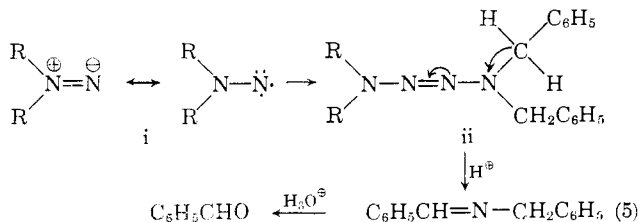


mmoles of difluoroamine as described above. Ethylene was isolated in 80% yield. Similar treatment of azetidine¹⁷ gave cyclopropane in 40% yield. Dibenzylamine (30 mmoles) reacted with difluoroamine (4.4 mmoles) under similar conditions giving N₂ (3.5 mmoles) as the only gaseous product. Bibenzyl, m.p. 50–51° (uncor.), identified by its infrared spectrum, was isolated in 53% yield by extracting the semi-solid residue with ether, removing unconverted amine with aqueous hydrochloric acid solution, and chromatographing over silica gel. Benzaldehyde was also obtained as a by-product.¹⁸

N-Cyclopropylmethyl-*p*-toluenesulfonamide (V) was prepared from 4.0 g. of cyclopropylcarbonylamine,¹⁹ 10.8 g. of *p*-toluenesulfonyl chloride and 25 ml. of pyridine by the general procedure outlined by Vogel.²⁰

(17) W. R. Vaughan, R. S. Klonowski, R. S. McElhinney and B. B. Millward, *J. Org. Chem.*, **26**, 138 (1961).

(18) This aldehyde probably arises by the sequence shown in eq. 5, R = benzyl. Dimerization of intermediate i could produce tetrazene ii which



would be expected to undergo decomposition during acid work-up. Formation of tetrazene ii could also account for the failure to observe quantitative N₂ evolution. See G. G. Overberger, *Rec. Chem. Progr. (Kresge-Hooker Sci. Lib.)*, **21**, 40 (1960), and W. R. McBride and H. W. Kruse, *J. Am. Chem. Soc.*, **79**, 572 (1957).

(19) J. D. Roberts and R. M. Mazur, *ibid.*, **73**, 2509 (1951).

N-Cyclopropylmethyl-*p*-toluenesulfonamide was obtained in 76% yield, m.p. 57–58° (uncor.)

Anal. Calcd. for C₁₁H₁₅NSO₂: C, 58.64; H, 6.71; N, 6.22. Found: C, 59.05; H, 6.95; N, 6.20.

Decomposition of N-Cyclopropylmethyl-*p*-toluenesulfonamide with Hydroxylamine-O-sulfonic Acid.—The general procedure described by Nickon and Sinz³ was followed with the exception that a gas trap, cooled in liquid nitrogen and protected by drying tubes, was connected to the exit end of the reflux condenser. After completion of the reaction, which was conducted with 2.25 g. of sulfonamide V and 28.3 g. of hydroxylamine-O-sulfonic acid (Eastman Kodak Co.), the contents of the gas trap were fractionated on a vacuum line, giving 0.8 mmole of butene-1, identified by its infrared and mass spectrum.

Reduction of N-Nitrosoazetidine.—N-Nitrosoazetidine¹³ was reduced with sodium hydrosulfite by the method described for reduction of N-nitrosodibenzylamine.¹⁴ Cyclopropane was identified in the escaping gases by its mass spectrum.

3,5,5-Trimethylpyrazoline and Difluoroamine.—Addition of 5 mmoles of difluoroamine to 2.24 g. (20 mmoles) of 3,5,5-trimethylpyrazoline¹⁶ in the manner described above for cyclopropylamine liberated 2.7 mmoles of N₂ and vacuum line fractionation yielded 2.1 mmoles of isobutylene and 0.7 mmole of acetonitrile, identified by their infrared and mass spectra. Only that acetonitrile in the gas phase was measured. According to the infrared spectrum, additional acetonitrile was present in the liquid fraction which collected in the Dry Ice-acetone trap.

Acknowledgments.—This investigation was supported by the Advanced Research Projects Agency under Army Ord. Contract DA-01-021 ORD-11909. We are grateful to Mr. Kirt Keller for technical assistance and to Dr. Grover Paulett for mass spectral analyses.

(20) A. I. Vogel, "Practical Organic Chemistry," second edition, Longmans, Green and Co., London, 1951, p. 625.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Carbenes from Alkyl Halides and Organolithium Compounds. V. Formation of Alkylcyclopropenes by Ring Closure of Alkenyl Substituted Carbenoid Intermediates^{1,2}

BY GERHARD L. CLOSS AND LISELOTTE E. CLOSS

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Reactions of 1,2-dimethylpropenyllithium and 2-methylpropenyllithium with methylene chloride give 1,3,3-trimethylcyclopropene and 3,3-dimethylcyclopropene, respectively. Product formation is conveniently accounted for in terms of a mechanism invoking alkenyl substituted intermediates. This hypothesis is strengthened by the observation that α -dehydrochlorination on 1-chloro-2,3-dimethyl-2-butene and α -debromination on 1,1-dibromo-2,3-dimethyl-2-butene with alkyllithium compounds give 1,3,3-trimethylcyclopropene, as well. Other possible mechanisms are discussed.

Introduction

The chemistry of alkylcarbenes has attracted considerable interest in recent years.³ Although rigorous proof for the intermediacy of free carbenes has not yet been brought forth in all cases, the following three reaction types are generally assumed to lead to alkyl substituted carbenoid species: (a) Photolysis or pyrolysis of diazoalkanes is probably the most versatile method for the formation of these intermediates. Frequently, the diazoalkane is produced *in situ* via the base-catalyzed decomposition of *p*-toluenesulfonylhydrazones of aldehydes and ketones in aprotic solvents.⁴ (b) Alkyl halides may be converted to carbenes through α -dehydrohalogenation with such strong bases as organoalkali metal compounds.^{5a-e} A preparative valuable

(1) Supported in part by a grant (NSF-G19927) from the National Science Foundation.

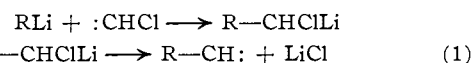
(2) Part of this work was reported in preliminary communications; G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **83**, 1003, 2015 (1961).

