Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.32; H, 6.41.

The infrared spectrum of the ester is grossly consistent with the structure assigned and shows weak bands at 5.12 and 5.40 μ. Of trisubstituted benzene derivatives, these bands are characteristic only of 1,2,3-trisubstituted products.[6] Accordingly, the acid is tentatively identified as 2-carboxy-3-methylphenylacetic acid (IV).

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[6] We are indebted to Prof. R. C. Lord for interpretation of the spectrum.

WILMINGTON 98, DELA.

[CONTRIBUTION NO. 523 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

A New Synthesis of Cyclopropanes[1]

BY HOWARD E. SIMMONS AND RONALD D. SMITH

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A new stereospecific synthesis of cyclopropanes is described which involves treatment of olefins with methylene iodide and a zinc–copper couple. Olefins with a wide variety of substitutents have given cyclopropanes in yields of 10–70%. Evidence is presented bearing on the mechanism of the reaction.

Introduction.—Organic structures containing small rings have received increasing attention in recent years, and cyclopropane derivatives in particular have played important roles in theoretical and synthetic studies. In the past, several methods for the preparation of cyclopropanes have been developed, most of which suffer from a lack of generality. From the standpoint of the organic chemist, the addition of a divalent carbon intermediate to carbon–carbon unsaturation, especially when stereospecific, presents a highly general approach.

Syntheses utilizing this concept have been realized in the classical reaction of aliphatic diazo compounds with olefins[2] and in the addition of halocarbenes to olefins.[3] The reaction of diazo esters with olefins, which leads to carbalkoxycyclopropanes,[2] has been investigated widely. Diazomethane adds to the olefinic bond of α,β-unsaturated esters[4–6] or ketones[7] giving pyrazolines, which lose nitrogen on heating, usually forming a mixture of the cyclopropane derivative and the β-methyl analog of the original ester or ketone. The light-induced reaction of diazomethane with simple olefins gives large amounts of difficultly separable, isomeric hydrocarbons along with the desired cyclopropane.[8] Dihalocarbenes add to olefins to give stereospecifically[9,10a] and in high yields 1,1-dihalocyclopropanes, which, however, must undergo further treatment in order to be transformed into halogen-free structures.

The direct addition of a methylene group to an olefin has been accomplished with methylene radicals produced from the photolysis of ketene. It has been shown that the methylene radicals from this source, as well as those from the photolysis of diazomethane[8,10a] have a high energy[10b,11] and do not discriminate between the olefinic and carbon–hydrogen bonds.

In general, no completely satisfactory method for the stereospecific addition of an unsubstituted methylene group to an olefin to form the corresponding cyclopropane in useful yields and in a high state of purity seems to have been recorded. A method meeting these requirements has now been developed in these laboratories.[1,12]

Thirty years ago Emschwiller reported the reactions of methylene iodide with magnesium[13] and zinc–copper couple[14] in ether.[15] He presented evidence that iodomethylzinc iodide (I) was formed in the latter reaction, while only the crystalline, unusually unreactive Grignard reagent II was isolated in the former. Titration data and some chemical observations seemed to confirm these conclusions. An ethereal solution of I, which was formed to the extent of 40%, gave methylene iodide and methyl iodide when treated with iodine and water, respectively, and the corresponding inorganic products were also isolated. It was further noted that when solutions of I were heated at prolonged

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[1] A preliminary report of the work described in this paper was given by H. E. Simmons and R. D. Smith, THIS JOURNAL, **80**, 5323 (1958).

[2] See R. Huisgen, *Angew. Chem.*, **67**, 439 (1955), for an excellent review of the reactions of diazo compounds.

[3] W. von E. Doering and A. K. Hoffman, THIS JOURNAL, **76**, 6162 (1954).

[4] K. v. Auwers and F. König, *Ann.*, **496**, 252 (1932).

[5] W. G. Young, L. J. Andrews, S. L. Lindenbaum and S. J. Cristol, THIS JOURNAL, **66**, 810 (1944).

[6] L. N. Owen and H. M. B. Somade, *J. Chem. Soc.*, 1030 (1947).

[7] L. I. Smith and W. B. Pings, *J. Org. Chem.*, **2**, 23 (1937).

[8] W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, THIS JOURNAL, **78**, 3224 (1956).

[9] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 3409 (1956).

[10] (a) W. von E. Doering and P. LaFlamme, *ibid.*, **78**, 5447 (1956); (b) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry & Industry*, 1039 (1957).

[11] H. M. Frey, THIS JOURNAL, **80**, 5005 (1958).

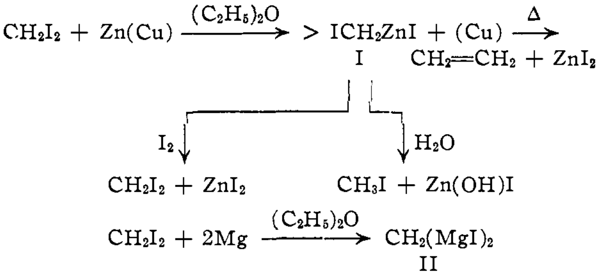
[12] At the request of Professor A. C. Cope, we converted cyclohepten-2-yl acetate to 2-acetoxybicyclo[5.1.0]octane; see A. C. Cope and P. E. Peterson, THIS JOURNAL, **81**, 1643 (1959).

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

[14] G. Emschwiller, *Compt. rend.*, **188**, 1555 (1929).

[15] Reactions of methylene iodide with metals have attracted the attention of chemists since A. Butlerow, *Ann.*, **120**, 356 (1861), recorded its reaction with copper to give ethylene. J. J. Sudborough, *J. Soc. Chem. Ind.*, **16**, 408 (1897), obtained similar results from the reaction of methylene iodide with powdered silver. Organometallic compounds have been reported in the reactions of methylene iodide with mercury (J. Sakurai, *J. Chem. Soc.*, **37**, 658 (1880); **39**, 485 (1881); **41**, 360 (1882)), aluminum (M. Faillebin, *Compt. rend.*, **174**, 112 (1922)) and tin (K. A. Kozeshkov, *Ber.*, **61B**, 1659 (1928); *J. Russ. Phys. Chem. Soc.*, **60**, 1191 (1928)). Much attention has been given to the generation of methylene radicals by reaction of methylene iodide with sodium vapor (C. E. H. Bawn and W. J. Dunning, *Trans. Faraday Soc.*, **35**, 185 (1939); C. E. H. Bawn and J. Milsted, *ibid.*, **35**, 889 (1939); C. E. H. Bawn and C. F. H. Tipper, *Disc. Faraday Soc.*, **2**, 104 (1947)) and by the photolysis of methylene iodide (R. A. Gregory and D. W. G. Style, *Trans. Faraday Soc.*, **32**, 724 (1936)).

reflux, ethylene in considerable quantity was slowly evolved. This latter observation was ascribed to a simple coupling reaction.

