both XIVa and XIVb were converted in high yields to a single hydrocarbon product (XV) on treatment with I.

Reaction of XIVb with Phenyl Azide.—Freshly distilled phenyl azide (0.081 g., 0.00069 mole) and XIVb (0.100 g., 0.00069 mole) were dissolved in pentane (2 ml.). After standing overnight, the mass of colorless crystals was filtered and weighed 0.157 g. (87%), m.p. 130-133°. Recrystallization from boiling hexane gave an analytical sample of 10-phenyl-10,11,12-triazapentacyclo[6.5.1.0^{2,7}.0^{3,8}.0^{9,13}]tetradec-11-ene (XVIIIa). The infrared spectrum of XVIIIa was discussed above. A mixture of XIVa and phenyl azide in pentane solution gave no evidence of reaction on standing 1 week at 25°.

Anal. Calcd. for C₁₇H₁₉N₃: C, 76.95; H, 7.22; N, 15.83. Found: C, 76.86; H, 7.14; N, 16.09.

***exo*-Dicyclopentadiene.**—The procedure of Bartlett and Goldstein⁴⁵ was followed employing pure *endo*-dicyclopentadiene. The procedure involved addition of aqueous hydriodic acid to the *endo* isomer to give an iodide of *exo* configuration, which was dehydrohalogenated with alcoholic potassium hydroxide. This procedure has been stated to give pure *exo*-dicyclopentadiene; g.p.c. analysis of the product (2 m., 20% tris-cyanoethyl glyceryl ether on 40-60 mesh Columpak, 124°, helium flow rate 65 ml./min.) showed it to consist of a 3:1 mixture of the isomers (*exo:endo*). The close retention times of the *endo* and *exo* isomers, 5.65 and 5.25 min., respectively, made preparative separation tedious. With similarly packed, larger columns, repeated separations gave 30 g. of pure *exo*-dicyclopentadiene, b.p. 170°, n_D^{25} 1.5078. The infrared spectrum was discussed above and showed many strong bands that were characteristic and absent in the spectrum of the *endo* isomer; e.g., 9.92 and 12.55 μ .

Anal. Calcd. for C₁₀H₁₂: C, 90.85; H, 9.15. Found: C, 90.81; H, 9.26.

Reaction of *exo*-Dicyclopentadiene with Methylene Iodide and Zinc-Copper Couple.—Pure *exo*-dicyclopentadiene (13.2 g., 0.10 mole), methylene iodide (80.4 g., 0.30 mole), zinc-copper couple (29.0 g., 0.40 g.-atom of zinc), and ether (100 ml.) were allowed to react under conditions identical with those employed for the *endo* isomer. The reaction mixture was worked up in the same manner, and the product was distilled to give the following fractions.

Frac- tion	B.p. (10 mm.), °C.	n_D^{25}	Wt., g.	Per cent		
				XVIa	XVIb	XVII
1	62-76	1.5126	0.44	44	33	...
2	76-78	1.5159	0.36	67	21	...
3	78-79	1.5173	0.93	75	12	0.4
4	79-81	1.5179	0.23	73	6	0.7
5	81-86	1.5184	0.56	66	3	1
6	86-88	1.5184	0.50	44	1	3
7	88-91	1.5184	0.40	23	0.5	73
8	91-93	1.5183	0.43	13	0.4	81
9	93	1.5183	2.37	2	...	94
10	93	1.5183	3.31	98
11	93	1.5184	2.12	93
12	93	1.5186	0.42	81

The percentage composition of the fractions was determined by g.p.c. (2-m., 20% tris-cyanoethyl glyceryl ether on 40-60 mesh "Columpak," 124°, helium flow rate = 110 ml./min.). The *exo*-dicyclopentadiene used as starting material was shown to be of 99% purity on the same column. The retention times of XVIa, XVIb and XVII were 7.5, 5.0 and 13.5 min., respectively. The products were separated by preparative g.p.c. on a similar, larger column.

Pure tetracyclo[5.3.1.0^{2,6}.0^{8,10}]undec-3-ene (XVIa) was isolated in 14% yield (2.10 g.), b.p. 207° (microdetermination), n_D^{25} 1.5183.

Anal. Calcd. for C₁₁H₁₄: C, 90.37; H, 9.63. Found: C, 90.40; H, 9.85.

Pure tetracyclo[6.2.1.0^{2,7}.0^{3,5}]undec-9-ene (XVIIb) was isolated in 2.5% yield (0.37 g.), b.p. 199° (microdetermination), n_D^{25} 1.5069.

Anal. Calcd. for C₁₁H₁₄: C, 90.37; H, 9.63. Found: C, 89.99; H, 9.58.

Pure pentacyclo[6.3.1.0^{2,7}.0^{3,5}.0^{8,11}]dodecane (XVIII) was isolated in 52% yield (8.36 g.), b.p. 91° (8 mm.), n_D^{25} 1.5184. The infrared spectra of the products were discussed above.

Anal. Calcd. for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 90.08; H, 10.18.

In separate experiments, both XVIIa and XVIIb were treated with reagent I and were converted in high yields to XVIII.