(3) For a recent review, see, W. Kirmse, *Angew. Chem.*, **73**, 161 (1961).

(4) J. W. Powell and M. C. Whiting, *Tetrahedron*, **7**, 305 (1959); L. Friedman and H. Shechter, *J. Am. Chem. Soc.*, **81**, 5512 (1959); **82**, 1002 (1960); **83**, 3159 (1961).

(5) (a) G. L. Closs and L. E. Closs, *ibid.*, **81**, 4996 (1959); **82**, 5723 (1960); (b) W. Kirmse and W. v. E. Doering, *Tetrahedron*, **11**, 266 (1960); W. v. E. Doering and W. Kirmse, *ibid.*, **11**, 272 (1960); (c) L. Friedman and J. G. Berger, *J. Am. Chem. Soc.*, **82**, 5758 (1960); **83**, 492, 500 (1961); (d) G. L. Closs and L. E. Closs, *Tetrahedron Letters*, **24**, 26 (1960); (e) P. S. Skell and A. P. Krapcho, *J. Am. Chem. Soc.*, **83**, 754 (1961).

variation of this method is the reaction of geminal polyhalides with organolithium compounds. Here one halogen atom, preferentially a bromine atom undergoes the halogen-metal exchange reaction while a remaining one serves as the anionic leaving group.^{6a,b} (c) Finally, the product distribution in the reaction of organolithium compounds with methylene chloride is conveniently interpreted by invoking alkylcarbenes as intermediates.⁷



In this reaction (sequence 1) the initially formed chloro-carbene can be thought to insert between the carbon-lithium bond of the lithium reagent to form the hypothetical α -chloroalkyllithium. The free carbene may then be formed by elimination of lithium chloride.⁸

Previous work carried out on the latter reaction led us to explore the possibilities of extending this scheme to the synthesis of carbenes with unsaturated substituents. Particularly, since alkenyllithium compounds are

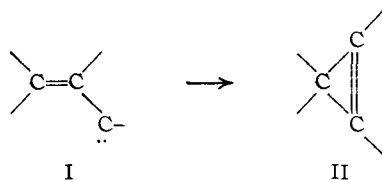
(6) (a) W. T. Miller, Jr., and C. S. Y. Kim, *ibid.*, **81**, 5008 (1959); (b) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960); W. R. Moore, H. R. Ward and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

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

(8) Although intermediacy of a free carbene explains the available data best, it has not been excluded that the α -chloroalkyllithium is the direct precursor of the resulting products⁷ (see also footnote 18).

readily available from the corresponding halides,⁹ this sequence (eq. 1, R = alkenyl) offers an attractive route to the hitherto undescribed alkenylcarbenes. In addition, extension of the remaining methods, successfully employed for the formation of alkylcarbenes and referred to above, appears potentially possible if suitable reactants could be found.

Alkenylcarbenes may be expected to undergo reactions in principle similar to those which lead from alkylcarbenes to stable products.³ In addition to rearrangements and intramolecular insertions, however, the possibility of cyclization to cyclopropenes is of special interest. This transformation (I → II) might be thought of as an intramolecular addition of the carbenoid carbon to the α,β -double bond. It was with this particular reaction in mind that the present investigation was initiated.



Results and Discussion

For reasons which will become apparent in the later part of the discussion the reaction of 1,2-dimethylpropenyllithium (III) with methylene chloride appeared to be well suited to test the hypothesis of cyclopropene formation in reactions possibly proceeding through the intermediacy of alkenylcarbenes. A solution of III in tetrahydrofuran was readily prepared from the corresponding bromide and lithium at -30° . Addition of methylene chloride at -30 to -40° followed by hydrolysis yielded besides 2-methyl-2-butene a hydrocarbon C_6H_{10} as major product.¹⁰ The structure of 1,3,3-trimethylcyclopropene (IV) was assigned to this compound on the basis of chemical and spectral evidence.

Confirmation of the carbon skeleton was obtained from catalytic hydrogenation yielding 1,1,2-trimethylcyclopropane (V) in good yield. The position of the double bond is evident from the nuclear magnetic resonance (n.m.r.) spectrum of the olefin. Two narrowly spaced doublets at 8.94 and 8.00 τ with line separations of 0.7 and 1.1 c.p.s. are assigned to the resonances of the *geminal* and allylic methyl protons, respectively. In addition, an only partially resolved symmetrical multiplet is centered at 3.35 τ . The integrated intensities of these line groups approach the ratios 6:3:1, in further support of structure IV. The observed spin-spin couplings between the vinyl and methyl protons are of the expected magnitude for spin interactions through four bonds in a partially unsaturated system.¹¹ Additional support for structure IV is given by the infrared spectrum which excludes the presence of an exocyclic double bond.¹² A medium-strong band at 1768 cm^{-1} is attributed to the carbon-carbon double bond stretching vibration.¹³

When the reaction was modified by attempting to distil directly from the solution the product without preceding hydrolysis no cyclopropene was obtained.

(9) E. A. Braude, "Progress in Organic Chemistry," Vol. 3, 1955, p. 172.

(10) An acetylenic hydrocarbon is formed as a by-product. Elucidation of its structure and mechanism of its formation will be discussed in a separate paper.

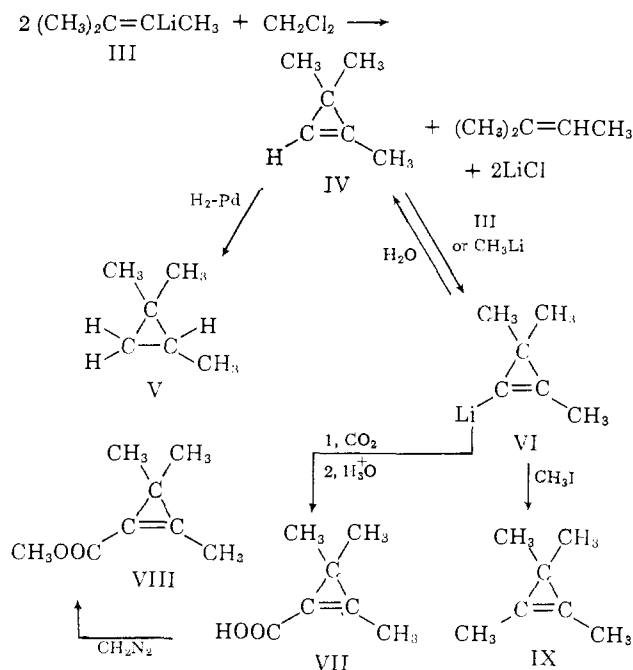
(11) For a discussion of "long range" coupling in unsaturated systems see: E. I. Snyder and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 1582 (1962), and references cited there.