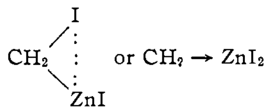


$$CH_2I_2 + Zn(Cu) \xrightarrow{(C_2H_5)_2O} ICH_2ZnI + (Cu) \xrightarrow{\Delta} CH_2{=}CH_2 + ZnI_2$$

$$CH_2I_2 + 2Mg \xrightarrow{(C_2H_5)_2O} CH_2(MgI)_2$$

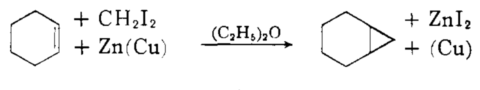
II

Cyclopropane Synthesis.—In light of modern concepts, iodomethylzinc iodide might be considered a complex of methylene and zinc iodide (structure III). Accordingly, the carbon atom in



III

iodomethylzinc iodide might be expected to exhibit enhanced electrophilic character similar to carbenes. This expectation was realized when it was found that Compound I, prepared in diethyl ether solution, reacted smoothly with cyclohexene to give a 48% yield of pure bicyclo[4.1.0]heptane.[1]

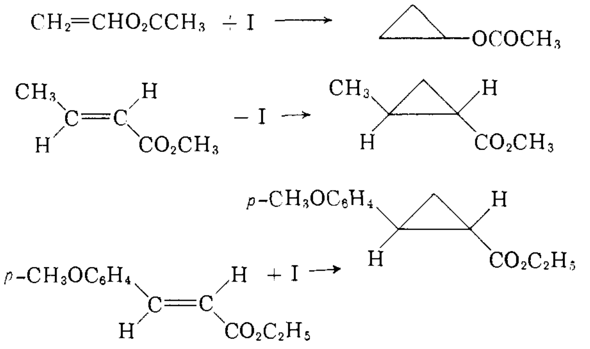


The scope of the reaction has not been fully investigated with respect to applicable unsaturated structures and reaction conditions; however, a synthesis giving reproducible yields with a large number of olefinic compounds has been devised. Table I lists some of the unsaturated compounds which gave the expected cyclopropanes. In general, yields in favorable cases were of the order of 30–50% when one mole of methylene iodide was heated at reflux with zinc–copper couple (containing one mole of zinc) in anhydrous diethyl ether solution in the presence of one mole of olefin. In some cases, yields were as high as 70%. The use of excess methylene iodide and couple usually gave increased conversions of olefin to cyclopropane. The reactions were carried out under anhydrous conditions for periods of 4–72 hours and were sensitive to the nature of the solvent and the source of the couple. A nitrogen atmosphere did not increase the yields.

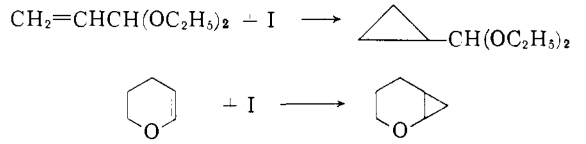
All alkyl-substituted monoölefins examined afforded the expected cyclopropane. 1,1,2,2-Tetramethylcyclopropane was obtained from tetramethylethylene in 45% yield, and ethylene gave cyclopropane in 29% yield when the reaction was carried out in a steel bomb under autogenous pressure. From the reaction of unconjugated dienes, such as 1,5-hexadiene, products were obtained incorporating one and two methylene units, the yields of either product being determined by the amounts of reagents employed. Cyclic olefins, such as cyclopentene and cyclohexene, behaved normally in the synthesis giving bicyclic hydrocarbons. Bicyclic olefins (*e.g.*, bicyclo[2.2.1]heptene and bicyclo[2.2.1]heptadiene) gave the expected products based on spectral considerations (see Table I). Conjugated olefinic hydrocarbons, such as styrene and propenylbenzene, functioned normally in the reaction.

In preliminary experiments, aliphatic acetylenes gave mixtures of unidentified products which contained cyclopropane derivatives on the basis of the infrared spectra.

Organozinc iodides are known to be unreactive toward ester, ketone and unactivated halogen functions. Iodomethyl-zinc iodide tolerated these substituents when present in the olefin, but, in general, the presence of electronegative groups near the point of olefinic unsaturation resulted in lower yields of cyclopropanes. Preliminary observations have indicated that when electronegative groups are removed from the site of unsaturation, yields of cyclopropane products are not lowered. The presence of ether functions frequently facilitated the reaction. Vinyl acetate, methyl crotonate and ethyl *trans*-*p*-methoxycinnamate gave cyclopropyl acetate, methyl *trans*-2-methylcyclopropanecarboxylate and ethyl *trans*-2-(*p*-methoxyphenyl)-cyclopropanecarboxylate[16] in 31, 9 and 29% yields, respectively. Acrolein diethyl acetal and dihydropyran, representative of acetals and vinyl ethers,



gave cyclopropanecarboxaldehyde diethyl acetal and 2-oxabicyclo[4.1.0]heptane in 12 and 65% yields, respectively.[17]



This method of introducing cyclopropane functions has proved valuable in the modification of

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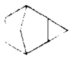
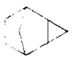
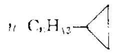
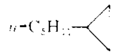
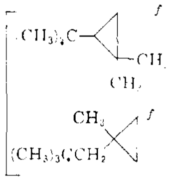
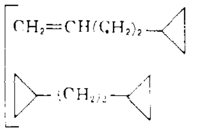
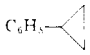
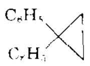
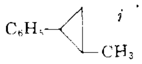
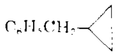
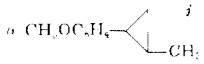
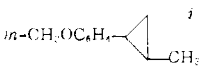
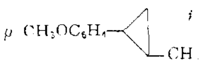
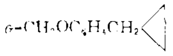
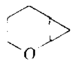
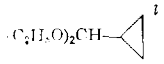
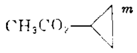
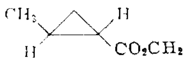
[16] When the ethyl 2-(*p*-methoxyphenyl)-cyclopropanecarboxylate obtained in the reaction was saponified, only *trans*-2-(*p*-methoxyphenyl)-cyclopropanecarboxylic acid was isolated. Recently the *trans*-acid has been unequivocally synthesized by E. N. Trachtenberg and G. Odian, This Journal, **80**, 4015 (1958). Since the starting cinnamic ester was of *trans* configuration, these results suggested that cyclopropane formation occurred stereospecifically. However, the possibility of epimerization during saponification cannot be ruled out. Similar considerations apply to the reaction of methyl crotonate. The ester products in these cases were assigned the *trans* configuration on the basis of the results of the study of *cis*- and *trans*-3-hexene (see below and Experimental).

[17] Zinc iodide is a strong Lewis acid capable of polymerizing styrenes, vinyl ethers and vinyl esters, and these classes of compounds sometimes gave lower yields of cyclopropanes due to polymerization.

