From the reaction of the cation with cyanide a 5% yield of α-phenylcinnamaldehyde also was recovered, but no other product could be detected.

pK_{R^+} Determinations.—Standard spectrophotometric methods were used for the pK determinations, both for the Hammett indicators used to establish acidity functions in our media and for the cyclopropenyl cation derivatives. The spectra of solutions of the cation did not change appreciably in the time periods of less than an hour used in the measurements, and isosbestic points at 300 and 313 mμ were observed (*cf.* Fig. 1), which indicated that there was no problem with insolubility.

[CONTRIBUTION FROM THE ORGANIC CHEMICAL RESEARCH SECTION, LEDERLE LABORATORIES DIVISION, AMERICAN CYANAMID CO., PEARL RIVER, N. Y.]

Unsaturated Cyclopropanes. III.[1] Synthesis and Properties of Alkylidenecyclopropanes and Spiropentanes

BY EDWIN F. ULLMAN AND WILLIAM J. FANSHAWE

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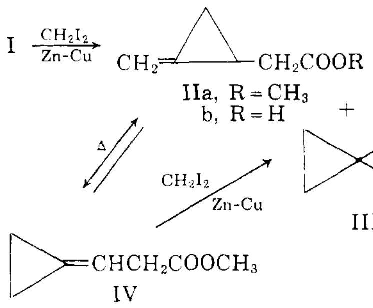
A method is described for the conversion of allenes to alkylidenecyclopropanes and thence to spiropentanes with methylene iodide–zinc–copper couple. Some reactions of these compounds are discussed.

The recent discovery of a simple general method for the synthesis of cyclopropanes from olefins with methylene iodide-zinc-copper couple[2] presents the possibility that heretofore difficulty obtainable unsaturated cyclopropanes may now be prepared from suitable multiply-unsaturated precursors. Indeed, the synthesis of sterculic acid from stearolic acid[3] has already demonstrated the practicability of the method as applied to the synthesis of cyclopropenes. We now wish to report the successful use of this reagent for the synthesis of alkylidenecyclopropanes and spiropentanes.

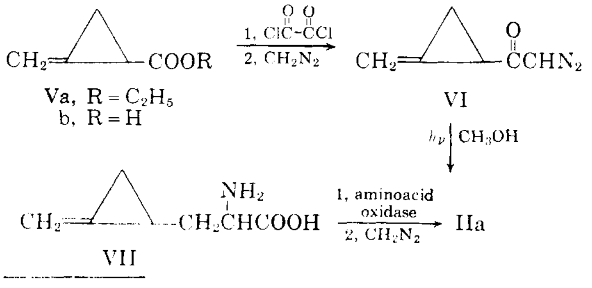
Aside from the classical preparation of spiropentane from pentaerythrityl tetrabromide[4] and the formation of chlorospiropentane by photochlorination of the hydrocarbon,[5] the only other synthesis of this system appears to be the recently reported reaction of 7,7-dibromonorcarane with an alkyllithium and an olefin.[6,6a] The use of an allene in the Simmons–Smith cyclopropane synthesis appeared to afford a simple route to this system. Methyl 3,4-pentadienoate[7] (I) was chosen for initial study.

$$CH_2{=}C{=}CHCH_2COOCH_3$$
I

When Compound I was treated with an eightfold excess of methylene iodide and zinc-copper couple, two products were isolated by vapor-phase chromatography in roughly equal amounts along with a little of the unreacted allene. The faster moving component was found to have intense terminal methylene absorption in the infrared at 11.15 μ which, together with its nuclear magnetic resonance spectrum (see Experimental) and combustion analysis, provided strong support for its formulation as IIa. The second chromatographic peak was a saturated compound with spectral characteristics not inconsistent with the spiropentane III. By increasing the reagent to allene ratio to 10:1 the ratio of III to IIa increased to about 4.5:1. Unexpectedly, no methyl β-cyclopropylidenepropionate (IV) could be detected in the reaction mixture even though it was subsequently found that IIa, III and IV were readily separable by vapor-phase chromatography.



Chemical evidence for structure IIa was provided by an independent synthesis from ethyl methylenecyclopropanecarboxylate (Va)[8] which, after hydrolysis to the corresponding acid Vb, was subjected to the Arndt–Eistert sequence.



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[1] For papers I and II of this series see (a) E. F. Ullman, *J. Am. Chem. Soc.*, **81**, 5386 (1959); (b) **82**, 505 (1960).