(12) Methylene cyclopropane shows a carbon-carbon double bond stretching frequency of 1730 cm^{-1} ; K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

(13) The spectral properties of the cyclopropene derivatives will be discussed more fully in a separate publication.

However, the immediate liberation of IV upon addition of water to the distillation residue suggested that the cyclopropenyllithium compound VI might have been the ultimate product. The correctness of this speculation was readily confirmed by carbonation of the reaction mixture. Work-up for carboxylic acids afforded 2,3,3-trimethylcyclopropenecarboxylic acid (VII) in good yield. Diazomethane converted this moderately stable acid at -30° to the methyl ester VIII from which the acid could be regenerated by mild alkaline hydrolysis. Structures of both acid and ester are confirmed by their n.m.r. spectra which show the resonances of the *geminal* dimethyl (VII, 8.88 τ ; VIII, 8.98 τ) and allylic methyl (VII, 7.82 τ ; VIII, 7.93 τ) protons. In addition, the methoxy hydrogens in VIII and the carboxyl proton in VII give the expected signals (6.42 and $-2.28\text{ }\tau$). All lines have the proper relative intensities. The ultraviolet (VII, λ_{max} , hexane $237\text{ m}\mu$, ϵ 7,000; VIII, λ_{max} , hexane $226\text{ m}\mu$, ϵ 7,700) and infrared spectra (VII, C=C, 1685 ; C=C, 1835 cm^{-1} ; VIII, >C=O, 1700 ; >C=C<, 1840 cm^{-1}) further corroborate the structure assignment.¹³

Similarly, the addition of methyl iodide to the crude reaction mixture resulted in alkylation of the cyclopropenyllithium VI since tetramethylcyclopropene (IX) was isolated in good yield. The structure of this compound follows unambiguously from its elemental analysis and n.m.r. spectrum. Two sharp singlets of equal intensities at 9.01 and 8.10 τ arise from *geminal* dimethyl and allylic methyl protons, respectively.



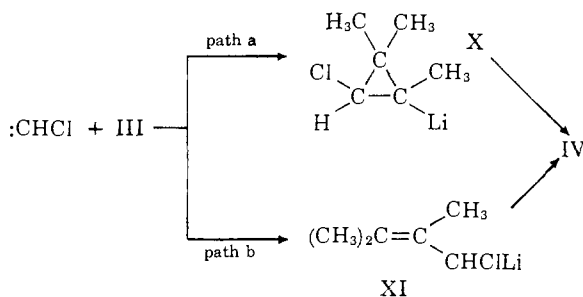
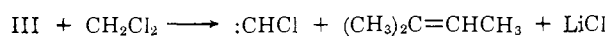
The fact that the cyclopropene is present in the reaction mixture as its lithium derivative VI is readily explained on the basis of the generally accepted theory of hybridization changes of the atomic orbitals with increasing "ring strain." Accordingly, one can expect a considerably larger degree of s-character of the atomic orbitals engaged in carbon-hydrogen bond formation than the classical structure indicates.¹⁴ Keeping in mind the correlation of degree of s-character with carbon hydrogen acidity,¹⁵ a rapid hydrogen-lithium interchange between the alkenyllithium III and cyclopropene IV appears to be quite likely.¹⁶ This assumption

(14) J. E. Kilpatrick and R. Spitzer, *J. Chem. Phys.*, **14**, 463 (1946); C. A. Coulson and W. E. Moffitt, *ibid.*, **15**, 151 (1947); A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(15) A. D. Walsh, *Disc. Faraday Soc.*, **2**, 118 (1947).

was readily verified by demonstrating that IV is indeed quantitatively converted by either III or methyllithium to its lithium derivative. Carbonation of the reaction mixture gave an excellent yield of the corresponding carboxylic acid VII.

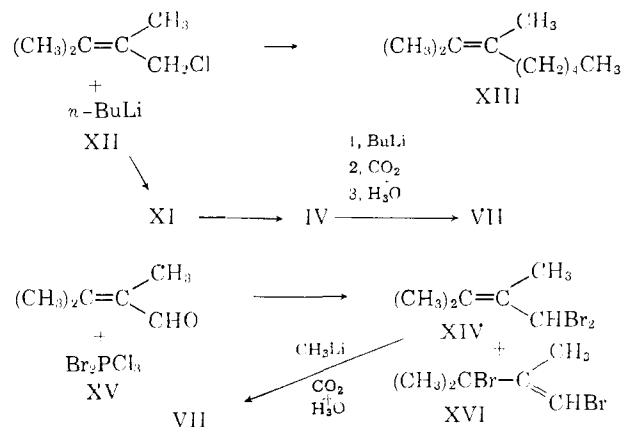
Once it had been established that a cyclopropene derivative is indeed the major product of the reaction of an alkenyllithium compound with methylene chloride, securing information pertaining to the reaction sequence of this novel synthesis became the goal of this investigation. Two possible pathways come immediately to mind. Both schemes are based upon the initial formation of chlorocarbene, a reasonable assumption in view of previous work on the reaction of alkyllithium with methylene chloride.^{5a} However, two different positions for attack of the electrophilic carbene on the lithium compound can be visualized. Reaction may either occur with the π -electrons of the double bond in III to yield the β -chloro-cyclopropyllithium X (path a) or, more likely, with the carbon-lithium bond (path b) as previously observed for the reaction of alkyllithium with chlorocarbene.⁷ Both resulting intermediates (X and XI, respectively) can be expected to yield the observed cyclopropene.



More weight could be lent to the hypothesis that XI might serve as precursor to the cyclopropene IV if the same or a similar intermediate could be generated by a different, more direct route. It was therefore attempted to effect hydrogen-lithium interchange on 2,3,3-trimethylallyl chloride (XII) with *n*-butyllithium. Carbonation of the reaction mixture produced besides 2,3-dimethyl-2-octen (XIII) a low yield of 2,3,3-trimethylcyclopropenecarboxylic acid (VII) indicating the initial formation of cyclopropene IV.

