Hydrogenation of I to *cis*- and *trans*-1,3-Dimethylcyclohexane.—A solution of 2.6 g. of I in 60 ml. of glacial acetic acid containing 0.3 g. of platinum oxide catalyst was shaken in a hydrogenation apparatus at room temperature and 40 lb./sq. in. hydrogen pressure. The reaction appeared to be complete after 1.25 hours. The resulting mixture was filtered and the filtrate was cooled to −80°. Excess 20% sodium hydroxide solution was added to the partially solid mixture. Petroleum ether was added and the organic layer was separated, washed with water and dried over magnesium sulfate. The petroleum ether was removed by distillation and the remaining liquid was distilled to obtain 1.6 g. of colorless liquid, b.p. 58° (97 mm.), $n^{25}\mathrm{D}$ 1.4173–1.4208, that was identified as a mixture of *cis*- and *trans*-1,3-dimethylcyclohexane by comparison of the infrared spectrum with those of authentic *cis*- and *trans*-1,3-dimethylcyclohexane.

Thermal Stability of I.—Compound I (4.8 g.) containing 0.1 g. of phenothiazine was refluxed under nitrogen at an oil-bath temperature of 145–150° for 6.5 hours. Distillation gave 3.2 g. (66%) of I. The product remaining in the distillation flask set to a glass-like material.

Silver Nitrate Complex of I.—The reaction of I with finely ground silver nitrate in ethanol yielded white crystals, m.p. 77–79° (sealed capillary, bath preheated to 70°). The complex was light sensitive. 3,5-Dimethylenecyclohexene was recovered by dissolving the complex in deaerated water and adding ammonium hydroxide until the silver oxide that initially separated had redissolved.

Isomerization of 3,5-Dimethylene-1(and 2)-methylcyclohexene (III).—Compound III was isomerized in chloroform solution with *p*-toluenesulfonic acid monohydrate catalyst. The product obtained, b.p. 83° (53 mm.), $n^{25}\mathrm{D}$ 1.4951–1.4975, was shown by infrared analysis to be principally 1,3,5-trimethylbenzene containing a small amount of 1,2,4-trimethylbenzene. The literature values are: 1,3,5-trimethylbenzene, b.p. 164°, $n^{25}\mathrm{D}$ 1.4967; 1,2,4-trimethylbenzene, b.p. 169°, $n^{25}\mathrm{D}$ 1.5025.[6]

Isomerization of 3,5-Dimethylene-1(and/or 2)phenylcyclohexene (IV).—Compound IV was heated in a solution of chloroform containing a small amount of *p*-toluenesulfonic acid monohydrate. Distillation yielded an aromatic product, b.p. 75° (0.11 mm.), $n^{25}\mathrm{D}$ 1.5930. The infrared and proton magnetic resonance spectra indicated the liquid to be a mixture of dimethylbiphenyls.

Preparation of 3,5- and 3,6-Dimethylenecyclohexene.—In two separate experiments a total of 160 g. (4 moles) of allene was treated with approximately 6.35 moles of acetylene at 80–85° and autogenous pressure in the presence of 10 g. of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst and 400 ml. of benzene. The combined product (634 g.) was distilled through a short column to separate it from the catalyst, and the distillate was redistilled through a packed column. There was obtained 91.5 g. of colorless liquid, b.p. 91° (200 mm.) to 69.5–70° (87 mm.), $n^{25}\mathrm{D}$ 1.5289–1.5300. A fraction, b.p. 75° (104 mm.), $n^{25}\mathrm{D}$ 1.5281, was analyzed.

Anal. Calcd. for C_8H_{10}: C, 90.50; H, 9.50. Found: C, 90.89; H, 9.61.

The infrared spectrum of this product was quite similar to that of I, but the proton magnetic resonance spectrum was considerably different. The components of the mixture were separated by vapor-phase chromatography using a column packed with Celite saturated with silver nitrate at room temperature. The column was heated to 75° and helium was used as the carrier gas. The first fraction, which comprised 42% of the mixture, was identified as 3,6-dimethylenecyclohexene on the basis of spectral analyses. The proton magnetic resonance spectrum was in agreement with the proposed structure and the ultraviolet spectrum showed $\lambda_{\max}$ 273 mμ (ϵ 20,150), 262.5 mμ (ϵ 28,000) and 254 mμ (ϵ 23,800). These data are in agreement with recently reported values[3] for this compound. The infrared spectrum showed absorption at 3.25 and 3.3 (=CH), 3.45 and 3.5 (CH), 6.15, 6.45 and 6.65 (conjugated C=C) and 11.2 μ (=CH_2).