[2] H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958); **81**, 4256 (1959).

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

[4] (a) Gustavson, *J. prakt. Chem.*, [2] **54**, 97 (1896). For additional references see (b) D. E. Applequist, G. F. Fanta and B. W. Henrikson, *J. Org. Chem.*, **23**, 1715 (1958).

[5] D. E. Applequist, G. F. Fanta and B. W. Henrikson, *J. Am. Chem. Soc.*, **82**, 2368 (1960).

[6] W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).

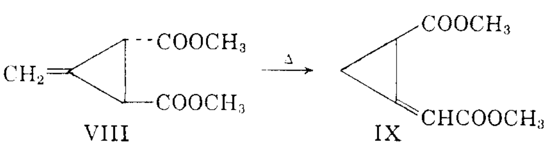
[6a] NOTE ADDED IN PROOF.—Recently a second communication on the formation of spiropentanes from cyclopropyl carbenes has appeared; W. M. Jones, *J. Am. Chem. Soc.*, **82**, 6200 (1960). In addition, D. E. Applequist and G. F. Fanta, *ibid.*, **82**, 6393 (1960), have recently reported some transformations of chlorospiropentane leading to spiropentane derivatives.

[7] *Cf.* E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.*, 3201 (1954).

[8] (a) J. A. Carbon, W. B. Martin and L. R. Swett, *J. Am. Chem. Soc.*, **80**, 1002 (1958); (b) U. S. Patent 2,956,077. We wish to thank Dr. Carbon for providing us with details of the preparation of ethyl 2-bromo-2-methylcyclopropanecarboxylate.

The resulting ester and IIa proved to be identical with each other and with the methyl ester of an enzymatic degradation product of hypoglycin A (VII) which had been assigned structure IIb.[9]

Pyrolysis of methyl methylenecyclopropaneacetate (IIa) in benzene solution at 210° failed to effect a detectable change, in contrast to the rapid rearrangement of Feist's ester VIII to give IX under these conditions.[1] However, an increase in temperature to 250° for 1.5 hours provided nearly quantitatively a two-component mixture which could be resolved by vapor-phase chromatography into the starting ester IIa and an isomer lacking the strong terminal methylene infrared absorption of IIa. The isomer appeared to be methyl cyclopropylidenepropionate (IV) on the basis of the Feist's ester analogy and the nuclear magnetic resonance spectrum which showed signals at 4.15 (C=CH—multiplet), 6.37 (OCH_3), 6.90 (=CH_2-CO doublet, J = 7.0 c.p.s., showing additional fine structure due to interactions with the ring protons), and 8.95 (ring protons, weakly split multiplet).[10] Further support for IV as well as for the spiropentane III was obtained by conversion of IV to III with the methylene iodide-zinc-copper couple reagent.

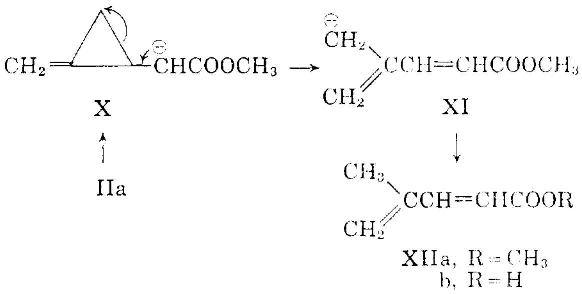


VIII IX

The pyrolytic conversion of methyl methylenecyclopropaneacetate (IIa) to methyl cyclopropylidenepropionate (IV) is noteworthy in that it represents the only example of this type of rearrangement other than the Feist's ester pyrolysis (VIII→IX) and thus demonstrates the lack of dependence of the reaction on electronegative groups attached to the cyclopropane ring. By comparison to the Feist's ester reaction in which an equilibrium product–starting material ratio of roughly 94:6 obtains[1b] due to the added conjugation of the double bond in IX, an equilibrium ratio of about 58:42 was observed in the present case, a result which is in accord with the expected small increase in stability of the pyrolysis product IV over IIa due to the additional double bond substituent.[11]

Pyrolytic rearrangements were also attempted on ethyl methylenecyclopropanecarboxylate (Va) and dimethyl methylenecyclopropane-1,1-dicarboxylate,[1a] but unlike the previous examples the reactions led to mixtures of products with formation of much tarry material. Similar conditions were without apparent effect on the spiropentane III.