Halogen-metal interchange on 1,1-dibromo-2,3-dimethyl-2-butene (XIV) with an alkyllithium compound promised to be a more effective route to the bromo analog of XI. Reaction of 2,3-dimethylcroton aldehyde (XV) with phosphorus dibromotrichloride produced a modest yield of XIV. Unfortunately, as the n.m.r. spectrum revealed, 25% of the allylic isomer XVI was also present.¹⁷ Structures were assigned according to the infrared carbon-carbon double bond stretching frequencies, which were found at 1628 for XVI and 1677 cm^{-1} for XIV, respectively. Comparison of these frequencies with those of 1-bromo-2-methylpropene (1635 cm^{-1}) and 1-chloro-2,3-dimethyl-2-butene (XII) (1670 cm^{-1}) supports this choice as does the fact that the low field resonance (3.6 τ) of the n.m.r. spectrum of the minor isomer shows long range coupling (1.1 c.p.s.) to a methyl group. Reaction of this mixture with methyllithium at -30° followed by carboxylation gave 40% of the cyclopropenecarboxylic acid VII. Assuming that no allylic rearrangement occurred during

the reaction, the yield indicates that at least part of the cyclopropene must have been produced from the *geminal* dibromide.



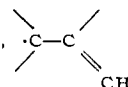
Cyclopropene formation *via* α -elimination from both XII and XIV strongly supports the original hypothesis that vinyl substituted carbenoid species may undergo ring closure by intramolecular "addition" to the double bond.

Ring closure of XI to a cyclopropene is sufficiently unusual to merit further discussion. Loss of lithium halide to give the free carbene XVII may be assumed to be the next step. It should be pointed out, however, that any transformation of the *free* carbene might undergo can in principle be formulated for its precursor XI as well. Usually free carbenes have been postulated in cases in which α -halolithium compounds are generated,¹⁸ but evidence for a distinct α -elimination of lithium halide resulting in a carbene as a true intermediate is rather circumstantial and has mostly relied upon unproved assumptions.¹⁹ But whether or not a free carbene is involved in the reaction under discussion, the apparent difficulty with visualizing ring closure is the necessity of rotation of the *geminal* dimethyl group through 90° around a bond with high degree of double bond character. Even in the free carbene resonance structures such as XVIII with a single bond between the β - and γ -carbon will contribute very little to the ground state of the molecule because of large charge separation.²⁰ On the other hand, it should be kept in mind that during the process of rotation (XIX \rightarrow XX) when overlap between the γ - and β -p-orbitals is diminishing, overlap of the former with the sp^2 doubly occupied orbital extending into the plane of the incipient ring will become increasingly important. This, and the fact that in the probably most stable electronic configuration of the carbene XIX the "empty" p-orbital at the α -carbon is geometrically favorably arranged to accommodate the π -electrons to form the new double bond, will substantially lower the energy of the transition state.²¹

(18) The difference between a free carbene mechanism and one in which the α -halolithium compound is assumed to be the reacting species bears a remarkable resemblance to the much better studied classification of nucleophilic displacement into $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ and eliminations into $\text{E}1$ and $\text{E}2$ mechanisms, respectively.

(19) The most widely quoted evidence for the intermediacy of free carbenes is the formation of products resulting from intramolecular insertions.^{18,17} However, the possibility that an α -halolithium compound may undergo this reaction as well can not be ruled out *a priori*.

(20) It is of course possible to invoke a diradical structure,

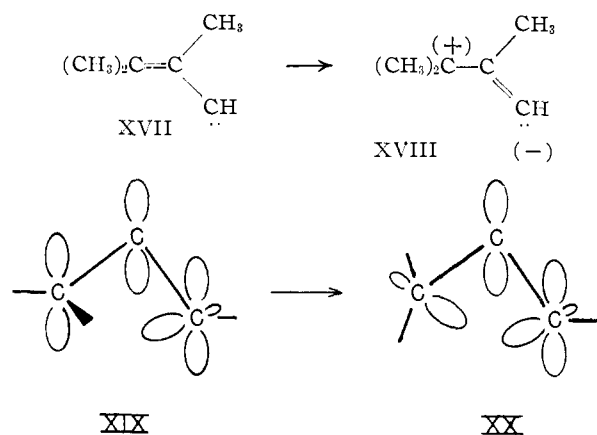


to circumvent this difficulty.

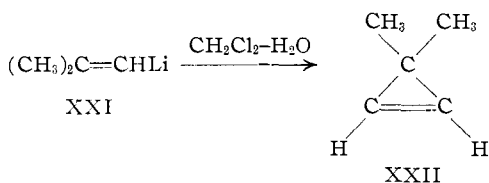
(21) This ring closure is the equivalent process to the one proposed by Cram and Hatch for the formation of 1-azirenes as intermediates in the Neber rearrangement; D. J. Cram and M. J. Hatch, *J. Am. Chem. Soc.*, **75**, 33, 38 (1953). Similarly, the recently discovered formation of azirenes from

(16) For deuterium exchange on a short-lived cyclopropene derivative see: K. B. Wiberg, R. K. Barnes and J. Albin, *J. Am. Chem. Soc.*, **79**, 4994 (1957).

(17) A similar rearrangement is known to occur in the reaction of acrolein with phosphorus pentabromide (F. Stitz, *Oesterr. Chem. Z.*, **48**, 186 (1947)).



These considerations lead to the conclusion that the presence of two methyl substituents at the γ -carbon will facilitate the reaction in two ways. First, with progressive rotation a decrease of π -electron density will take place at this carbon due to the formation of the new α,β -double bond. Alkyl substitution will of course favor this build-up of a partial positive charge. In addition, reduced non-bonded interactions in the transition state between the γ - and β -methyl groups will also lower the activation barrier. Consideration of these factors led us to choose this particular system for the initial study. That this choice was not a bad one became obvious when the reaction was extended to include 2-methylpropenyllithium (XXI). The expected 3,3-dimethylcyclopropene (XXII), the structure of which was conclusively established by catalytic hydrogenation to 1,1-dimethylcyclopropane, was formed in considerably poorer yield. The steric factor outlined above gives a reasonable explanation for this reduced efficiency of the ring closure.²²



In summary, it has been shown that all three methods usually employed for generating alkylcarbenes and based on α -elimination on halides, will give cyclopropenes when extended to suitable unsaturated systems. In another paper, to be published shortly, we will show that the fourth general method for producing carbenes, the decomposition of diazo compounds, yields cyclopropenes, as well, when extended to the appropriate diazoalkenes. These observations make it very likely that alkenylcarbenes or their immediate precursors are involved in these novel cyclopropene syntheses,²³ although direct proof of this hypothesis is still outstanding.