The retention time and infrared spectrum for the second component (57%) were the same as those of authentic I. A third component, which was present in approximately 1% concentration, was not identified.

An analysis of the entire reaction product from a similar preparation indicated the presence of 57.5% of the 3,6-isomer and 41.5% of the 3,5-isomer. Similarly, the product obtained from the reaction of allene with acetylene at atmospheric pressure in the presence of bis-(triphenyl phosphite)-nickel dicarbonyl catalyst contained 40.5% of the 3,6-isomer and 57.4% of the 3,5-isomer.

Isomerization of these products with 10% palladium-on-charcoal catalyst gave a mixture of *m*- and *p*-xylene.

The triene mixture was separated by use of vapor-phase chromatography.[7] A 1.6 cm. × 183 cm. copper tube was packed with 4-methyl-4-nitroheptanedinitrile on fire brick and heated to 100°. Helium was used as the carrier gas at about 500 ml./min. for 2.5-ml. samples of the triene mixture. The 3,6-isomer was obtained in a pure state as shown by spectral and gas chromatographic analyses, b.p. 75° (100 mm.), $n^{25}\mathrm{D}$ 1.5419.[3]

Acknowledgments.—The authors gratefully acknowledge the determination and interpretation of infrared and ultraviolet absorption spectra by Miss N. E. Schlichter and Mr. C. B. Matthews, and of the n.m.r. spectra by Dr. H. Foster and Dr. W. D. Phillips.

[7] We are indebted to Dr. B. C. Anderson for this study.

WILMINGTON 98, DELA.

[CONTRIBUTION NO. 503 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Chemistry of Allene. III. Chemistry of 3,5-Dimethylenecyclohexene

BY R. E. BENSON, R. V. LINDSEY, JR., AND B. C. ANDERSON

RECEIVED OCTOBER 29, 1958

The chemistry of 3,5-dimethylenecyclohexene, which is readily accessible from allene and acetylene, has been studied. Reactions with electrophilic and nucleophilic reagents have led to the formation of aromatic derivatives, whereas reactions proceeding *via* free-radical processes have yielded non-aromatic structures.

The synthesis of 3,5-dimethylenecyclohexene (I) in 45% yield from allene and acetylene was reported previously.[1] This unusual triene was found to isomerize readily to *m*-xylene with *p*-toluenesulfonic acid, potassium *t*-butoxide or palladium-on-carbon catalysts. It was, however, quite stable thermally in the absence of oxygen. Further studies of I are now reported.

Reactions of the triene with electrophilic, nucleophilic and free-radical reagents have been examined. Most of the reactions appear to proceed by attack of the reagent at the exocyclic conjugated methylene group. With the exception of free radical-type reactions, the ultimate products were aromatic derivatives.

The triene I was extremely sensitive to air and reacted with oxygen at 0–5° in the absence of added catalyst to yield a viscous, polymeric peroxide. The

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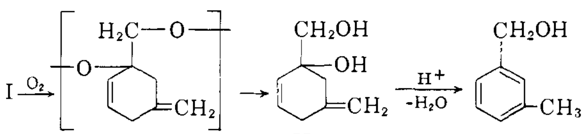
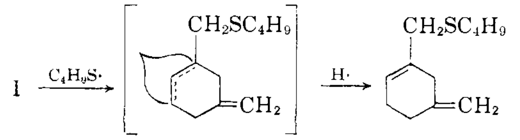
[1] R. E. Benson and R. V. Lindsey, Jr., THIS JOURNAL, **81**, 4250 (1959).

infrared absorption spectrum of this product indicated that 1,2-addition of oxygen had occurred at the conjugated exocyclic methylene group. Reduction of the peroxide with lithium aluminum hydride yielded a glycol, presumably II. Treatment of II with *p*-toluenesulfonic acid in chloroform brought about dehydration and rearrangement to *m*-methylbenzyl alcohol.

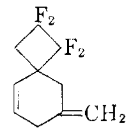


II

1-Butanethiol reacted slowly with I in the presence of ultraviolet light to give a low conversion to a 1:1 adduct identified as 2-butylthiomethyl-4-methylenecyclohexene by elemental and spectral analyses, including proton magnetic resonance. The intensity of the hydrogen attached to unsaturated carbon of the ring indicated that isomerization of the double bond had occurred. The same product was obtained in low conversion by use of benzoyl peroxide catalyst. Spectral examination of the fractions containing I recovered from these reactions failed to show the presence of *m*-xylene, thus indicating the stability of I under these conditions.