A study of the effects of alkaline reagents on II, III and IV was suggested by the observation, during an attempted Wolff rearrangement of the diazoketone VI with silver oxide in methanol, that a complex mixture of products was obtained including IIa and a doubly unsaturated ester having strong ultraviolet absorption at 250 mμ. The structure of the latter was shown to be methyl 4-methyl-2,4-pentadienoate (XIIa) by comparison with an authentic sample prepared from the previously reported 4-methyl-2,4-pentadienoic acid[12] (XIIb). The formation of the unsaturated ester XIIa in this reaction proved to be the result of alkaline attack on the initially formed methyl methylenecyclopropaneacetate (IIa) as shown by the observation that the same product was formed when IIa was treated with sodium hydride in cyclohexane containing a little methanol. Although the transformation represents a not unknown reaction of cyclopropylcarbinyl anions,[1a, 13,14] this example is of some interest in that it requires the conversion of a strongly carbonyl-stabilized anion X to the less stabilized allylic anion XI, the increase in energy apparently being offset by the considerable relief of strain resulting from ring scission.[15] In contrast, when alkaline cleavage of methyl spiropentaneacetate (III) was attempted, the relief of strain was apparently in-



X XI IIa

XIIa, R = CH$_3$
b, R = H

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[9] E. C. De Renzo, K. W. McKerns, H. H. Bird, W. P. Cekleniak, B. Coulomb and E. Kaleita, *Biochem. Pharm.*, **1**, 236 (1958). We wish to thank Dr. De Renzo for supplying a sample of the hypoglycin A degradation product.

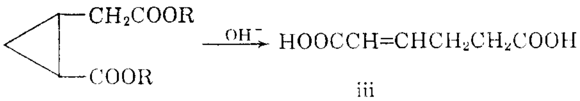
[10] Nuclear magnetic resonance spectra were taken using CCl_4 as solvent with tetramethylsilane as an internal standard. Chemical shifts are recorded in τ-values; G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[11] Compare the difference of only 0.5 kcal./mole in the heats of hydrogenation of *trans*-CH_3CH=$CHCH_2COOR$ and CH_3CH=CH_2; R. W. Taft, Jr., and M. M. Kreevoy, *J. Am. Chem. Soc.*, **79**, 4011 (1957).

[12] T. Lennartz, *Ber.*, **76B**, 1006 (1943)

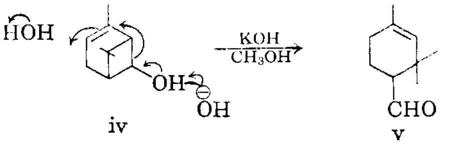
[13] (a) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951); (b) M. S. Silver, P. R. Shafer, J. E. Nordlander, C. Rüchardt and J. D. Roberts, *ibid.*, **82**, 2647 (1960).

[14] A recently observed example of a cyclopropylcarbinyl anion rearrangement is the facile ring opening of i during an attempted saponification. We are indebted to Dr. L. Crombie for identifying the product of this reaction as *trans-α*-dihydromuconic acid (iii) rather than the erroneously reported cyclic acid ii (see ref. 1a).



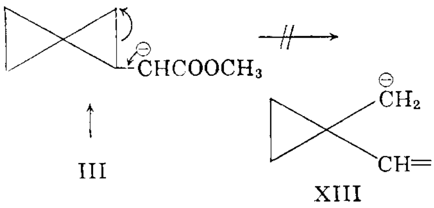
i, R = CH$_3$
ii, R = H
iii

[15] Recently a related ring cleavage reaction (iv → v) which may also involve an allylic carbanion has been observed; J. J. Hurst and G. H. Whitham, *J. Chem. Soc.*, 2864 (1960). The authors imply that ring scission of iv may occur with simultaneous protonation of the double bond, a mechanism that cannot be rigorously excluded in the present case. However it is noteworthy that when homogeneous conditions were used (sodium methoxide in methanol) almost no cleavage of IIa was observed.

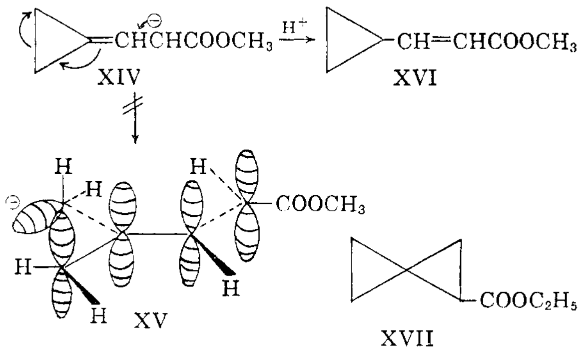


iv v

sufficient to balance the large increase in energy necessary to form the requisite non-resonance stabilized carbanion XIII, and no reaction occurred.