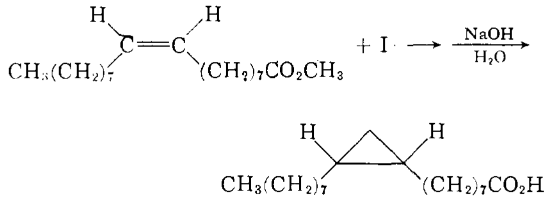
TABLE I

REACTIONS OF OLEFINS WITH METHYLENE IODIDE/ZINC-COPPER COUPLE

Olefin	Olefin, mole	CH_2I_2, mole	Zn(Cu), mole	I_2, mole	Reaction time, hr.	Product	Yield, %	B.p. (mm.), °C.	n^{25}D
Cyclohexene	0.30	0.15	0.22	0.02	48		48	116.5[a]	1.4546[a]
Cyclopentene	.45	.30	.36	.02	72	 [b]	27	81-82[c]	1.4373[c]
Bicyclo[2.2.1]heptene	.21	.30	.35	.02	48	 [d]	47	136-137	1.4778
Bicyclo[2.2.1]-heptadiene	.45	.30	.35	.02	48	 [d]	7	67-68 (100)	1.4874
1-Octene	.37	.19	.19	0	15		70	148	1.4160
1-Heptene	.40	.20	.27	0.02	30		47	128-129	1.4105
Diisobutylene[e]	.15	.25	.20	.02	25	 [f] [f]	31[g] 37[g]	124-125 120-121	1.4160 1.4210
1,5-Hexadiene	.125	.30	.35	.02	60		18 36	96-97 128-129	1.4181 1.4289
Styrene	.28	.19	.19	0	20		32	69 (22)[h]	1.5309[h]
1,1-Diphenylethylene	.09	.30	.36	0.02	72		24	110-111 (1.3)[i]	1.5847[i]
1-Phenylpropene	.20	.30	.35	.03	48	 [j]	54	78-79 (20)[k]	1.5204[k]
3-Phenylpropene	.30	.20	.30	.02	72		49	122-124 (102)	1.5132
1-(o-Methoxyphenyl)-propene	.18	.30	.35	.02	48	 [j]	70	98-99 (9)	1.5298
1-(m-Methoxyphenyl)-propene	.20	.30	.35	.02	48	 [j]	60	98 (6.3)	1.5443
1-(p-Methoxyphenyl)-propene	.135	.30	.35	.02	72	 [j]	63	95-97 (4)	1.5260
3-(o-Methoxyphenyl)-propene	.20	.30	.35	.02	48		48	102-103 (10)	1.5245
Dihydropyran	.12	.20	.25	.001	16		65	121	1.4488
Acrolein diethyl acetal	.15	.20	.26	.02	72	 [l]	12	97-100 (93)	1.4154
Vinyl acetate	.37	.19	.19	0	20	 [m]	31	112	1.4099
Metnyl crotonate	.30	.20	.30	0.02	48		9	69-70 (95)	1.4189

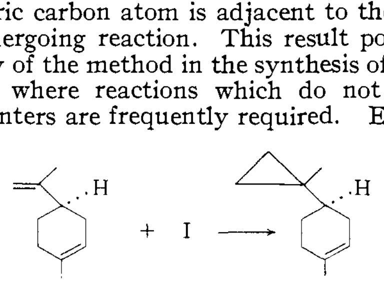
[a] Ref. 3 reported b.p. 116°, n^{25}_D 1.4550. [b] M. S. Kharasch, J. S. Sallo and W. Nudenberg, *J. Org. Chem.*, **21**, 129 (1956), obtained hydrocarbon mixtures containing bicyclo[3.1.0]hexane, which was not isolated. [c] N. Zelinsky and M. Ouchakoff, *Bull. soc. chim. France*, [4] **35**, 484 (1924), reported b.p. 78.5–79.5° (740 mm.), n^{18}_D 1.4326. [d] Examination of scale atomic models indicates that *exo* configurations of the cyclopropane rings are more likely in that they involve considerably less non-bonded hydrogen repulsions than *endo* configurations. The same conclusions are predicted by consideration of the transition states. [e] A mixture of 2,4,4-trimethyl-1-pentene (predominant) and 2,4,4-trimethyl-2-pentene obtained from Matheson, Coleman and Bell was used. [f] Structures were assigned on the basis of product ratio and infrared spectral considerations. The intensities of the 3.25 μ (C–H) stretching and 9.90 μ ring deformation bands were considerably lower in 1-*t*-butyl-2,2-dimethylcyclopropane than in 1-methyl-1-neopentylcyclopropane. [g] Yield ratio is approximate, determined by distillation. [h] F. H. Case, THIS JOURNAL, **56**, 715 (1934), reported b.p. 79–80° (37 mm.), n^{20}_D 1.5285; also see N. Kishner, *J. Russ. Phys. Chem. Soc.*, **45**, 950 (1913), who reported b.p. 173.6° (758 mm.), n^{15}_D 1.5342. [i] H. Wieland and O. Probst, *Ann.*, **530**, 274 (1937), reported analyses but no physical constants (see Table II). [j] The starting olefin was presumably a *cis–trans* mixture, and no attempts were made to separate the isomeric cyclopropane products. [k] D. Davidson and J. Feldman, THIS JOURNAL, **66**, 488 (1944), reported b.p. 184–186°, n^{20}_D 1.5237, but no analyses were given (see Table II). [l] The infrared spectrum was in accord with the assigned structure and showed the expected absorption at 3.25 and 9.82 μ. However, traces of hydroxyl and carbonyl impurities prevented acceptable analyses. [m] J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 3176 (1951), reported b.p. 111.8°, n^{25}_D 1.4058.

natural products. The total synthesis of DL-*cis*-9,10-methyleneoctadecanoic acid (dihydrosterculic acid) has been achieved in 51% yield in one step from methyl oleate.



Hofmann, Orochena and Yoho have recently reported an elegant but lengthy synthesis of dihydrosterculic acid.[18]

D-Limonene, $[\alpha]^{23}_D$ +106° (methanol), gave only one product in 50% yield when treated with an excess of I in ether, and infrared spectral studies showed that addition occurred exclusively in the isopropenyl group. The fact that the D-limonene recovered from the reaction was optically pure and the product had a high optical rotation, $[\alpha]^{23}_D$ +51° (methanol), suggests that little or no racemization occurred during cyclopropane formation. This case is particularly important since the single asymmetric carbon atom is adjacent to the double bond undergoing reaction. This result points out the utility of the method in the synthesis of natural products, where reactions which do not disturb optical centers are frequently required. Examination of molecular models showed that the double bond in the ring is the least accessible on steric grounds to the approach of a bulky reagent, and this internally competitive system offers convincing evidence of considerable steric requirements in the reaction of I with double bonds.



Methylene chloride and bromide did not react with zinc–copper couple under the reaction conditions which are described in the Experimental section. Cyclopropanes could be obtained when chloroiodomethane was employed, but the yields were lower.

The method of preparation of the zinc–copper couple is an important factor in determining its reactivity toward methylene iodide and in achieving reproducible yields of pure products. Couples prepared by heating together granulated zinc and copper powder[19] gave cyclopropanes, but in erratic yields, while those prepared by the thermal decomposition of cupric citrate in the presence of zinc dust[20] or by the precipitation of copper from cupric sulfate solutions with excess zinc dust reacted with difficulty with methylene iodide. Zinc dust activated by iodine or hydrochloric acid failed to react with the diiodide. An active couple was obtained by heating a mixture of zinc dust and cupric oxide to 500° in an atmosphere of hydrogen.[21] This couple, which contained 90% zinc and 10% copper, gave reproducible results in the cyclopropane synthesis and was used in all of the work described in this paper. When this couple was activated by the addition of a few crystals of iodine before the introduction of the other reagents, subsequent initiation frequently proceeded more smoothly but with no apparent effect on yield. During the course of the reaction, the gray color of the couple disappeared as finely divided red copper precipitated.

No systematic study of the effect of solvents has been made. Of the solvents investigated, diethyl ether consistently gave highest yields and most easily controlled reactions. Bicyclo[4.1.0]heptane was obtained from cyclohexene in ethyl acetate, ethylene glycol dimethyl ether, and tetrahydrofuran, but white, crystalline $CH_2(ZnI)_2$ was formed in a side reaction. Mixed solvents, such as ether and tetrahydrofuran, offered no advantages.

Mechanism.—Although no detailed investigation of the mechanism of the reaction of olefins with methylene iodide and zinc–copper couple has been made, several experimental observations have suggested a reasonable interpretation.

(1) The reaction of I with olefins occurs with discrimination, in that only double bonds are attacked by the reagent. No isomeric hydrocarbons which would be expected if free methylene were an intermediate[3,10a] were detected in the reaction mixtures.[22]

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(18) K. Hofmann, S. F. Orochena and C. W. Yoho, THIS JOURNAL, **79**, 3608 (1957).

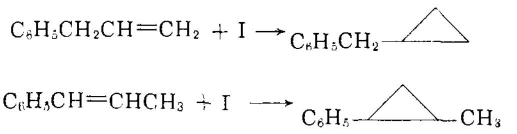
(19) E. Krause and A. von Grosse, "Die Chemie der Metallorganischen Verbindungen," Borntraeger, Berlin, 1943, p. 63.