Condensation of I with tetrafluoroethylene at 150° gave a 1:1 adduct and higher-boiling products. The monoadduct, formed in 47% yield, was identified as 4-methylene-7,7,8,8-tetrafluorospiro[3.5]nonene (III) on the basis of elemental and spectral analyses.

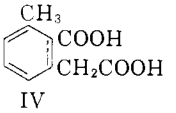


III

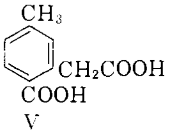
3,5-Dimethylenecyclohexene (I) reacted with bromine in carbon tetrachloride in the presence of sodium bicarbonate at room temperature to give a 70% yield of α,α'-dibromo-*m*-xylene and an 11% yield of α-bromo-*m*-xylene. In the absence of sodium bicarbonate, the yield of the monobromo derivative was increased at the expense of the dibromo compound.

Despite the facile acid-catalyzed isomerization to *m*-xylene, addition of I to a sulfuric acid–tetrahydrofuran solution containing formaldehyde gave β-(*m*-tolyl)-ethanol in 36% yield. This reaction presumably involved initial reaction of the $[CH_2OH]^+$ species with the conjugated exomethylene group.

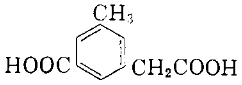
Reaction of I with two moles of butyllithium in ether gave a yellow solid that was converted to an acid salt with carbon dioxide. Acidification and recrystallization gave a white solid, m.p. 173.5–175°, that was characterized as an aromatic dibasic acid by elemental and spectral analyses and by neutralization equivalent. The proton magnetic resonance spectrum of the disodium salt of the acid, determined in heavy water, showed a ratio of aromatic protons to methyl protons to α-methylene protons of 3:3:2. The combined data prescribe a trisubstituted benzene derivative containing methyl, carboxy and carboxymethyl substituents. If it is assumed that 1,3-orientation of the methylene groups of I is preserved in the formation of the acid, only four isomer possibilities exist.



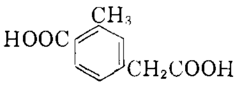
IV



V



VI

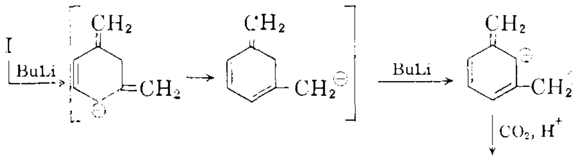


VII

Of these acids, only VII appears to have been reported, m.p. 198.5–199.5°.[2]

An attempt to convert the unknown acid to a tricarboxylic acid derivative by oxidation with alkaline potassium permanganate yielded isophthalic acid. This suggested that the unknown compound might be *m*-phenylenediacetic acid, m.p. 171–172°,[3] despite spectral evidence to the contrary. Comparison of the infrared absorption spectrum of the unknown with that of authentic *m*-phenylenediacetic acid eliminated this possibility.

The acid was converted to the dimethyl ester with diazomethane. The infrared absorption spectrum of this product showed weak bands at 5.12 and 5.40 μ, characteristic of 1,2,3-trisubstituted benzene derivatives. On the basis of this evidence, the acid is assigned structure IV. The formation of this product from I can be accounted for by the reaction scheme



IV

Experimental

Reaction of 3,5-Dimethylenecyclohexene (I) with Bromine.—A mixture of 10 g. (0.0944 mole) of I, 150 ml. of carbon tetrachloride and 40 g. of sodium bicarbonate was stirred and cooled in an ice-bath. Approximately two-thirds of a solution of 47 g. (0.294 mole) of bromine in 80 ml. of carbon tetrachloride was added dropwise until a slight bromine color persisted after 25 minutes. The mixture was filtered and the filtrate was heated on a steam-bath to remove the solvent. Distillation through a 4-inch Vigreux column gave 1.9 g. of α-bromo-*m*-xylene (11% yield) and 17.6 g. of oil that solidified in the receiver, b.p. 120–130° (2.5 mm.). There was 1.5 g. of residue in the distillation flask. Recrystallization of the solid from *n*-heptane gave α,α'-dibromo-*m*-xylene as white needles, m.p.

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[2] K. von Auwers and W. Julicher, *Ber.*, **55B**, 2167 (1922).

[3] A. A. Morton, E. L. Little, Jr., and W. O. Strong, Jr., This Journal, **65**, 1339 (1943).

75–76°, mixed melting point with authentic α,α'-dibromo-*m*-xylene, 75–76°. The yield of the crude dibromo compound was 71%.