Not unexpectedly, similar alkaline treatment of methyl cyclopropylidenepropionate (IV) also failed to produce ring cleavage. Unlike the intermediate anion X in the alkaline ring cleavage of methyl methylenecyclopropaneacetate (IIa), the anion XIV that would be initially formed from methyl cyclopropylidenepropionate (IV) may be unable to rearrange by reason of (a) its inability to assume a geometry suitable for backside attack of the free electron pair on a ring methylene carbon atom; and (b) the instability of the incipient carbanion XV in which the charge-bearing carbon atom not only lacks effective *resonance* stabilization due to its unfavorable stereochemistry, as is also the case in the reaction X → XI, but also can receive little *inductive* stabilization from the only partially formed γ,δ-double bond. The only product formed in the reaction was the isomeric methyl β-cyclopropylacrylate (XVI), identified by comparison with an authentic sample.[16]



Several preliminary attempts have been made to apply the Simmons–Smith cyclopropane synthesis to the preparation of other spiropentanes, although with only limited success. With Feist's ester VIII the reaction leads to several difficultly separable products and with dimethyl methylenecyclopropane-1,1-dicarboxyoate[1a] the products were mostly polymeric. However, ethyl methylenecyclopropanecarboxylate (Va) smoothly provided the expected ethyl spiropentanecarboxylate (XVII).

Experimental[17]

Methyl 3,4-Pentadienoate (I).—An ether solution of 11.9 g. of 3,4-pentadienoic acid[7] was added to excess ethereal diazomethane and the mixture allowed to stand at room temperature for 1 hour. The excess reagent and ether were evaporated and the remaining liquid distilled to give 8.9 g. (67%) of the ester, b.p. 44–46° (15 mm.), n^{25}_D 1.4519. The compound showed typical terminal allene absorption at 5.10 and 11.63 μ.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.04; H, 7.20.

Reaction of Methyl 3,4-Pentadienoate (I) with Methylene Iodide–Zinc–Copper Couple.—A mixture of 5.2 g. (0.08 mole) of zinc–copper couple,[18] 19.3 g. (0.072 mole) of methylene iodide, 0.09 g. of iodine and 15 ml. of ether was refluxed with stirring for 30 minutes, and a solution of 1.01 g. (0.009 mole) of methyl 3,4-pentadienoate in 2 ml. of ether was then added to it. Refluxing and stirring were continued for 48 hours after which the reaction mixture was cooled, filtered, and washed successively with several portions each of dilute hydrochloric acid, dilute ammonium hydroxide and water. After drying over sodium sulfate, the resulting ether solution was concentrated and vapor-phase chromatographed. Two peaks having about equal areas were observed after 13 and 24 minutes, respectively. The faster moving component, methyl methylenecyclopropaneacetate, showed terminal methylene absorption in the infrared at 11.15 μ. Its ultraviolet spectrum showed only end absorption and its n.m.r. spectrum[10] showed multiplets at 4.70 ($C{=}CH_2$), 7.83 ($-CH_2COO-$) and 8.20–9.45 (ring protons) which was completely consistent with structure IIa.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 67.08; H, 8.36.

The slower moving peak, methyl spiropentaneacetate (III), showed no terminal methylene absorption in the infrared. The n.m.r. spectrum[10] was in accord with the proposed structure, showing multiplets at 7.80 ($-CH_2COO-$) and 8.22–9.62 (ring protons).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.10; H, 8.82.

When the above reaction was repeated using a 10:1 ratio of methylene iodide–zinc–copper couple to allene the ratio of spiropentane to methylenecyclopropane increased to about 4.5:1.

In both of these reactions the over-all yields of the isolated products amounted to only about 35% because of considerable losses during chromatography. Observed losses of about 50% of mixtures of known compounds on the vapor-phase chromatography instrument that was used suggest that the actual yields in the cyclopropane synthesis are about 70%.

