

unlabeled acid in 200 ml. of dry chloroform was added 24.0 g. (0.238 mole) of triethylamine, followed by the addition of 24.0 g. (0.221 mole) of ethyl chlorocarbonate over a 10-min. period. The mixture was allowed to stand at room temperature for 1.5 hr. and then cooled in an ice-bath and about 40 ml. of anhydrous dimethylamine vaporized and bubbled in. After 17 hr. at room temperature, the greater part of the solvent was evaporated under reduced pressure, 20 ml. of water was added, and the aqueous phase was extracted six times with 50-ml. portions of chloroform. The combined chloroform extracts were dried over sodium sulfate and the solvent distilled at atmospheric pressure. The residue distilled at 102–105° (35 mm.) and gave 19.8 g. (75%) of *N,N*-dimethylcyclopropanecarboxamide-*carboxyl*-¹³C of a purity higher than 99%, as shown by v.p.c. Unlabeled carboxamide (1.5 g.) was added to the residue and distilled into the labeled material, giving a total of 21.1 g. of amide. The ¹³C content of the final product was calculated to be about 22%.

methyl-¹³C-Cyclopropane.—Lithium aluminum diethoxyhydride was prepared by adding a solution of 8.9 g. (0.10 mole) of ethyl acetate over a 1-hr. period to 100 ml. of a magnetically stirred, ice-cooled 1.0 *N* lithium aluminum hydride solution in ether. The resulting mixture was added to a stirred solution of 21.1 g. (0.186 mole) of *N,N*-dimethylcyclopropanecarboxamide-*carboxyl*-¹³C in 80 ml. of dry ether at 0° over 30 min. The mixture was stirred at room temperature for 30 min., then heated under reflux for 30 min., and finally ice-cooled and treated with 2 *N* sulfuric acid to decompose the aluminum complexes. The ether layer was separated and the aqueous suspension extracted eight times with 50-ml. portions of ether. The combined ether solutions were dried over sodium sulfate and concentrated by distilling the solvent through a 100-cm. Helipak column.¹⁰

The residue was cooled in ice, and 25 ml. of ethylene glycol and 20 ml. of 85% hydrazine hydrate were added. The mixture was allowed to stand at room temperature for 15 min., and a solution of 25 g. of potassium hydroxide in 125 ml. of ethylene glycol was then added. The flask was equipped with a magnetic stirring bar and connected to a 30-cm. semi-

(10) In a separate experiment it was found that 70% of cyclopropanecarboxaldehyde could be isolated from this concentrate as its semicarbazone; cf. H. C. Brown and A. Tsukamoto, *J. Am. Chem. Soc.*, **81**, 502 (1959).

micro column.¹¹ The mixture was stirred and heated in an oil-bath, the temperature of which was raised gradually to 160°. The distillate that collected to this point was discarded. A new receiver was then attached that was connected through a short reflux condenser to two traps cooled in Dry Ice-acetone. The bath temperature was raised over 30 min. up to 220° and kept at that temperature for 30 min. The liquid that condensed in the first trap was distilled through a calcium chloride tube into the second trap. Approximately 6 ml. of methyl-¹³C-cyclopropane was obtained, which was identified by its infrared spectrum. The n.m.r. spectrum of the product is shown in Fig. 1.

Photochlorination of methyl-¹³C-Cyclopropane.—Approximately 6 ml. of methyl-¹³C-cyclopropane was chlorinated in the apparatus described earlier.^{4a} The oil-bath surrounding the boiler was raised to 50° toward the end of the reaction, but there was still excess methylcyclopropane when the chlorination was stopped.¹² The chlorination products amounted to 4.0 g., which v.p.c. showed to be a complex mixture with cyclopropylcarbonyl-*α*-¹³C chloride and allylcarbonyl-*α*-¹³C chloride present in an approximate ratio of 65:35. No cyclobutyl chloride could be detected. Besides ring-chlorinated methylcyclopropane, considerable quantities of other products were present with longer retention times, probably polychlorinated products.

Cyclopropylcarbonyl and allylcarbonyl chlorides were separated from the crude chlorination product using a Perkin-Elmer vapor fractometer equipped with a preparative column A (diisodecyl phthalate) at 68° and employing helium as carrier gas at 5 p.s.i. About 0.35 ml. of allylcarbonyl-*α*-¹³C chloride and 0.6 ml. of cyclopropylcarbonyl-*α*-¹³C chloride were collected and sealed in n.m.r. tubes for analysis. The allylcarbonyl chloride so obtained was contaminated with perhaps 3% of *cis*- or *trans*-2-chloro-1-methylcyclopropane as evidenced by the slight high-field n.m.r. absorptions shown in Fig. 1.

(11) C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(12) A marked decrease in yield of allylcarbonyl chloride was observed when attempts were made to complete the reaction, probably because of addition of chlorine to the double bond. Even when the reaction was not run to completion, v.p.c. showed that there were considerable variations in the ratio of the monochlorinated products in experiments at different chlorine flow rates.

[CONTRIBUTION FROM HICKRILL CHEMICAL RESEARCH LABORATORY, KATONAH, N. Y.]

Comparative Reactivity of Methylene, Carbomethoxycarbene and Bis-carboethoxycarbene toward the Saturated Carbon-Hydrogen Bond

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The series of carbenes, CH₂, CHCOOCH₃ and C(COOC₂H₅)₂, reacts with the carbon-hydrogen bond with increasing discrimination in the sense 3° > 2° > 1°. The presence of carbalkoxy groups decreases the absolute reactivity of the carbene. The enhanced discrimination points to the contribution of polar structures in the transition state.