(20) R. C. Krug and P. J. C. Tang, THIS JOURNAL, **76**, 2262 (1954).

(21) The method developed is based on one described by F. L. Howard, *J. Research Natl. Bur. Standards*, **24**, 677 (1940); *cf.* a similar application by F. R. Buck, B. B. Elsner, E. J. Forbes, S. H. Morrell, J. C. Smith and E. R. Wallsgrove, *J. Inst. Petroleum*, **34**, 339 (1948).

(22) Pure olefin, methylene iodide and the couple described above gave only one product, the expected cyclopropane. During work-up, it is desirable to remove the zinc iodide completely before distillation, since some cyclopropanes may be isomerized under these conditions.

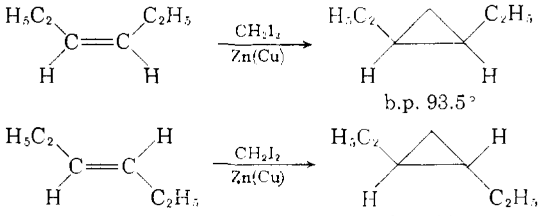
(2) No rearranged cyclopropanes were formed from olefins which are susceptible to prototropic rearrangements.[22] For example



In these cases, only the isomer shown was detected. Thus, compound I showed no carbanion character sufficient to rearrange the starting olefin.

(3) When Compound I was prepared in ether and the reaction mixture was filtered through a fine sintered-glass plug, a colorless, solid-free solution was obtained that was stable at room temperature or below for several hours. The addition of cyclohexene caused a mild exothermic reaction to occur accompanied by the slow precipitation of zinc iodide, and the only product isolated was bicyclo[4.1.0.]heptane.[23] Further the solid salts isolated from the homogeneous reaction were shown to contain no more than 50 p.p.m. of copper by emission spectroscopy.[24] It thus seems unlikely that copper plays an important role in the reactions of I with olefins[25]; however, a large catalytic effect by the very small amount of copper present cannot be ruled out.

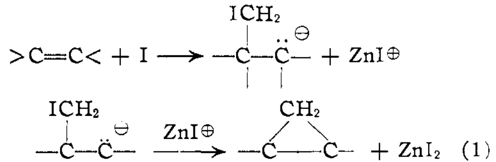
(4) Cyclopropane formation occurs stereospecifically.[1] Highly purified samples of *cis*- and *trans*-3-hexene reacted smoothly with I in ether, giving diethylcyclopropanes boiling at 93.5° and 86.5°, respectively. Vapor-phase chromatographic analysis of each reaction mixture showed the presence only of *unchanged* olefin and a *single* cyclopropane. Although the configurations of the two diethylcyclopropanes have not been determined chemically, assignments were made as indicated on the basis of the Auwers–Skita rule, which appears to be valid for rigid rings and predicts the *cis* isomer of this hydrocarbon pair to have the higher boiling point.[26] The recovery of unisomerized olefin in the reactions of *cis*- and *trans*-3-hexene suggests that no strong, reversible coördination of I and the olefin occurred prior to transfer of the methylene group.



(5) Experience has shown that high electron density at the double bond undergoing reaction favors increased yields and rates of cyclopropane formation.

(6) An unpredictable steric effect seems to influence the success of some of the reactions. The internal competition exhibited in the case of D-limonene is best explained on the grounds of steric requirements.

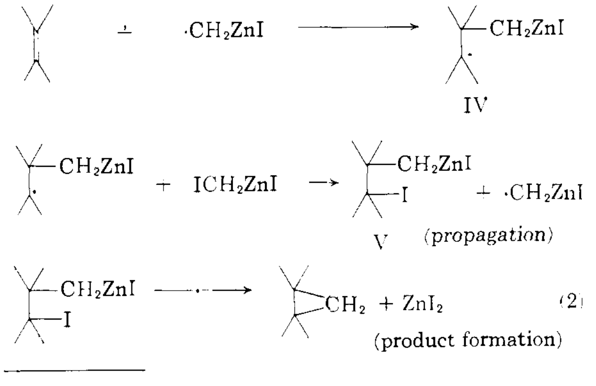
A possible mechanism which explains cyclopropane formation involves addition of I as a carbanion to the olefinic bond followed by cyclization by intramolecular displacement.



Very reactive organometallic compounds, such as sodium[27a] and aluminum[27b] alkyls, are known to add to unactivated olefins. The less reactive Grignard reagents and organozinc iodides do not undergo addition reactions with such olefins. It seems reasonable that iodomethylzinc iodide would be similarly unreactive in a carbanion-addition mechanism as pictured in equation 1. Carbanion intermediates are also unlikely in view of observations 2 and 4. Moreover, (5) suggests that an electrophilic rather than a nucleophilic species is involved in the addition.

A mechanism based on the homolytic dissociation of I and a free radical chain process (equation 2) was considered in view of the radical character of

$ICH_2ZnI \longrightarrow I\cdot + \cdot CH_2ZnI$[28] (initiation)



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[23] This observation may be important in synthetic applications when a homogeneous reaction is required or when it is desirable to avoid contact of reactants or products with the couple surface.

[24] This small amount of copper probably was not in solution. The copper metal which is released during reaction is in an extremely finely divided form, and such amounts may have passed the filter.

[25] P. Yates, THIS JOURNAL, **74**, 5376 (1952) has offered convincing evidence of the role of copper in modifying carbene reactivity.

[26] J. Braudrenghien, *Bull. soc. chim. Belg.*, **38**, 172 (1929); also see ref. 10a in which Doering has accepted this criterion in assigning the configuration of *cis*- and *trans*-1,2-dimethylcyclopropane. ADDED IN PROOF.——Recent proton magnetic resonance spectral studies by Dr. D. B. Chesnut of this laboratory have confirmed these absolute assignments of configuration. The 1,2-diethylcyclopropane obtained from *cis*-3-hexene showed a 30 mc. (spinning) proton spectrum consisting of three high-field lines relative to water at 118, 130 and 160 c.p.s. (peak areas, 10:3:1). The *cis*-isomer would be expected to exhibit such a spectrum if the ten ethyl protons, three ring protons *trans* to the ethyl groups and single ring proton *cis* to the ethyl groups are differentiated by the magnetic field in that order. The product from *trans*-3-hexene showed a two line spectrum with peaks at 120 and 145 c.p.s. (peak areas, 10:4). In this case the ten ethyl protons are again in evidence while the ring protons, although of two kinds, are sufficiently similar to give a single line at low fields of the expected intensity.

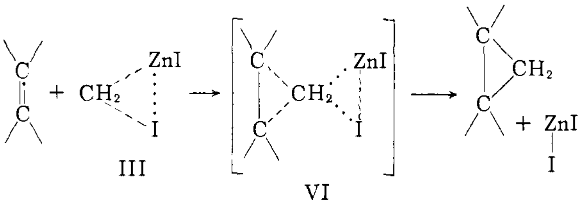
[27] (a) H. Pines, J. A. Vesely and V. N. Ipatieff, THIS JOURNAL, **77**, 554 (1955); see also ref. 9; (b) K. Ziegler, H. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 91 (1954).

[28] Other schemes of homolytic initiation, such as $ICH_2ZnI \rightarrow ICH_2\cdot + \cdot ZnI$, require similar steps of propagation and product formation.