Experimental

All boiling points are uncorrected. N.m.r. spectra were recorded on a Varian V 4300-B spectrometer operating at 40 m.c. Infrared spectra were obtained on a Beckman IR-7. Reported frequencies supercede frequencies published in the preliminary communications² which were obtained on an inferior instrument. Ether and tetrahydrofuran were distilled from sodium immediately prior to use.

α,β -unsaturated azides by photolysis has been postulated to proceed through an equivalent intermediate; G. Smolinsky, *J. Am. Chem. Soc.*, **83**, 4483 (1961).

(22) One can expect that any factor reducing the rate of ring closure will have an adverse effect on the yield of cyclopropene, since the hypothetical intermediates XI can undergo a variety of side reactions.

(23) A study of the chemical and physical properties of the cyclopropenes here reported will be the subject of a separate paper.

1,2-Dimethylpropenyllithium.²⁴—A solution of 2-bromo-3-methyl-2-butene (75 g., 0.5 mole) in tetrahydrofuran (280 ml.) was slowly added to a suspension of finely cut lithium wire (10 g., 1.4 g. atoms) in tetrahydrofuran (80 ml.). The reaction was carried out under a protective atmosphere of argon (nitrogen gave a considerably poorer yield) and with magnetic stirring. The initial addition was begun at -20° and as soon as the lithium surface became shiny the reaction temperature was lowered to -30° . Total addition time was about 40 minutes. The solution was allowed to warm to -10° within 1 hour. The yield (50–60%) was determined by the double titration method by Gilman.

It should be mentioned that smooth reaction and good yields in this reaction depend on the purity of the bromide (b.p. 119.5°) and the quality of the lithium used. Certain batches of lithium wire (Lithium Corporation of America, Inc.) failed to give the reaction.

1,3,3-Trimethylcyclopropene.—A solution of 1,2-dimethylpropenyllithium (0.325 mole) in tetrahydrofuran (320 ml.) was prepared from 2-bromo-3-methyl-2-butene (86 g., 0.375 mole) and lithium wire (11 g., 1.57 g. atoms) as described above. The solution was separated from excess lithium wire by pushing it with argon or nitrogen through a thin tube into another three-neck flask. This flask was fitted with an addition funnel, a low-temperature thermometer and a distillation head with receiving flask (without condenser). The gas outlet of the distillation head served as nitrogen inlet. The solution was cooled to -45° and a solution of methylene chloride (9.2 g., 0.11 mole) in tetrahydrofuran (30 ml.) was added dropwise with magnetic stirring, keeping the temperature between -40 and -45° . A deep purple color developed during the addition. After addition was complete the solution was allowed to warm to -30° , the dropping funnel and the thermometer were replaced by stoppers and the receiving flask was immersed in liquid nitrogen. The nitrogen inlet was then connected with a vacuum line and about half (180 ml.) of the solvent distilled into the receiving flask at less than 1 mm. pressure. No bath was needed for the reaction flask. This operation removed most of the 2-methyl-2-butene. The distillation flask was then filled with nitrogen and cooled with Dry Ice-acetone. Ice-water (200 ml.) was added while the flask was shaken by hand. The temperature inside the flask was not allowed to exceed 10° .

Heptane (100 ml.) was added to the hydrolysis mixture and most of the tetrahydrofuran was washed out by washing three times with ice-water (400 ml. each time). During this operation the separatory funnel was cooled with ice.

The remaining hydrocarbon mixture was dried with sodium sulfate and fractionally distilled over an efficient Helipac column. The fraction boiling from 39 to 44° (6.0 g.) was collected. Infrared analysis showed this material to be 74% trimethylcyclopropene (0.055 mole, 50% based on methylene chloride as limiting reagent). Repeated distillation afforded pure material, b.p. 43.3° , n_D^{20} 1.3892. The compound is stable at room temperature for several months.

Anal. Calcd. for C_8H_{10} (82.14): C, 87.73; H, 12.27. Found: C, 87.67; H, 12.30.

Carboxylation of Reaction Mixture of 1,2-Dimethylpropenyllithium with Methylene Chloride.—1,2-Dimethylpropenyllithium (0.060 mole) in tetrahydrofuran (60 ml.) was prepared and separated from excess lithium wire as described above. The solution was cooled to -45° and methylene chloride (1.6 g., 0.019 mole) in tetrahydrofuran (5 ml.) was added under vigorous magnetic stirring keeping the temperature between -45 and -40° . The reaction flask was then removed from the cold bath and allowed to warm up to -30° and kept at this temperature for 10 minutes to complete the metalation. After cooling the mixture to -70° , a fast stream of dry carbon dioxide was bubbled through until the exothermic reaction subsided. The mixture was then poured onto ice-water (40 ml.) and extracted with ether. The ether layer was re-extracted with sodium bicarbonate solution and the combined aqueous layers were washed three times with small amounts of ether. The whole extraction process was carried out as rapidly as possible and the solutions were kept close to 0° . After addition of some ice the aqueous solution was acidified with 2 *N* sulfuric acid and twice extracted with ether. After drying over magnesium sulfate the ether was evaporated leaving the impure trimethylcyclopropenecarboxylic acid as a slightly brownish oil (3.2 g.; infrared analysis showed this material to be about 65% pure). The impure material polymerized rather rapidly at room temperature. Purification of the acid was accomplished through esterification and hydrolysis, as described below.

Methyl Trimethylcyclopropenecarboxylate.—The impure trimethylcyclopropenecarboxylic acid (3.0 g.) obtained as described above was dissolved in ether (20 ml.) and cooled to -25° . A solution of diazomethane (0.021 mole) in ether (30 ml.) was slowly added to the stirred solution keeping the temperature between -25 and -30° . The slight excess of diazomethane was removed with acetic acid.