Reaction of XVIIb with Phenyl Azide.—Freshly distilled phenyl azide (0.081 g., 0.00069 mole) and XVIIb (0.100 g.,

0.00069 mole) were dissolved in pentane (2 ml.). After standing overnight the mass of colorless crystals was filtered and weighed 0.147 g. (81%), m.p. 150–155°. Recrystallization from boiling hexane gave an analytical sample of 10-phenyl-10,11,12-triazapentacyclo[6.5.1.0^{2,7}.0^{3,5}.0^{8,13}]tetradec-11-ene (XIX), m.p. 154–155°. The infrared spectrum of XIX was discussed above. A mixture of XVIIa and phenyl azide in pentane solution was allowed to stand at 25° for 1 week with no evidence of reaction.

Anal. Calcd. for C₁₇H₁₈N₃: C, 76.95; H, 7.22; N, 15.83. Found: C, 76.81; H, 7.33; N, 15.91.

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The Synthesis and Reactions of an α -Lactam, 1-*t*-Butyl-3,3-dimethylaziridinone

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1-*t*-Butyl-3,3-dimethylaziridinone (2) was prepared from 2-bromo-*N-t*-butyl-2-methylpropionamide (1) by dehydrobromination with potassium *t*-butoxide. In refluxing ether, this α -lactam isomerized to *N-t*-butylmethacrylamide (3, major product) and smaller amounts of acetone and *t*-butyl isocyanide. In the reactions with nonionic nucleophiles (water, *t*-butyl alcohol, benzylamine, α -toluenethiol, and ethyl glycinate) ring opening occurred preferentially with preservation of the amide linkage. Potassium *t*-butoxide converted *N-t*-butyl-2-chloropropionamide (11) into *t*-butyl 2-*t*-butylaminopropionate (13) in good yield. Similarly, the reaction of 2-bromo-2-methyl-*N-n*-propylpropionamide (7) with potassium *t*-butoxide produced *t*-butyl 2-methyl-2-*n*-propylaminopropionate (9) and 2-*t*-butoxy-2-methyl-*N-n*-propylpropionamide (10). In the latter two cases an intermediate α -lactam (12 and 8) was detected by the characteristic infrared band at 1840 cm.⁻¹.

In recent years there has been an increasing interest in α -lactams (aziridinones). In 1949, 1-phenylaziridinone was suggested as a possible intermediate in the reaction of phenyl isocyanate with diazomethane.¹ A claim that certain α -haloamides with sodium hydride produce aziridinones² has been questioned.³ Hydrolysis of several dichloroaziridines lead to α -chloroamides with ring opening^{4,5} rather than to α -lactams.

Baumgarten and co-workers were the first to find spectral evidence for the existence of an aziridinone,⁶ and more recently reported in a short communication⁷ the isolation of 1-*t*-butyl-3-phenylaziridinone from the interaction of potassium *t*-butoxide and *N*-chloro-*N-t*-butylphenylacetamide (prepared *in situ* and not characterized). No suggestion has been put forward as to the possible mechanism of the reaction.

We now wish to report the preparation and some typical reactions of an α -lactam, 1-*t*-butyl-3,3-dimethylaziridinone (2).⁸ In the choice of our precursor, we

were influenced by the known stabilizing effect of substituents in the β -lactam⁹ and β -thiolactone series.¹⁰

N-Carbobenzoxypenicillamine (β,β -dimethylcysteine) forms a thiolactone in high yield,¹⁰ whereas *N*-carbobenzoxycysteine itself tends to polymerize¹¹ and the corresponding thiolactone was obtained only in very low yield.¹²

Preliminary experiments indicated that 2-bromo-2-methyl-*N-t*-butylpropionamide¹³ (1) reacted with potassium *t*-butoxide to give a good yield of a product having the characteristic α -lactam band in the infrared at 1840 cm.⁻¹.^{6,7} Substitution of potassium *t*-butoxide by metallic potassium as the base under otherwise identical conditions gave the same product but in lower yield. When the reaction was carried out in ether at -25°, the by-product formation could be practically eliminated. Separation from unchanged starting material was achieved by low-temperature fractional crystallization (only starting material precipitated from a *n*-pentane solution) and subsequent fractional low-temperature vacuum sublimation. By this technique we obtained a product with the chemical and spectral properties expected for an α -lactam: only one band was observed in the carbonyl region of the infrared (1837 cm.⁻¹; carbon tetrachloride); no band was detected in the 3100–3500 cm.⁻¹ region. The n.m.r. spectrum (carbon tetrachloride) had a singlet signal at 8.67 τ ascribable to the *N-t*-butyl group¹⁴ and a singlet at 8.55 τ cor-

still no independent, published confirmation of the alleged preparation of 1,3,3-triphenylaziridinone.

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(8) After the preparation of this manuscript, a short communication appeared: H. E. Baumgarten, *et al.*, *ibid.*, **85**, 3303 (1963), which described the preparation of an α -lactam (1-*t*-butyl-3-phenylaziridinone) by a very similar reaction. This type of reaction had been investigated previously by Sarel and Leader² and by Sheehan and Frankenfeld.³ The former authors claimed isolation of an α -lactam, but the second investigators isolated only compounds of the oxindole and indoxyl type in the specific example mutually studied. The present authors (J. C. S. and I. L.) have prepared a number of α -lactams by the dehydrohalogenation of α -haloamides and have found that the substituents present profoundly affect the stability of α -lactams (Ph.D. Thesis, I. L., M.I.T., September, 1963, pp. 11, 12, and 19). In the case originally tried by Sarel and Leader (α -chloro- α,α -diphenylacetamide) and reinvestigated by Sheehan and Frankenfeld, no α -lactam was isolated even by the recent modifications. There is