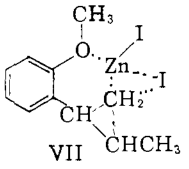
other reactions of organometallic compounds, *e.g.*, Grignard reagents in the presence of certain metals and metal salts.[29] The presence of metal salts and metal surfaces, especially copper, might also promote homolytic reactions of I. Evidence that this is not the case is strongly suggested by the discrimination (1) and stereospecificity (2) shown in the reaction. Skell and Woodworth[30] have shown that the addition of trichloromethyl radical to *cis*- and *trans*-2-butene, which involves an intermediate radical similar to IV, gives mixtures of diastereomeric products. The product of the chain process (V) would also be a mixture of diastereomers, and the subsequent elimination of zinc iodide to give a single cyclopropane would be highly unlikely.

An interpretation of the reaction based on free methylene[8] or a less energetic form modified by copper,[25,34] $CH_2 \rightarrow Cu$, is objectionable because of considerations 1 and 3, especially in view of the stability of ethereal solutions of I and the absence of copper in reactions carried out using filtered solutions. Furthermore, iodomethylzinc iodide reacts with both ethylene and tetramethylethylene, whereas dichlorocarbene reacts only with the latter. The additions of dihalocarbenes, which are determined chiefly by electronic considerations,[31] are stereospecific[9,10a] and subject to small steric effects. We have concluded that reactions of I with olefins are influenced more by steric effects than are the corresponding reactions of dichlorocarbene.

A mechanism consistent with the above observations considers iodomethylzinc iodide as a relatively strongly bonded complex of methylene and zinc iodide (III), the carbon atom of which is electrophilic in character.[32] Structure III suggests that considerable (C–I) and (C–Zn) bond weakening and (I_C–Zn) bond strengthening exist over that implicit in the conventional structure I. Reaction probably occurs through a three center transition state VI, which would account for the stereospecificity observed. Transition state VI, which includes a molecule of zinc iodide, will obviously make heavier steric demands on the success of the addition of a methylene group than will transition states involving a free carbene.[3,8,9,10a] Steric effects may assist (and direct)[33] addition in certain cases. For example, 1-(*o*-methoxyphenyl)-propene gave a higher yield of a cyclopropane than did the *m*- and *p*-isomers. Coördination of I with the ether oxygen may stabilize the transition state (structure VII) in the case of the *o*-isomer.



III VI



VII

Other Attempts to Prepare Cyclopropanes.—In the course of this study, several other reagents were investigated as potential systems for the transfer of methylene groups to olefins. The reaction of methylene iodide with magnesium in ether in the presence of cobaltous chloride and cyclohexene gave no detectable amount of the cyclopropane derivative. Attempts were made to prepare cyclopropanes through the intermediate formation of methylene copper, $CH_2 \rightarrow Cu$[25,34]; however, the reaction of methylenedimagnesium diiodide with cuprous chloride in ether solution in the presence of olefins gave no cyclopropanes.

The preparation of iodomethylmercuric iodide, ICH_2HgI, has been reported from the reaction of mercury with excess methylene iodide.[15] On repetition of the preparation, it was found that the reaction proceeded very slowly with liquid mercury to give mercuric iodide and low yields of impure iodomethylmercuric iodide. A much faster reaction occurred when finely divided mercury was used with irradiation from an ultraviolet source. Attempts to purify the crude iodomethylmercuric iodide by recrystallization from methylene iodide[15] resulted in decomposition at 140–150° with the formation of a viscous tar and mercuric iodide. It is possible that the following reactions occurred.

$$CH_2I_2 + Hg \longrightarrow ICH_2HgI$$

$$ICH_2HgI \xrightarrow{150^\circ} HgI_2 + CH_2:$$

$$xCH_2: \longrightarrow —(CH_2—)_x$$

A report in the literature[35] describes the reaction of phenyllithium with trimethylsulfonium iodide to form polymethylene and dimethyl sulfide. In an effort to trap any methylene intermediates formed, this reaction was repeated in the presence of cyclohexene. Although dimethyl sulfide was detected among the reaction products, no bicyclo[4.1.0.]heptane was isolated.

Experimental[36]

Materials.—The unsaturated compounds employed in the cyclopropane syntheses were commercial reagent grade chemicals, which were distilled before use, or were synthe-

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[29] K. Ziegler, E. Eimers, W. Hechelhammer and H. Wilms, *Ann.*, **567**, 43 (1950), have reported the free-radical coupling of olefins in the presence of butylmagnesium chloride and cupric chloride.

[30] P. S. Skell and R. C. Woodworth, THIS JOURNAL, **77**, 4638 (1955).

[31] (a) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958). (b) For interesting discussions of the electronic configuration of transition states involved in the addition of dihalocarbenes to olefins, see P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956); R. C. Woodworth and P. S. Skell, *ibid.*, **79**, 2542 (1957).

[32] Structure III does not necessarily imply the usual π-complex, *cf.* M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 18.

[33] See ref. 12; the addition of I to cyclohepten-2-yl acetate gave predominantly one isomer.

[34] Similar intermediates may be involved in the copper-induced decomposition of ethyl diazoacetate; see W. von E. Doering and L. H. Knox, THIS JOURNAL, **78**, 4947 (1956).

[35] G. Wittig and H. Fritz, *Ann.*, **577**, 39 (1952).

[36] All melting points are corrected and boiling points are uncorrected.

sized by conventional methods. In all cases, the physical constants of the unsaturated compounds were in accord with quoted literature values. Methylene iodide, obtained from Matheson, Coleman and Bell, was distilled before use and stored over bright iron wire. Commercial anhydrous diethyl ether was dried over sodium.

Spectral Data.—Infrared spectra were determined for all of the cyclopropanes prepared in this work on a Perkin-Elmer model 21 double beam infrared spectrometer equipped with NaCl optics (2–15 μ). Spectra were obtained on pure liquids or in potassium bromide wafers and were in accord with the assigned structures. It is interesting to note that all of the cyclopropane products showed characteristic absorption in the 3.2 and 9.8 μ regions. A compilation of the spectral data will be published elsewhere.

Preparation of the Zinc–Copper Couple.—A couple containing approximately 90% zinc and 10% copper was prepared by a variation of a method in the literature.[21] Mallinckrodt A.R. wire form cupric oxide (30 g.) was ground to a fine powder in a mortar and mixed with 240 g. of Mallinckrodt A.R. zinc dust. The mixture was placed in a Vycor combustion boat lined with copper foil, and a thermocouple was embedded in the powder. The boat was placed in a Vycor tube heated by a muffle furnace. A mixed gas (hydrogen, 65 l./hr., nitrogen, 25 l./hr.) was passed through the tube while the temperature was raised to 500° during 4 hours. The mixture was kept at 500° for 30 minutes, and the tube was allowed to cool to room temperature in a hydrogen atmosphere. The couple was obtained as dark gray lumps, which were ground to a fine powder in a mortar before use. In some instances, there was also found in the mixture a small amount of material which had apparently melted and agglomerated during heating. This shiny, metallic material was easily separated from the powdered couple and was not used in the reactions with methylene iodide. No loss of activity was noticed in samples of the couple on storage, even when atmospheric moisture and oxygen were not rigorously excluded.

Synthesis of Cyclopropanes.—The general procedure used for the synthesis of cyclopropanes from olefins is described below, and the details are given in Tables I and II. The reactions were carried out in a round-bottomed flask equipped with a magnetic stirrer, reflux condenser and drying tube. The couple, iodine and anhydrous ether (100–150 ml.) were placed in the flask and stirred until the iodine color faded. Methylene iodide and the olefin were added, and the stirred mixture was heated at gentle reflux for the specified time. Usually a mildly exothermic reaction occurred after a short induction period and lasted for approximately 30 minutes. At the end of the reaction, most of the gray couple had been replaced by finely divided copper. The cool mixture was filtered, and the filtrate was washed successively with cold 5% hydrochloric acid,[37] 5% sodium bicarbonate solution and water. After the solution had been dried over anhydrous magnesium sulfate, ether was removed by distillation, and the residue was fractionated through a semi-micro spinning-band column.[38] Vapor-phase chromatographic (v.p.c.) analyses of several of the cyclopropanes initially indicated contamination by hydrocarbon impurities. Subsequent studies showed that the use of pure methylene iodide and olefin with the couple described above gave reproducible yields of pure cyclopropanes. Yields, in general, were based on the limiting component (olefin or methylene iodide), and in most cases unreacted olefin was recovered, indicating high conversions to cyclopropanes.