(24) Compare E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 331 (1955).

Small amounts of unidentified basic material were removed by extraction with chilled 1 *N* sulfuric acid. After washing with saturated sodium chloride solution the ether phase was dried over magnesium sulfate. The solvent was distilled off and the residue was distilled at reduced pressure. The ester (1.40 g., 0.010 mole) was collected at 48.5–50.0° at 13 mm.

Saponification of Methyl Trimethylcyclopropenecarboxylate.—Methyl trimethylcyclopropenecarboxylate (0.568 g., 0.004 mole) was stirred with 0.2 *N* sodium hydroxide (24 ml.) at 10° for 30 minutes. During this time the solution had become homogeneous. Any remaining nonacidic material was removed by extraction with ether. The aqueous layer was acidified with 2 *N* sulfuric acid and extracted with ether. The extract was washed with saturated sodium chloride solution and dried with magnesium sulfate. The solvent was removed at reduced pressure whereupon the residue crystallized. Sublimation at 0.02 mm. gave pure trimethylcyclopropenecarboxylic acid (0.278 g., 0.0022 mole, 55%) melting at 48.5 to 49.0°.

Anal. Calcd. for C₇H₁₀O₂ (126.15): C, 66.64; H, 7.99. Found: C, 66.62; H, 8.04.

Methylation of the Reaction Mixture of 1,2-Dimethylpropenyllithium and Methylene Chloride.—A solution of 2,3,3-trimethylcyclopropenyllithium (0.30 mole in tetrahydrofuran (300 ml.) and methylene chloride (8.5 g., 0.10 mole) dissolved in tetrahydrofuran (30 ml.) at –40° as described above. About one-half (150 ml.) of the solvent was removed under reduced pressure (0.1 mm.) and low temperature (–30 to –50°). The remaining solution was then allowed to warm up to –10° and methyl iodide (14.2 g., 0.10 mole) was added dropwise. The resulting mixture was poured onto water (500 ml.) and the hydrocarbon component was extracted with paraffin oil (75 ml.). The oil layer was washed twice with ice-water (400 ml.) to remove all tetrahydrofuran. The volatile component of the extract was distilled from the paraffin oil at reduced pressure (0.01 mm.) at room temperature using a trap cooled with liquid nitrogen as a receiver. The distillate (8.6 g.) was fractionated over a 3-ft. column, collecting the fraction boiling at 66–67° (750 mm.). The material collected this way (5.50 g.) was shown by infrared analysis to be 90% pure (52% yield) tetramethylcyclopropene. Repeated fractionation gave pure material boiling at 67.0° (755 mm.), *n*_D²⁰ 1.4021.

Anal. Calcd. for C₇H₁₂ (96.17): C, 87.42; H, 12.58. Found: C, 87.43; H, 12.32.

Hydrogenation of 1,3,3-Trimethylcyclopropene.—1,3,3-Trimethylcyclopropene (0.82 g., 0.01 mole) was dissolved in ethanol (5 ml.) and hydrogenated using 5% palladium-on-charcoal (50 mg.) at 0°. Hydrogen uptake (0.013 mole) was complete within 10 minutes. Vapor phase chromatography of the filtered reaction mixture using a 12-ft. column of tricresyl phosphate on firebrick at 30° showed the presence of two major components in a three-to-one ratio. The major component was trapped from the v.p.c. in the conventional manner. The identity of this material with authentic 1,1,2-trimethylcyclopropane was established by comparison of infrared and n.m.r. spectra and v.p.c. retention times. The minor component having a shorter retention time was not identified.

Metalation of 1,3,3-Trimethylcyclopropene. (a) Using Methylithium in Ether.—Methylithium (0.024 mole) in ether (18 ml.) was placed under a protective atmosphere of nitrogen into a two-neck flask equipped with an efficient reflux condenser and nitrogen inlet tube. The solution was cooled to 0° and 1,3,3-trimethylcyclopropene (2.04 g., 0.023 mole) was added. The flask was then allowed to warm up to room temperature whereupon slow methane evolution was observable. After a period of 40 hours a sample was withdrawn and the n.m.r. spectrum recorded. Absence of the multiplet at 3.35 τ indicated the completeness of the reaction. The mixture was cooled to –70° and a rapid stream of dried carbon dioxide was bubbled through the solution. Work-up for the carboxylic acid was carried out as indicated in the description of the carboxylation above. The crude 2,3,3-trimethylcyclopropenecarboxylic acid (2.26 g., 0.018 mole, 78%) crystallized on chilling. Final purification was achieved by sublimation at 0.02 mm. and 40°, yielding 2.0 g. of acid melting at 48.5–49°. This method is recommended for the preparation of the acid.

(b) Using 1,2-Dimethylpropenyllithium in Tetrahydrofuran.—1,2-Dimethylpropenyllithium (0.020 mole) in tetrahydrofuran (25 ml.) was prepared as described above. The solution was cooled to –30° and 1,3,3-trimethylcyclopropene (1.65 g., 0.020 mole) was added. The solution was allowed to sit at –30 to –40° for 30 minutes. Carboxylation and work-up was carried out in the manner as described above yielding 2,3,3-trimethylcyclopropenecarboxylic acid (1.80 g., 0.014 mole, 72%) melting at 48°.

Reaction of 1-Chloro-2,3-dimethyl-2-butene with *n*-Butyllithium.—1-Chloro-2,3-dimethyl-2-butene²⁵ (11.8 g., 0.10 mole) was dissolved in ether (15 ml.). A solution of *n*-butyllithium (0.090 mole) in ether (65 ml.) was added at 5 to 10° under nitrogen within

1 hour. Lithium chloride precipitated during the addition. The addition of butyllithium was followed with the addition of methylithium²⁶ (0.040 mole) in ether (25 ml.) to complete the metalation. The reaction mixture was allowed to sit for 3 days and was then carboxylated in the manner as described above. The crude acidic material was shown by infrared analysis to contain 2,3,3-trimethylcyclopropenecarboxylic acid (0.006 mole, 6%).²⁷ By dissolving the crude oily material in pentane and cooling to –40° the acid was obtained crystalline. Sublimation at 40° (0.02 mm.) yielded pure acid (0.32 mole, 2.5%) melting at 47–48°.