When the reaction of bromine with I in carbon tetrachloride at room temperature was conducted in the absence of sodium bicarbonate, a lower yield of bromine-containing products was obtained, and the ratio of mono- to dibromo-*m*-xylene was higher. Presumably, the hydrogen bromide formed in the reaction catalyzed the isomerization of I to *m*-xylene. Under similar conditions, no reaction resulted when bromine was added to *m*-xylene.

Reaction of I with Oxygen.—Triene I (33 ml.) was placed in a 15-mm. o.d. tube cooled by circulating water at wet-ice temperature. A fine stream of oxygen was passed through the liquid for 2.5 days in the absence of light. At the end of this time, two layers had formed; the upper layer comprised approximately 20% of the mixture. A small amount of the lower, viscous layer was removed for analysis. The peroxide content was determined potentiometrically with arsenous acid and iodine.[4] The crude product was 47.2% peroxide, assuming it to have a composition of $(C_8H_{10}O)_x$. The product reacted readily with bromine in carbon tetrachloride. Infrared analysis of a similar sample indicated the presence of an exocyclic methylene group (11.25 μ) and of ring unsaturation (6.0 μ). The absence of conjugated double bond absorption indicated attack of oxygen at the 3-position of 3,5-dimethylenecyclohexene.

For reduction of the peroxide, a 4-necked, 3-l. flask was flushed with nitrogen and 300 ml. of dry ether and 23 g. of lithium aluminum hydride (0.62 mole) was added. A solution of the peroxide (47.2% peroxide, approximately 0.15 mole) in 200 ml. of dioxane was added dropwise. A precipitate formed immediately and the addition was conducted over 1.5 hours to give a gray mixture that was stirred overnight.

The resulting mixture was decomposed with ethyl acetate, and aqueous sodium hydroxide was added. The aqueous layer was extracted continuously with ether for 18 hours. The ether layer was separated, dried, and the ether and dioxane were removed by distillation. The remaining product was distilled through a small vapor-bath still to give 3.5 g. of product, b.p. 100–138° (0.2 mm.). The main fraction gave a 1,2-glycol test with periodic acid and reacted readily with bromine in carbon tetrachloride to give a pink solution.

A small amount of the glycol was heated with *p*-toluenesulfonic acid monohydrate in chloroform and the product was isolated by distillation. The infrared spectrum of this product is identical to that of an authentic sample of *m*-methylbenzyl alcohol. Presumably, this alcohol was formed by dehydration and rearrangement of the glycol.

Reaction of I with 1-Butanethiol.—A mixture of 16.7 g. (0.161 mole) of I and 34 ml. (29.2 g., 0.325 mole) of 1-butanethiol was flushed with nitrogen and sealed in a Pyrex brand glass tube. The tube was rotated while being irradiated with an ultraviolet lamp for 4 days. The tube was opened and the liquid was distilled. Approximately 29 ml. of 1-butanethiol and more than 8 g. of I was recovered. In addition, there was obtained 3.5 g. of colorless liquid, b.p. 78–79° (0.9 mm.), $n^{25}\text{D}$ 1.5124, and 2.4 g. of viscous residue remained in the distillation flask. The distillate was identified as 2-butylthiomethyl-4-methylenecyclohexene on the basis of analytical data and infrared and proton magnetic resonance studies.

Anal. Calcd. for $C_{12}H_{20}S$: C, 73.40; H, 10.27; S, 16.23. Found: C, 73.23; H, 10.32; S, 16.24.

Infrared analysis of the fraction containing recovered I failed to detect the presence of *m*-xylene.

Benzoyl peroxide was also examined as a catalyst for this reaction. A solution of 9.7 g. (0.0915 mole) of I, 21 ml. (0.2 mole) of 1-butanethiol and 1 g. of benzoyl peroxide in 100 ml. of dry *t*-butyl alcohol was refluxed under nitrogen for 18 hours. The resulting solution was poured into water, extracted with petroleum ether, and phenothiazine was added. Distillation gave an approximate 10% conversion to 2-butylthiomethyl-4-methylenecyclohexene, b.p. 70° (0.2 mm.), $n^{25}\text{D}$ 1.5135. About two-thirds of I was recovered. Infrared analysis of this fraction failed to detect the presence of *m*-xylene.

4-Methylene-7,7,8,8-tetrafluorospiro[3.5]nonene (III).—A Carius tube was charged with 10.6 g. (0.01 mole) of I and 24 g. (0.24 mole) of tetrafluoroethylene. The tube was sealed and heated for 12 hours at 150°. The colorless reaction product was distilled to give 9.65 g. (47% yield) of colorless liquid, b.p. 68–78° (23 mm.). Redistillation gave pure III, b.p. 68° (23 mm.), $n^{25}\text{D}$ 1.4264.