Ethyl 2-Bromo-2-methylcyclopropanecarboxylate.[8]—A solution of 164 g. (1.44 moles) of ethyl diazoacetate in 200 ml. of 2-bromopropene was added over an 8-hour period to a stirred refluxing mixture of 200 ml. of 2-bromopropene, 1.8 g. of freshly ignited anhydrous copper sulfate and 0.5 g. of copper–bronze powder (purchased from The Belmont Smelting Works, Brooklyn, N. Y.). The mixture was heated for a total of 9 hours, allowed to stand at room temperature overnight, and then filtered. The filtrate was distilled at atmospheric pressure to remove excess 2-bromopropene and then at 19 mm. to give 45 g. of a colorless liquid, b.p. 80–100°, and a second fraction containing mostly diethyl fumarate, b.p. 100–106°. The first fraction was treated in the cold with excess aqueous potassium permanganate (22 g.) and the resulting mixture filtered. The filtrate and filter cake were extracted with ether and the extracts dried over sodium sulfate, concentrated to a small volume and distilled; b.p. 65–88°, 28.1 g. An additional 5.3 g. of product was obtained by permanganate treatment and redistillation of the 100–106° boiling fraction; total yield 11%.

Anal. Calcd. for $C_7H_{11}BrO_2$: C, 40.60; H, 5.32; Br, 38.61. Found: C, 40.82; H, 5.08; Br, 38.93.

Ethyl Methylenecyclopropanecarboxylate (Va).[8]—To a refluxing mixture of 10.0 g. (0.048 mole) of ethyl 2-bromo-2-methylcyclopropanecarboxylate and 8.7 g. (0.18 mole) of sodium hydride (49.6% oil suspension) in 125 ml. of ether was added approximately 1 ml. of ethanol. The mixture

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[16] *Cf.* L. I. Smith and E. R. Rogier, *J. Am. Chem. Soc.*, **73**, 3831, 4047 (1951).

[17] Chloroform and methanol were used as solvents for the infrared and ultraviolet spectra, respectively. Vapor-phase chromatographic separations were carried out using a 5-foot silicon GE-SF 96 column purchased from Wilkens Instrument and Research, Inc. A flow rate of 30 ml. of helium per minute and a temperature of 110° were used unless otherwise noted.

[18] R. S. Shank and H. Schechter, *J. Org. Chem.*, **24**, 1825 (1959).

was vigorously stirred under nitrogen for 3.75 hours and the excess hydride decomposed with glacial acetic acid in ether. Water was then added and the aqueous layer extracted with ether. The combined ether solutions were washed with aqueous sodium bicarbonate, dried over sodium sulfate and concentrated to a small volume. Distillation of the concentrate gave 3.1 g. (51%) of a colorless liquid, b.p. 150–153° (atm.).

Methylenecyclopropanecarboxylic Acid (Vb).—A solution of 3.4 g. (0.027 mole) of ethyl methylenecyclopropanecarboxylate (Va) in 96 ml. of 5% aqueous potassium hydroxide was refluxed for 7 minutes, cooled, and washed with ether. The aqueous solution was acidified and extracted with ether and the resulting extracts dried over sodium sulfate. Removal of the solvent and distillation of the product gave 1.5 g. (58%) of the acid, b.p. 94–98° (22 mm.); $\lambda\lambda_{max}$ 5.84μ(COOH), 11.05μ (=CH$_2$).

Anal. Calcd. for $C_5H_6O_2$: C, 61.21; H, 6.17. Found: C, 60.70; H, 6.54.

Diazoacetylmethylenecyclopropane (VI).—A solution of 8.2 g. (0.084 mole) of methylenecyclopropanecarboxylic acid (Vb) in 54 g. (0.43 mole) of oxalyl chloride was refluxed for 2 hours, concentrated at atmospheric pressure, and finally distilled at 30 mm. to give 8.3 g. (85%) of the acid chloride, b.p. 47–48°. A solution of this product in ether was added to 0.2 mole of ethereal diazomethane and the mixture allowed to stand at room temperature for 30 minutes. The ether and excess reagent were removed with a stream of nitrogen and the residual diazoketone (10 g.) used directly in the following reactions.