TABLE II

ANALYTICAL DATA

Cyclopropane	Elemental analyses, % Calcd. C	H	Found C	H
Bicyclo[3.1.0]hexane	87.73	12.27	88.19	12.27
Tricyclo[3.2.1.$0^{2,4}$]octane	88.82	11.18	88.86	11.12
Tricyclo[3.2.1.$0^{2,4}$]-6-octene	90.50	9.50	90.52	9.43
n-Hexylcyclopropane	85.63	14.37	86.16	14.61
n-Amylcyclopropane	85.64	14.36	85.63	14.29
1-*t*-Butyl-2,2-dimethylcyclopropane	85.63	14.37	85.33	14.23
1-Methyl-1-neopentylcyclopropane	85.63	14.37	85.92	14.41
4-Cyclopropyl-1-butene	87.42	12.58	87.07	13.01
1,2-Bis-(cyclopropyl)-ethane	87.19	12.81	87.79	12.80
1,1-Diphenylcyclopropane	92.74	7.26	92.89	7.59
1-Methyl-2-phenylcyclopropane	90.85	9.15	91.08	9.16
Benzylcyclopropane	90.85	9.15	91.26	9.30
1-Methyl-2-(*o*-methoxyphenyl) cyclopropane	81.44	8.70	81.59	8.61
1-Methyl-2-(*m*-methoxyphenyl)-cyclopropane	81.44	8.70	81.52	8.54
1-Methyl-2-(*p*-methoxyphenyl)-cyclopropane	81.44	8.70	81.57	8.87
o-Methoxybenzylcyclopropane	81.44	8.70	81.46	8.81
2-Oxabicyclo[4.1.0]heptane	73.43	10.27	73.65	10.32
Methyl *trans*-2-methylcyclopropanecarboxylate	63.13	8.83	63.34	8.94

Preparation of Bicyclo[4.1.0]heptane in a Homogeneous System (Filtered Reaction).—A solution of iodomethylzinc iodide was prepared by stirring a mixture of methylene iodide (50.0 g., 0.19 mole) and zinc–copper couple (13.5 g., 0.19 mole of zinc) in anhydrous ether (200 ml.) at reflux for 4 hours. The cooled solution was filtered by suction in a nitrogen atmosphere through a fine sintered glass funnel to give a water-white filtrate. Cyclohexene (15.3 g., 0.19 mole) was added by a syringe and a cloudiness developed within 30 seconds. The mixture was stirred and heated at reflux for 18 hours, during which time white zinc iodide precipitated. The reaction appeared to be complete after 1 hour. The reaction mixture was worked up in the usual manner and gave 2.1 g. (11.5%) of bicyclo[4.1.0]heptane, b.p. 115–116°, $n^{25}\text{D}$ 1.4538. Infrared spectral studies and v.p.c. showed the sample to be homogeneous. The aqueous washings were evaporated to dryness, and the crude solid was analyzed by emission spectroscopy. Copper was determined to be present in a concentration of no more than 50 p.p.m.

Bicyclo[4.1.0]heptane from Chloroiodomethane.—A mixture of zinc–copper couple (14.5 g., 0.20 mole of zinc), chloroiodomethane (26.3 g., 0.15 mole) and cyclohexane (24.6 g., 0.30 mole) was stirred in 50 ml. of dry tetrahydrofuran. After a gentle exothermic reaction had subsided, the mixture was stirred under reflux for 70 hours. The cool mixture was diluted with 50 ml. of ether and filtered. The filtrate was washed with 5% hydrochloric acid, water, and 5% sodium sulfite solution and then was dried over anhydrous magnesium sulfate. Distillation gave 1.11 g. (8%) of bicyclo[4.1.0]heptane, b.p. 115–116°, $n^{25}\text{D}$ 1.4546.

Synthesis of Cyclopropane from Ethylene.—Zinc–copper couple (22.0 g., 0.30 mole of zinc), iodine (5.0 g., 0.02 mole), anhydrous ether (80 ml.) and methylene iodide (53.6 g., 0.20 mole) was placed in a 200-ml. bomb equipped with a glass liner. The bomb was sealed, and ethylene (10.0 g., 0.36 mole) was added. The mixture was shaken at 60° under autogenous pressure for 48 hours. The tube was cooled to room temperature, and the gaseous products (30 g.) were bled into an evacuated stainless steel cylinder cooled in liquid nitrogen. Analysis of the products by v.p.c. showed the presence of 2.4 g. (29%) of cyclopropane, the identity of which was confirmed by infrared spectroscopy.

1,1,2,2-Tetramethylcyclopropane.—A mixture of tetramethylethylene (b.p. 73°, $n^{25}\text{D}$ 1.4085) (15.7 g., 0.19 mole), methylene iodide (50.0 g., 0.19 mole), zinc–copper couple (20.4 g., 0.28 mole), a crystal of iodine, and anhydrous ether (80 ml.) was stirred and heated under reflux while maintaining anhydrous conditions. After 15 hours, the mixture was cooled and decanted into a separatory funnel, and the solids were washed with ether. The combined ether solutions were washed with cold 5% hydrochloric acid, 5% sodium bicarbonate solution and water and were dried over anhydrous magnesium sulfate. The ether was removed through an efficient packed column, and the residue was distilled through a semi-micro spinning-band column.[38] Five fractions boiling over the range 72.5–74.0°, $n^{25}\text{D}$ 1.4046–

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[37] The zinc salts were removed from acid-sensitive products by washing first with water or ammonium chloride solution and then with aqueous ammonium hydroxide solution.

[38] R. G. Nester, *Anal. Chem.*, **28**, 278 (1956).

1.4020, were taken, the total weight of the distillate being 12.1 g.

Vapor phase chromatography showed that all of the fractions were composed of three components in the ratio 61:38:1. The major component was isolated by v.p.c. and was shown by mass spectrographic and infrared analyses to be pure 1,1,2,2-tetramethylcyclopropane, n^{25}D 1.3955. The yield was calculated to be 42%. The second component was shown to be recovered tetramethylethylene by its retention time and infrared spectrum. The third component, which was not isolated, increased from 0.5 to 1% in concentration over the fractions. This increase was paralleled by the appearance and increase in intensity of weak bands at 6.05 and 11.15 μ in the spectra of the fractions, indicating the presence of a terminal olefin.

The terminal olefin appears to arise as a rearrangement product of tetramethylethylene in contact with the couple and zinc iodide. Control experiments were carried out which showed that 1,1,2,2-tetramethylcyclopropane was unchanged after heating under reflux in ether solution in the presence of the couple and zinc iodide. The infrared spectrum of a sample of tetramethylethylene, which had been treated under the same conditions, showed the presence of a small amount of a terminal olefin which absorbed at 6.05 and 11.15 μ.