Anal. Calcd. for $C_{10}H_{10}F_4$: C, 58.25; H, 4.89; F, 36.86. Found: C, 58.71; H, 5.04; F, 39.36.

The infrared spectrum showed absorption at 3.25 (=CH), 3.4 and 3.5 (—CH), 6.03 (C=C), 7–9 (CF) and 11.13 μ (terminal methylene).

β-(*m*-Tolyl)-ethanol.—A mixture of 55 g. of pure tetrahydrofuran, 8.0 g. of 96% sulfuric acid and 7.5 g. (0.25 mole) of paraformaldehyde was stirred and cooled to 0°. Triene I (10.6 g., 0.01 mole) was added dropwise during 0.5 hour. The ice-bath was removed and at 20–25° an exothermic reaction occurred causing the reaction mixture to warm spontaneously to 45°. The reaction mixture was stirred for 16 hours and poured onto excess ice and water. The product was extracted with ether. The ether extracts were dried with magnesium sulfate and potassium carbonate and the residue was distilled through a small column. There was obtained 4.89 g. (36% yield) of β-(*m*-tolyl)-ethanol, b.p. 68–75° (0.25 mm.), n^{25}_{D} 1.5260–1.5263, lit.[5] b.p. 115–118° (10 mm.). The infrared spectrum was in accord with the proposed structure.

The product was treated with phenyl isocyanate to give β-(*m*-tolyl)-ethylphenylurethan, m.p. 61–62° after recrystallization from hexane, lit.[5] m.p. 59–60°.

Anal. Calcd. for $C_{16}H_{17}NO_2$: C, 75.27; H, 6.71; N, 5.49. Found: C, 75.53; H, 6.93; N, 5.50, 5.58.

Unknown Acid IV.—A 500-ml., four-necked flask was fitted with a nitrogen inlet tube, stirrer, thermometer, and a wide-mouth funnel. Dry ether (200 ml.) and lithium wire (about 3.0 g.) were placed in the flask and cooled to 5°. Then 30.0 g. (0.22 mole) of *n*-butyl bromide was added to the cooled, stirred solution during 30 minutes. The mixture was stirred for 0.5 hour and allowed to warm to 10°. It was filtered through a glass wool plug into a dropping funnel and added dropwise to 10.6 g. (0.1 mole) of I in 100 ml. of dry ether cooled to −10°. The solution soon turned red-orange and after about 0.5 hour a yellow solid began to separate. The mixture was heated to reflux and maintained at that temperature for 3 hours. The mixture was cooled and poured onto 200 g. of solid carbon dioxide in 50 ml. of ether. The resulting mixture was allowed to stand until the excess carbon dioxide had evaporated, then 200 ml. of water was added and the ether was separated. The water solution was acidified with cold concentrated hydrochloric acid and the acid solution was extracted with three 300-ml. portions of ether. The extracts were combined, dried with magnesium sulfate, and the ether was distilled. The residue was a pasty mixture which was crystallized from ethyl acetate to yield 6.0 g. of IV. Recrystallization of IV from ethyl acetate–cyclohexane gave white needles, m.p. 173.5–175°. The infrared spectrum indicated the product to be an aromatic acid.

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19; neut. equiv., 97. Found: C, 62.12; H, 5.40; neut. equiv., 98, 99.

The nuclear magnetic resonance spectrum of the anhydrous disodium salt was determined in deuterium oxide. The spectrum was in accord with that expected for 2-carboxy-3-methylphenylacetic acid, with three separate peaks corresponding to aromatic protons, methyl protons and α-methylene protons and having an area corresponding to 3:3:2, respectively.

Dimethyl Ester of Unknown Acid.—The unknown acid, 1.80 g., was mixed with 25 ml. of anhydrous ether and a solution of diazomethane in ether was added until the yellow color of diazomethane persisted. The ether solution was washed with saturated sodium bicarbonate solution, iced dilute sulfuric acid, and water and dried with magnesium sulfate. The product was distilled through a semimicro column affording 1.2 g. of the diester. A center cut had b.p. 103–104° (0.15 mm.) and $n^{25}\text{D}$ 1.5073.

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(4) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 102.

(5) M. T. Bogert and D. M. Apfelbaum, THIS JOURNAL, **60**, 932 (1938).

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.86; 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.[5] 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.

[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

RECEIVED FEBRUARY 5, 1959

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)).