Wolff Rearrangement of Diazoacetylmethylenecyclopropane (VI). A.—A solution of 10 g. of the above crude diazoacetylmethylenecyclopropane (VI) in 160 ml. of methanol was irradiated in two batches in a water-cooled quartz apparatus with an Hanovia 100 watt ultraviolet lamp. After nitrogen evolution had ceased (about 22 hours per batch), the combined solutions were concentrated to a small volume and the remaining liquid distilled to give 4.2 g. (40% over-all yield from methylenecyclopropanecarboxylic acid, Vb) of methyl methylenecyclopropaneacetate (IIa), b.p. 60–65° (25 mm.), n^{25}D 1.4450. The compound was found to be identical by infrared and vapor-phase chromatography both to the more volatile component obtained from methylene iodide–zinc–copper couple treatment of methyl 3,4-pentadienoate (I), and also to the methyl ester of an hypoglycin A (VII) degradation product obtained by treatment of the amino acid with a snake venom L-amino acid oxidase preparation[9] followed by diazomethane esterification of the resulting acid IIb.

B.—A slurry of 3 g. of freshly precipitated silver oxide in methanol was added with stirring to a solution of 1.3 g. of crude diazoacetylmethylenecyclopropane (VI) in 15 ml. of methanol at 50°. The mixture was refluxed for 3 hours at which point nitrogen evolution had greatly decreased. An additional quantity of silver oxide was added and refluxing continued for another 3 hours. The cooled, filtered solution was then diluted with 250 ml. of water and extracted with several portions of ether. The combined extracts were dried over sodium sulfate and concentrated to a small volume. Vapor-phase chromatography of the concentrate demonstrated the presence of at least five components, one of which was the desired methyl methylenecyclopropaneacetate (IIa). The only other component positively identified was methyl 4-methyl-2,4-pentadienoate (Xa) which was identified by comparison with an authentic sample (*vide infra*).

C.—To an aqueous suspension of 3 g. of sodium carbonate, 1.8 g. of sodium thiosulfate and 1.2 g. of silver oxide kept at 58–62° was added dropwise with stirring over 30 minutes a solution of 5.2 g. of crude diazoacetylmethylenecyclopropane in 33 ml. of dioxane. After the addition was complete, the temperature of the mixture was increased to 85° and stirring continued for 1 hour. The resulting solution was cooled, filtered, acidified with dilute sulfuric acid, and extracted with ether. The extracts were dried over sodium sulfate and the solvent evaporated. The remaining liquid was distilled to give 0.8 g. (16% over-all yield from methylenecyclopropanecarboxylic acid, Vb) of methylenecyclopropaneacetic acid (IIb), b.p. 85–90° (20 mm.). An analytical sample of this compound was prepared by vapor-phase chromatography at 132°.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.02; H, 7.41.

Treatment of the acid IIb with excess diazomethane gave methyl methylenecyclopropaneacetate (IIa) which was identical to an authentic sample.

Pyrolysis of Methyl Methylenecyclopropaneacetate (IIa).—A solution of 0.046 g. of methyl methylenecyclopropaneacetate (IIa) in 1.4 ml. of dry benzene was heated in a sealed tube at 250° for 90 minutes. The resulting pale brown solution was concentrated to a small volume and the residue separated by vapor-phase chromatography. Two peaks were observed at 13 and 20 minutes, respectively. A total of 0.014 g. of the slower moving component, methyl cyclopropylidenepropionate (IV), and 0.010 g. of the more volatile starting material were collected. The product had no terminal methylene absorption in the infrared and only end absorption in the ultraviolet.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.38; H, 7.79.

When the reaction time was increased to 2 hours the product–starting material ratio remained unchanged. Although the total recovery of the two compounds ranged in several experiments from only 35–53%, little or no non-volatile material was formed in the reaction, and the recoveries were found to be of similar magnitude to those obtained from synthetic mixtures from the particular column used.

Pyrolysis of methyl spiropentaneacetate (III) under the same conditions failed to produce any change.

Methyl Spiropentaneacetate (III) from Methyl Cyclopropylidenepropionate (IV).—A mixture of 1.135 g. (0.0042 mole) of methylene iodide, 0.31 g. (0.0047 mole) of zinc–copper couple, 1.5 ml. of ether and a trace of iodine were stirred at reflux for 30 minutes and a solution of 0.033 g. (0.00026 mole) of methyl cyclopropylidenepropionate (IV) in 0.05 g. of benzene was added to it. The mixture was refluxed with stirring for an additional 6 hours and then stirred at room temperature for 64 hours. The solution resulting from dilution of the reaction mixture with ether was filtered, washed successively with several portions each of dilute hydrochloric acid and dilute ammonium hydroxide, filtered through sodium sulfate and concentrated. The concentrate showed a single vapor-phase chromatography peak that had an identical retention time and infrared spectrum to that of methyl spiropentaneacetate (III).