***cis*-1,2-Diethylcyclopropane.**—A mixture of *cis*-3-hexene[39] (b.p. 66.5°, n^{25}D 1.3920) (10.0 g., 0.12 mole), methylene iodide (31.6 g., 0.12 mole), zinc–copper couple (8.9 g., 0.12 mole of zinc) and anhydrous ether (60 ml.) was stirred and heated under reflux while maintaining anhydrous conditions. After 20 hours, the mixture was cooled and decanted into a separatory funnel, and the solids were washed with 30 ml. of ether. The combined ether solutions were washed with cold 5% hydrochloric acid, 5% sodium bicarbonate solution and water and were dried over anhydrous magnesium sulfate. The ether was removed through an efficient packed column, and the residue was distilled through a semi-micro spinning-band column.[38] There was recovered 4.4 g. of unreacted olefin, b.p. 66–67°, n^{25}D 1.3920. Pure ***cis*-1,2-diethylcyclopropane** was obtained as a colorless liquid, b.p. 93.5°, n^{25}D 1.4035. The yield was 4.0 g. (34.5%).

Anal. Calcd. for C_7H_{14}: C, 85.63; H, 14.37. Found: C, 85.89; H, 14.32.

All of the distillation fractions were examined by v.p.c. and showed only pure starting olefin and *cis*-1,2-diethylcyclopropane. In another experiment, the crude reaction mixture was analyzed directly with the same results. In the v.p.c. analyses, two columns were principally employed: (1) 7 ft. × 0.25 in. copper tubing packed with firebrick coated with 4-methyl-4-nitropimelonitrile and operated at 25° with helium flow rate = 1 cm.^{3}/sec., and (2) 7 ft. × 0.25 in. copper tubing packed with firebrick coated with the carbitol ester of N,N-diisobutyloxamide and operated at 25° with a helium flow rate = 1 cm.^{3}/sec. Other columns packed with firebrick coated with silicone oils and operated at higher temperatures gave the same analytical results. Column 1, operated under the above conditions, gave the following retention times with pure samples of *cis*- and *trans*-3-hexene and *cis*- and *trans*-1,2-diethylcyclopropane. Separation was complete and the limit of detection was better than 0.5%.

Compound	Retention time, min.
cis-3-Hexene	3.82
trans-3-Hexene	3.06
cis-1,2-Diethylcyclopropane	6.80
trans-1,2-Diethylcyclopropane	4.43

The infrared spectrum of *cis*-1,2-diethylcyclopropane showed the usual cyclopropane absorption at 3.25 and 9.80 μ. Characteristic absorption occurred at 9.16, 9.95, 10.95 and 11.80 μ regions which were blank in the *trans* isomer.

***trans*-1,2-Diethylcyclopropane.**—A mixture of *trans*-3-hexene[39] (b.p. 66.0°, n^{25}D 1.3920) (10.0 g., 0.12 mole), methylene iodide (31.6 g., 0.12 mole), zinc–copper couple (8.9 g., 0.12 mole of zinc) and anhydrous ether (60 ml.) was carried through the cyclopropane synthesis under conditions identical to those employed with the *cis*-olefin. There was recovered 5.5 g. of unreacted olefin, b.p. 66.5°, n^{25}D 1.3920, in addition to 1.8 g. (15.5%) of pure ***trans*-1,2-diethylcyclopropane**, b.p. 86.5°, n^{25}D 1.3982.

Anal. Calcd. for C_7H_{14}: C, 85.63; H, 14.37. Found: C, 85.54; H, 14.49.

Detailed v.p.c. studies, similar to those above, showed that the product was uncontaminated by the *cis*-isomer or other isomeric hydrocarbons and that the recovered olefin was the pure *trans* isomer. Synthetic mixtures of pure samples of *cis*- and *trans*-3-hexene and *cis*- and *trans*-1,2-diethylcyclopropane showed that detection of each component in unknown mixtures was reliable to better than 0.5%.

The infrared spectrum of *trans*-1,2-diethylcyclopropane showed the usual cyclopropane absorption at 3.25 and 9.78 μ. Characteristic absorption occurred at 9.05, 11.20, 11.34 and 13.32 μ, regions which were blank in the *cis* isomer.

1-Methyl-4-(1-methylcyclopropyl)cyclohexene.—The general procedure described above was followed employing D-limonene (b.p. 70° (26 mm.), n^{25}D 1.4710, $[\alpha]^{23}$D +106° in methanol, 13.6 g., 0.10 mole), methylene iodide (53.6 g., 0.20 mole), zinc–copper couple (18.2 g., 0.25 mole of zinc) and anhydrous ether (150 ml.). The mixture was stirred at reflux for 48 hours and was worked up in the usual manner. Distillation through a semi-micro spinning-band column[38] gave approximately 4 g. of recovered D-limonene, b.p. 55° (8 mm.), n^{25}D 1.4682, and 7.3 g. (50%) of pure **1-methyl-4-(1-methylcyclopropyl)cyclohexene**, b.p. 73° (8.5 mm.), n^{25}D 1.4679, $[\alpha]^{23}$D +51° in methanol.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.90; H, 12.10. Found: C, 87.87; H, 12.26.

V.p.c. studies proved the homogeneity of the product. D-Limonene shows absorption bands in the infrared at 5.96 (cyclohexene double bond, weak), 6.06 (terminal vinyl, strong), 11.27 (terminal vinyl, strong) and 12.52 μ (1-methylcyclohexene, (C–H) bending, strong). The cyclopropane product had a single band in the (C=C) stretching region at 5.96 μ of the same intensity as that in D-limonene, while the very strong band at 6.06 μ was absent. The region at 11.27 μ was blank in the product. The band at 12.52 μ due to (C–H) bending of the ring vinyl hydrogen was presently unchanged. Characteristic (C–H) stretching of the cyclopropane hydrogens was obscured by the vinyl hydrogen in the six-membered ring. The usual strong absorption at 9.94 μ was present while this region was blank in D-limonene. The spectra showed that cyclopropane formation occurred exclusively in the isopropenyl group.

The recovered D-limonene had an optical rotation, $[\alpha]^{23}$D +98°, and the infrared spectrum indicated contamination by traces of the cyclopropane product. Redistillation of a 1-g. sample gave almost total recovery of D-limonene, $[\alpha]^{23}$D +105°, showing that little or no racemization of the starting material occurred under the reaction conditions.

Ethyl *trans*-2-(*p*-Methoxyphenyl)-cyclopropanecarboxylate.—Zinc–copper couple (25.4 g., 0.35 mole of zinc), iodine (5.0 g., 0.02 mole), methylene iodide (80.4 g., 0.30 mole), ethyl *trans*-*p*-methoxycinnamate[40] (10.3 g., 0.05 mole) and anhydrous ether (100 ml.) were stirred under reflux for 48 hours. The cool reaction mixture was filtered, and the filtrate was washed successively with 5% hydrochloric acid, water, and 5% sodium sulfite solution. The ether was evaporated to leave a solid residue, which was crystallized from ethanol. There was obtained 3.14 g. (29%) of ethyl *trans*-2-(*p*-methoxyphenyl)-cyclopropanecarboxylate, m.p. 83–84°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.03; H, 7.38.

Two grams of the ester was saponified by heating under reflux for 8 hours with 2.0 g. of potassium hydroxide in 15 ml. of 85% ethanol. Dilution of the reaction mixture with 75 ml. of water, and acidification with concentrated hydrochloric acid gave the free acid. Crystallization from ethanol–water afforded 1.55 g. (89%) of *trans*-2-(*p*-methoxyphenyl)-cyclopropanecarboxylic acid, m.p. 114–114.5°.[41]

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[39] The *cis*- and *trans*-3-hexene were A.P.I. samples and were shown to be of at least 99.5% purity by v.p.c. on columns described below.