The neutral material was fractionally distilled collecting the fraction boiling at 156–160° (5.44 g.). Redistillation yielded a fraction boiling at 158–159° (*n*_D²⁰ 1.4276). The n.m.r. spectrum showed an integrated intensity of 8.3 allylic methyl protons assuming 20 protons as a total; physical constants reported²⁸ for 2,3-dimethyl-2-octene: b.p. 158.4–158.8°, *n*_D²⁰ 1.4280.

2,3-Dimethylcrotonaldehyde.²⁹—1,2-Dimethylpropenyllithium (0.325 mole) in tetrahydrofuran (300 ml.) was added to a solution of *N*-methylformylanilide (47.2 g., 0.35 mole) in tetrahydrofuran (150 ml.) at –70 to –50°. Addition was carried out by pressing the solution of the lithium compound with nitrogen pressure in small portions into the reaction flask. The reaction mixture was allowed to warm up to 0° and was then poured onto 2 *N* hydrochloric acid (400 ml.) containing enough ice to keep the solution below 5°. The mixture was extracted twice with ether (150 ml. each). The combined ether extracts were washed with 2 *N* hydrochloric acid, sodium bicarbonate, water and saturated sodium chloride solution, and then dried over magnesium sulfate. The ether and most of the remaining tetrahydrofuran were distilled off over a small Vigreux column. The residue was fractionated over a 3-ft. spiral column under reduced pressure. After collection of a small forerun consisting mainly of tetrahydrofuran, 2,3-dimethylcrotonaldehyde (29.6 g., 0.30 mole, 93%) was collected at 89–91° (85 mm.).

1,1-Dibromo-2,3-dimethyl-2-butene.—To a suspension of phosphorus trichloride (13.7 g., 0.10 mole) in methylene chloride (50 ml.) was added bromine (16 g., 0.10 mole) at 0° with vigorous stirring. This solution was then cooled to –70° and 2,3-dimethylcrotonaldehyde (9.8 g., 0.10 mole) in methylene chloride (25 ml.) was added. The mixture was stirred for 2 hours at this temperature and was then allowed to warm up within 1 hour to –30° and kept at this temperature for 15 minutes. Pentane (150 ml.) was added and the reaction mixture was poured onto crushed ice. After separation the organic layer was washed several times with ice-water and dried over magnesium sulfate. The solvent was stripped off at reduced pressure and the residue was distilled over a short Vigreux column at 0.01 mm. The fraction boiling at 26–30° was collected. Further purification was obtained by several redistillations until the sample did not show any carbonyl absorption in the infrared spectrum.

Anal. Calcd. for C₆H₁₀Br₂ (241.98): Br, 66.04. Found: Br, 65.44.

The sample thus obtained (8.9 g., 0.037 mole, 37%) proved to be a mixture of two components when analyzed by infrared and n.m.r. spectra; n.m.r. analysis revealed two low field resonances at 3.6 (quadruplet, 1.1 c.p.s. line separation) and 3.8 τ (single line). That the resonances were attributable to two different compounds was evident from the change in integrated intensities upon further fractional distillation. The infrared spectrum showed the corresponding change of the intensities of the two carbon-carbon double bond stretching frequencies at 1628 and 1674 cm.⁻¹, respectively. Integration of the low field n.m.r. lines gave a 3:1 ratio in favor of the compound with the higher chemical shift and the higher carbon-carbon double bond stretching frequency.

Reaction of Mixture of 1,1-Dibromo-2,3-dimethyl-2-butene and 1,3-Dibromo-2,3-dimethyl-1-butene with Methylithium.—The mixture of the isomeric bromides (5.0 g., 0.021 mole) obtained as described above was dissolved in ether (20 ml.) and cooled to –30°. Methylithium (0.065 mole) in ether (38 ml.) was added over a period of 30 minutes at this temperature. The solution was then allowed to warm up to room temperature and allowed to sit for 3 days to complete the metalation. Carboxylation at –70° and work-up for 2,3,3-trimethylcyclopropenecarboxylic acid was carried out as described above. The pure acid was obtained through dissolving the crude acidic material in *n*-pentane and crystallization at –30°. Sublimation at 40° (0.02 mm.) gave the pure acid (1.05 g., 0.0083 mole, 40%), m.p. 48–49°.

(26) In another run the metalation of the cyclopropene was accomplished by using excess butyllithium. However, the *n*-valeric acid formed by carboxylation of the excess is difficult to separate from the cyclopropenecarboxylic acid.

(27) The originally reported² yield of 16% was due to a misprint and should read 6%.

(28) F. C. Whitmore and W. L. Evers, *J. Am. Chem. Soc.*, **55**, 812 (1933).

(29) This is an improved procedure based on a method of E. A. Brande and E. A. Evans, *J. Chem. Soc.*, 3336 (1955).

(25) L. F. Hatch and G. E. Journeay, *J. Am. Chem. Soc.*, **75**, 3712 (1953).

Reaction of 2-Methylpropenyllithium with Methylene Chloride.—2-Methylpropenyllithium (0.70 mole) was prepared from 1-bromo-2-methylpropene (135 g., 1.0 mole) and lithium (20 g., 2.9 g. atoms) in ether (1000 ml.).³⁰ The lithium compound precipitated partially as a slightly yellow powder. Most of the ether (800 ml.) was removed by distillation under reduced pressure (80 mm.). To the remaining lithium compound was added tetrahydrofuran (700 ml.) and the solution was cooled to -30° . Methylene chloride (24 g., 0.28 mole) was slowly added under vigorous stirring keeping the solution between -35 and -30° . After the addition was complete the solution was kept an additional 10 minutes at this temperature. Then part of the solvent (600 ml.) was distilled into a trap cooled with liquid nitrogen under reduced pressure (1 mm.) thus removing most of the isobutene. During this distillation the reaction mixture was kept below -10° . Heptane (100 ml.) was added to the residue followed by ice-water. The organic layer was separated and washed three times with ice-water (200 ml.) keeping the separatory funnel in an ice-bath. After drying over magnesium sulfate, the most volatile components were distilled from the heptane solution using a 3-ft. Helipack column kept in a room below 15° . The cooling water of the reflux cold finger had a temperature of 3° .

(30) E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3324 (1955).