Reaction of Methyl Methylenecyclopropaneacetate (IIa) with Alkali.—To a suspension of 0.143 g. (0.006 mole) of sodium hydride, 1.5 ml. of cyclohexane and 0.093 g. (0.0007 mole) of methyl methylenecyclopropaneacetate (IIa) was added 0.15 ml. of methanol. The mixture was refluxed under nitrogen with stirring for 9 minutes and then poured into a mixture of 1 *N* hydrochloric acid and ether. The aqueous layer was extracted twice with ether and the combined ether solutions washed successively with dilute sodium carbonate and water, dried over sodium sulfate and concentrated to a small volume. Vapor-phase chromatography of the concentrate gave two peaks at 13 and 16 minutes, respectively. A total of 0.020 g. of starting material (13-min. peak) and 0.003 g. of product (16-min. peak) was collected. A substantial amount of non-volatile polymeric material was formed in the reaction.

Spectral comparisons demonstrated the identity of the product with the presumed methyl 4-methyl-2,4-pentadienoate (XIIa) obtained from the attempted Wolff rearrangement of diazoacetylmethylenecyclopropane (VI) using a silver oxide catalyst, and with authentic XIIa prepared by diazomethane esterification of 4-methyl-2,4-pentadienoic acid.[12] The compound showed infrared maxima in the double bond region at 5.85, 6.13 and 6.21 μ and an ultraviolet maximum at 250 mμ (ϵ 21,400), n^{23}D 1.4848, b.p. 64° (18 mm.), m.p. −23.5° to −21.0.

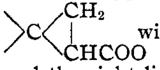
Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.49; H, 7.87.

When alkaline cleavage of methyl methylenecyclopropaneacetate (IIa) was attempted with sodium methoxide in methanol or cyclohexane only a trace of the unsaturated ester could be detected by ultraviolet spectroscopy even after 4.5 hours of heating. Only starting material and polymer were isolated from the reaction mixture.

Reaction of Methyl Cyclopropylidenepropionate (IV) with Alkali.—To a solution of 0.013 g. (0.0001 mole) of methylcyclopropylidenepropionate (IV) in 0.5 ml. of cyclohexane was added 0.022 g. (0.0009 mole) of sodium hydride followed by 0.05 ml. of methanol. The mixture was refluxed under nitrogen with stirring for 45 minutes. The resulting mixture was poured into cold 1 *N* hydrochloric acid and the aqueous solution extracted with ether. The combined organic layers were washed successively with dilute sodium carbonate and water, dried over sodium sulfate and evaporated to a small volume. The concentrate was vapor-phase chromatographed at 108°. A single peak appeared after 25 minutes. The infrared and ultraviolet spectra of the chromatographed product were identical to those of an authentic sample of methyl β-cyclopropylacrylate (XVI) prepared from the previously reported β-cyclopropylacrylic acid[16] with diazomethane; b.p. 76° (19 mm.), $n^{24}D$ 1.4777, λ_{max} 230.5 mμ (ε 16,600).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 67.05; H, 8.29.

Attempted Ring Cleavage of Methyl Spiropentaneacetate (III).—In contrast to the two preceding experiments, when methyl spiropentaneacetate (III) was refluxed with sodium hydride in cyclohexane or with sodium methoxide in methanol no ultraviolet chromophore appeared. Vapor-phase chromatography showed the compound to be largely unchanged.

Ethyl Spiropentanecarboxylate (XVII).—A stirred mixture of 10.5 g. (0.16 mole) of zinc–copper couple, 42.9 g. (0.16 mole) of methylene iodide, several crystals of iodine and 75 ml. of ether was heated at reflux for 30 minutes and 2.0 g. (0.016 mole) of ethyl 2-methylenecyclopropanecarboxylate in 5 ml. of ether was then added over a 5-minute period. After 24 hours the mixture was cooled, filtered and washed successively with several portions each of dilute hydrochloric acid, dilute ammonium hydroxide and water. The solution was then dried over sodium sulfate, concentrated to a small volume, and vapor-phase chromatographed. Two major peaks were obtained at 13 minutes (starting material) and 24 minutes (ethyl spiropentanecarboxylate, XIX), respectively. The structure of the latter was confirmed by its n.m.r. spectrum[10] which showed a typical 12 line ABX pattern[19] from the grouping  with the α-proton quartet centered at 7.98 and the eight lines from the methylene protons centered at 8.63. The protons of the unsubstituted ring showed a single peak at 9.05.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.96; H, 8.68.