[40] Ethyl *trans*-*p*-methoxycinnamate was prepared by the esterification of the acid obtained from the reaction of anisaldehyde with malonic acid in pyridine (piperidine catalyst), a procedure known to give *trans*-cinnamic acids; see W. J. Hinckenbottom and M. F. Ansell in E. H. Rodd, "Chemistry of the Carbon Compounds," Vol. III-B, Elsevier Publishing Co., New York, N. Y., 1956, p. 995.

[41] E. N. Trachtenberg and G. Odian, THIS JOURNAL, **80**, 4015 (1958), reported m.p. 112–113° and absorption maxima at 210 (ϵ 6400), 233 (ϵ 14,000) and 279 mμ (ϵ 1700).

The ultraviolet spectrum of the *trans*-acid showed absorption maxima at 232 (ϵ 14,200), 278 (ϵ 1700), 283 (ϵ 1650) and 288 mμ (ϵ 1170) in 95% ethanol.[41]

DL-*cis*-9,10-Methyleneoctadecanoic Acid (Dihydrosterculic Acid).—A mixture of 22.0 g. (0.30 mole of zinc) of zinc-copper couple, 5.0 g. (0.02 mole) of iodine, 53.6 g. (0.20 mole) of methylene iodide, 29.6 g. (0.10 mole) of distilled methyl oleate (b.p. 128–132° (0.4 mm.), n^{25}_D 1.4506) and 100 ml. of anhydrous ether was stirred under reflux for 48 hours. The cool reaction mixture was filtered, and the filtrate was washed successively with 5% hydrochloric acid, water, and 5% sodium sulfite solution. After the solution had been dried over anhydrous magnesium sulfate, the ether was evaporated, and the residue was distilled to give 7.95 g. of recovered methyl oleate, b.p. 132–134° (0.4 mm.), n^{25}_D 1.4506. The distillation residue (17 g.) was heated under reflux with 4.0 g. of potassium hydroxide in 75 ml. of ethanol for 4 hours. The hot solution was filtered, and the filtrate was diluted with 400 ml. of water. Acidification of the solution with concentrated hydrochloric acid, filtration and drying of the solid afforded 15 g. (51%) of crude DL-*cis*-9,10-methyleneoctadecanoic acid, m.p. 31–35°. Two crystallizations from petroleum ether at −30° raised the melting point to 34–37°. Liquid-solid countercurrent distribution of the urea complex of the acid[42] did not reveal the presence of any impurities and raised the melting point to 36–38°.[43] The infrared spectrum showed characteristic cyclopropane absorption at 3.25 and 9.90 μ and was identical with the published spectrum of dihydrosterculic acid.[43b] The amide was prepared and melted at 87–88° (lit.,[18] m.p. 86.4–87.6°).

Acknowledgment.—The authors acknowledge with pleasure the many helpful discussions with Dr. B. C. McKusick.

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[42] W. N. Sumerwell, THIS JOURNAL, **79**, 3411 (1957).

[43] (a) Dihydrosterculic acid has been reported to have m.p. 38.8–39.8° by J. R. Nunn, *J. Chem. Soc.*, 313 (1952), and (b) m.p. 39.7–40.5° by K. Hofmann, O. Jucker, W. R. Miller, A. C. Young, Jr., and F. Taussig, THIS JOURNAL, **76**, 1799 (1954). (c) Synthetic DL-*cis*-9,10-methyleneoctadecanoic acid has been reported to have m.p. 38.6–39.6°.[18]

WILMINGTON, DEL.

[CONTRIBUTION FROM GOESSMANN CHEMISTRY LABORATORY, UNIVERSITY OF MASSACHUSETTS]

Conjugation in Cyclopropanes. Attempted Acylation, Alkylation, Cyanoethylation and Deuterium Exchange[1]

BY GEORGE W. CANNON, ARTHUR A. SANTILLI AND POPKIN SHENIAN

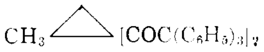
RECEIVED SEPTEMBER 18, 1958

Attempts to effect acylation, alkylation and cyanoethylation of diethyl 2-methylcyclopropane-1,1-dicarboxylate (I) and 1-benzoyl-1,2,2,-trimethylcyclopropane (II) failed. Attempted deuterium exchange with I, II, V and IX using sodium amide gave very low exchanges. These results are interpreted as indicating that transmission of electronic effects by the cyclopropane ring to methyl groups beta to electron-withdrawing groups is small in the transition state for carbanion formation.

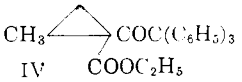
This paper describes attempts to chemically detect the transmission of conjugative effects to methyl groups by the cyclopropane ring.[2]

Our first effort to determine if there is transmission of electronic effects to contiguous methyl groups was the prosaic attempt to effect reactions typical of "active methyl" groups. Diethyl 2-methylcyclopropane-1,1-dicarboxylate (I) and 1-benzoyl-1,2,2-trimethylcyclopropane (II), neither of which has α-hydrogen atoms, were synthesized for this purpose. The reactions attempted were acylation with diethyl oxalate and benzoyl chloride, alkylation with alkyl halides and cyanoethylation. Sodium amide, sodium hydride, triphenylmethylsodium and potassium *t*-butoxide were employed as bases. The results of a number of these attempts are summarized in Table I. From 45 to 80% of the starting cyclopropanes were recovered,[3] none of the expected reaction products could be isolated and, with the exception discussed later, the cyclopropanes appeared to be essentially inert to the bases. For example, ketone II required 24 hours of refluxing with triphenylmethylsodium to change the color from blood-red to orange, only traces of ammonia were evolved on treatment with sodium amide and none of the anticipated reaction products could be isolated. These negative experiments are not very satisfying because small amounts of product may have escaped isolation.[4] However, the fact that glyoxylations at the γ-carbon of α,β-unsaturated esters, ketones and nitriles under comparable or less drastic conditions readily give products in 80–90% yields[5] and our own experience with conventional cases of these reactions lead us to believe that the formation of the expected products in appreciable quantity would have been detected.

The residue obtained from the attempted alkylation of I with methyl chloromethyl ether and triphenylmethylsodium (expt. 9) was refluxed with sodium hydroxide. Triphenylacetic acid (15% based on triphenylmethylsodium) was isolated. A possible source of the acid is cleavage by hydroxide ion of compounds III and/or IV formed by reaction of triphenylmethylsodium with the carbethoxyl groups of I. Support for this assumption is found



III



IV

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[1] Taken from the Ph.D. Theses of Popkin Shenian (1955) and Arthur A. Santilli (1958). This work was supported in part by the Office of Ordnance Research, U. S. Army, and a grant from the University of Massachusetts Teachers' Research Fund.

[2] For an excellent summary of the status of the problem of transmission of conjugation by the cyclopropane ring and leading references see E. N. Trachtenberg and G. Odian, THIS JOURNAL, **80**, 4018 (1958).

[3] Triphenylmethylsodium was used in all reactions in which the cyclopropane recovery was less than 65% and large residues remained. The low recoveries were due at least in part to difficulty in separating triphenylmethane from the reaction mixtures.

[4] A further criticism of this approach made by a referee is that "even if products were isolated in all cases showing that reactions other than those of the active methyl type had occurred, one is then in the unfortunate position of not knowing whether the active methyl type reaction has been shielded from view by the incurrence of some faster process."

[5] A. Lapworth, *J. Chem. Soc.*, **79**, 1276 (1901); W. Borsche and R. Manteuffel, *Ber.*, **65B**, 868 (1932); W. Borsche and R. Manteuffel, *Ann.*, **512**, 97 (1934); R. C. Fuson, R. E. Christ and G. M. Whitman, THIS JOURNAL, **58**, 2450 (1936); R. E. Christ and R. C. Fuson, *ibid.*, **59**, 893 (1937).