The gas outlet of the distillation head was connected with a trap cooled with Dry Ice and acetone. The fraction boiling at $12-16^{\circ}$ was collected (3.8 g.). Comparison of the infrared and n.m.r. spectra of this material with those obtained from a pure sample of 3,3-dimethylcyclopropene (b.p. 14.5°)² obtained by the base-catalyzed decomposition of the tosylhydrazone of β -methylcrotonaldehyde showed the presence of about 60% 3,3-dimethylcyclopropene (12% yield). The main impurities were isobutene and ether. The final purification was achieved by v.p.c. using a 5-ft. column with silicon 710 on firebrick, at 30° . The sample was trapped in the conventional manner; n.m.r. spectrum: triplet, centered at 9.07τ (0.7 c.p.s. separation) septuplet; centered at 3.00τ (0.7 c.p.s. separation); infrared spectrum: C=C stretching, 1632 cm.^{-1} .

Hydrogenation of 3,3-Dimethylcyclopropene.—3,3-Dimethylcyclopropene (0.478 g., 0.007 mole) was dissolved in ethanol (3 ml.) and hydrogenated over 5% palladium-on-charcoal (50 mg.) at 0° . Hydrogen uptake (0.0064 mole) was complete within 7 minutes; v.p.c. analysis showed the hydrogenation product to consist of 95% 1,1-dimethylcyclopropane with only one other component (unidentified). Isolation of the cyclopropane by v.p.c. was carried out on 12-ft. column using TCP on fire-brick as substrate at 22° . The material was identified by comparison of its infrared and n.m.r. spectrum with an authentic sample of 1,1-dimethylcyclopropane.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN 12, TEX.]

Substituent Effects in the Solvolysis and Thiosulfate Reactions of 3-, 4- and 3,5-Substituted α -Chlorotoluenes

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The rates of reaction of a series of 3-, 4- and 3,5-substituted α -chlorotoluenes with sodium thiosulfate in 60% acetone at 30° , and the rates of solvolysis in 50% ethanol at 60° have been measured. The present data together with previous work provide information on more than twenty compounds. The thiosulfate reaction rates may be represented by a series of U-shaped Hammett equation plots. 3-Substituents possess an intrinsic rate-depressing ability compared with 4-substituents of similar σ , and this effect is additive in the 3,5-disubstituted compounds. 4-Substituents capable of strong mesomeric electron release enhance rates compared with other substituents of similar σ . The solvolysis rates may be represented by a Hammett plot vs. σ^+ as three lines, or, alternatively, as a single curved line. The mechanistic implications are discussed.

For several decades there has been available a considerable body of rate data pertaining to the reactions of nucleophiles with benzyl halides (α -halotoluenes), and the effect of *m*- and *p*-substituents therein.² Attempted correlations with the Hammett equation have been unsuccessful in two ways: (1) plots of the reactivity of *p*-substituted benzyl halides with anions are U-shaped,^{2a,b,c,f,g,h} with the unsubstituted compound at the rate minimum, and for the reactions with amines the plots may be still more complex,^{2d} although tending to give negative values of ρ . (2) The rates of reaction of *m*-substituted benzyl halides^{2a-f} are consistently lower than would be predicted on the basis of σ -values, and are in certain cases^{2b-e} below that of the unsubstituted compound. There is also the possibility that the dissociation of salts in media of low ion-solvating ability, and, hence, the rate of nucleophilic attack by anions, may be affected by the polar nature of certain substituents.^{2f,h} This possibility has been greatly reduced in the present study by the choice of 60% acetone-40% water as the solvent. The use of the powerful nucleophile thiosulfate has also precluded solvolysis as a successfully competing reaction in all cases excepting that of the *p*-methoxy compound.

(1) Based on the Ph.D. dissertation of D.M.C., The University of Texas, 1962.

(2) (a) H. Franzen, *J. prakt. Chem.*, [2] **97**, 82 (1918); H. Franzen and I. Rosenberg, *ibid.*, [2] **101**, 333 (1921); (b) W. T. Miller, Jr., and J. Bernstein, *J. Am. Chem. Soc.*, **70**, 3600 (1948); (c) S. C. J. Olivier and W. P. Weber, *Rec. trav. chim.*, **53**, 869 (1934); (d) J. W. Baker, *J. Chem. Soc.*, 2631 (1932); 1128 (1933); 1448 (1936); (e) C. G. Swain and W. P. Langsdorf, *J. Am. Chem. Soc.*, **73**, 2813 (1951); (f) G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1815 (1935); A. G. Evans and S. D. Hamann, *Trans. Faraday Soc.*, **47**, 25 (1951); (g) R. Fuchs and A. Nisbet, *J. Am. Chem. Soc.*, **81**, 2371 (1959); (h) Other, less extensive series are cited in A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

The effect of substituents in the SN2 reactions of benzyl compounds has been considered by Swain³ in terms of "loose" and "tight" transition states. Electron-releasing substituents are said to facilitate the former by stabilization of the fractional positive charge developed on the benzylic carbon atom in the transition state; electron-withdrawing substituents place a fractional positive charge on the benzylic carbon atom of the initial state, and stabilize the somewhat more negative charge in the "tight" transition state. The rate-enhancing effect of +R substituents has been attributed in part to neighboring orbital overlap^{2h} when the entering and leaving groups are not first row elements; partial bonding of the nucleophile may occur at C-1 of the benzene ring of benzyl chlorides, with mesomeric delocalization of the fractional negative charge to a *p*-nitro group.

A recent publication⁴ further indicates that σ -values do not serve as a satisfactory basis for prediction of the rates of reaction of several 4-substituted 3-nitrobenzyl chlorides with thiosulfate. The Hammett plot for this series (using experimentally determined σ -values for 3-nitro-4-substituents⁵) describes a separate U-shaped curve similar to that for the 4-substituted benzyl chlorides. It was concluded⁴ that the 3-nitro group in each compound of the series exerts only a rather small effect on the absolute and relative rates of reaction.

Data on the rates of solvolysis of benzyl series are also available.^{2c,f,h,6} The solvolysis of α,α -dimethyl-

(3) C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.*, **73**, 2813 (1951).

(4) R. Fuchs and D. M. Carlton, *J. Org. Chem.*, **27**, 1520 (1962).

(5) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(6) (a) S. C. J. Olivier, *Rec. trav. chim.*, **41**, 301, 646 (1921); **42**, 516