A total yield of 0.42 g. (19%) of the chromotographed spiropentane was obtained. However, substantial losses occurred during chromatography (*vide supra*).

Acknowledgments.—We wish to thank Dr. S. R. Safir for helpful discussions during the course of this work and Dr. J. E. Lancaster for the determination and aid in interpretation of the n.m.r. spectra.

[19] J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 138.

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Addition of Iodine Halides to Fluorinated Olefins. II. The Addition of Iodine Monofluoride to Halogenated Olefins

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An excellent method for the addition of iodine monofluoride (considered to be formed "*in situ*") to perfluoro- and perfluorochloroölefins is described. The most effective source of iodine monofluoride was the system iodine and iodine pentafluoride ($2I_2 + IF_5 \rightarrow 5IF$) in the presence of a catalyst. The novel iodides CF_3CFICF_3, CF_3CFClI, CF_3CCl_2I, CF_3CHClI and CF_3CHFI were formed by the addition of iodine monofluoride to $CF_2{=}CFCF_3$, $CF_2{=}CFCl$, $CF_2{=}CCl_2$, $CF_2{=}CHCl$ and $CF_2{=}CHF$, respectively. The addition of iodine monofluoride to tetrafluoroethylene, preferably in the presence of a small amount of the "inhibitor" CF_2ClCCl_2I, to give a high yield of CF_3CF_2I is described. The iodides $CF_2ClCFClI$ and CF_3CH_2I were formed in the reactions of iodine and iodine pentafluoride with $CFCl{=}CFCl$ and $CF_2{=}CH_2$, respectively.

This paper relates to a novel and excellent method for adding iodine monofluoride to halogenated olefins.[1] A mixture of iodine and iodine pentafluoride in a molar ratio of 2:1 or slightly greater (preferably preheated usually to temperatures of 100–175° and in the presence of a catalyst) has been found to be an effective source of iodine monofluoride.

$$2I_2 + IF_5 \longrightarrow 5IF$$

It has been demonstrated that if perhaloölefins containing a terminal $=CF_2$ group are allowed to react with the above mixture high yields of the corresponding iodine fluoride adducts are obtained. Examples of such olefins include the perfluoroolefins $CF_2{=}CF_2$, $CF_2{=}CFCF_3$ and the perfluorochloroölefins $CF_2{=}CFCl$ and $CF_2{=}CCl_2$. Other olefins including $CFCl{=}CFCl$, $CF_2{=}CHCl$, $CF_2{=}CHF$ and $CH_2{=}CF_2$ have given low to moderate yields of the IF adduct.

The addition of iodine monofluoride to $CF_2{=}CCl_2$ was studied most extensively. This reaction represents the best route to the reactive iodide CF_3CCl_2I previously isolated as a rearrangement product from the reaction of ICl with $CF_2{=}CFCl$ in the presence of aluminum chloride.[2]

The initial reactions which were carried out at 20–25° using undistilled iodine pentafluoride (poured directly from a storage cylinder) gave conversions of 24 to 48% to mixtures of isomers containing about 90% of CF_3CCl_2I[2] and 10% of $CFCl_2CF_2I$.[2] The results were unsatisfactory when carefully distilled iodine pentafluoride was used and a search for catalysts for this reaction was then made. Aluminum iodide, aluminum chloride and aluminum fluoride were not effective catalysts when used alone. When aluminum wire containing 0.1% iron was used as the catalyst only a 6% conversion to a mixture of isomers containing 70% CF_3CCl_2I and 30% $CFCl_2CF_2I$ was obtained. Thus iron appeared to be detrimental not only in lowering the isomer content of

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[1] It should be noted that very recently A. Bowers, L. C. Ibanez, E. Denot and R. Becerra, *J. Am. Chem. Soc.*, **82**, 4001 (1960), reported the addition of an iodine and a fluorine atom across the double bonds of cyclohexene and unsaturated steroids by use of N-iodosuccinimide (a source of electrophilic iodine) and hydrogen fluoride in the presence of ether or tetrahydrofuran.

[2] Paper I, this series M. Hauptschein, M. Braid and A. H. Fainberg, *ibid.* **83**, June 5, (1961).