Insertion into the carbon-hydrogen bond is a novel reaction in the chemistry of carbenes. The firm establishment of a direct, single-step mechanism rests on labeling experiments in the reaction of the allylic carbon-hydrogen bond with methylene.² On the assumption that no intermediates are involved, the usual picture of a transition state incorporating the structural features of starting material and product is constructed.³⁻⁶ In such

(1) To whom inquiries may be directed: 1901-A Yale Station, New Haven, Conn.

(2) W. von E. Doering and H. Prinzbach, *Tetrahedron*, **6**, 24 (1959).

(3) J. Chanmugan and M. Burton, *J. Am. Chem. Soc.*, **78**, 509 (1956).

(4) W. von E. Doering and L. H. Knox, *ibid.*, **78**, 4947 (1956).

(5) P. S. Skell and R. C. Woodworth, *ibid.*, **78**, 4496 (1956).

(6) J. H. Knox and A. F. Trotman-Dickenson, *Chemistry & Industry*, 268 (1957).

a typically "no-mechanism" situation, where there are no catalysts to discuss, nor intermediates to define, the questions involve the hypothetical transition state. Has its geometry been correctly represented? Is it a useful working hypothesis by which to predict the effects of structural changes on rate?

In the insertion reaction the rates are so fast that structural changes make themselves felt as a change in degree of discrimination. Methylene itself reacts with the carbon-hydrogen bond without discrimination; that is, without being able to distinguish between different degrees of substitution.⁷ Analysis of the transition state along previous

(7) W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, *J. Am. Chem. Soc.*, **78**, 3224 (1956).

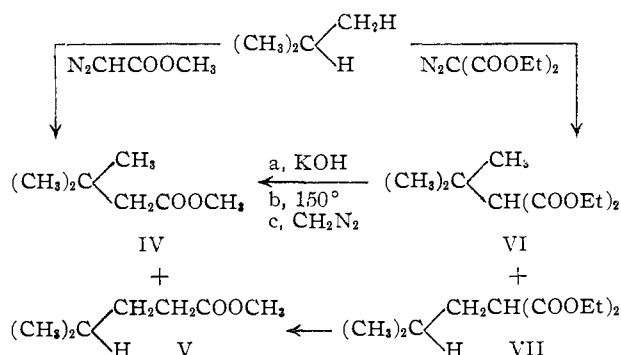
lines allows one to predict that substitution of the hydrogens in methylene by carbalkoxy groups should lead to an increasing discrimination in favor of the more highly substituted carbon-hydrogen bond, provided sufficient activation energy develops to permit the operation of discrimination.⁸ The main concern of this paper is with the photochemical decomposition of diazomalonic ester in saturated hydrocarbons and the comparison of its behavior with that of diazomethane and diazoacetic ester.

Diazomalonic ester (I), prepared from aminomalonic ester⁹ by the method of Lindemann and co-workers,¹⁰ was found to be grossly (45%) contaminated by ethyl diazoacetate after an orienting irradiation in cyclohexane had revealed large amounts of ethyl cyclohexylacetate in addition to diethyl cyclohexylmalonate. Consequently, subsequent experiments were conducted with diazoester of m.p. 7–8°, purified by distillation. The formation of diethyl cyclohexylmalonate from the photochemical decomposition of diazomalonic ester in cyclohexane is considered to constitute strong presumptive evidence for the intermediacy of bis-carboethoxycarbene. As a means of converting the carbon-hydrogen bond to a substituted malonic ester, the reaction may well have synthetic value.

The hydrocarbon 2,3-dimethylbutane, containing twelve primary and two tertiary hydrogen atoms, has been allowed to react with methylene,⁷ carbomethoxycarbene⁴ and now with bis-carboethoxycarbene. Inaccessibility of the products and analytical difficulties give these results a low order of precision. Diazomalonate was irradiated with light of $\lambda > 300 \text{ m}\mu$ in excess 2,3-dimethylbutane serving both as reactant and as solvent. The crude product was hydrolyzed, decarboxylated and converted to the methyl ester by diazomethane. Analysis by gas-liquid partition chromatography (g.l.p.c.) using hydrogen as the carrier gas indicated the mixture to consist of 67.6% of methyl 3,3,4-trimethylpentanoate (II) and 32.4% of methyl 4,5-dimethylhexanoate (III). Both substances were identical with those obtained previously⁴ (the structure of II, however, is assigned on the basis of analogy alone). The previously reported⁴ product of the reaction of 2,3-dimethylbutane and methyl diazoacetate has been re-analyzed with hydrogen instead of nitrogen as the carrier gas and is found to consist of 32.4% II and 67.6% III. In both experiments the difficultly avoidable assumption that the g.l.p.c. correction factor (c.f.) is unity casts doubt on the absolute accuracy, but does not jeopardize the comparative reactivities. The ratio of reactivity of tertiary hydrogen to primary ($3^\circ/1^\circ$) in 2,3-dimethylbutane (compensating for the statistical factor of 6:1) may be calculated: methylene, 1.2;¹¹ carbomethoxycarbene, 2.9; and bis-carboethoxycarbene, 12.5 (Table I).

Considerably more reliable results have been obtained in the reaction with isobutane. The prod-

ucts from both methyl diazoacetate [methyl *t*-butylacetate (IV) and methyl isobutylacetate (V)] and methyl isobutylacetate (V)] and diethyl diazomalonate [ethyl *t*-butylmalonate (VI) and ethyl isobutylmalonate (VII)] have been synthesized in order to permit checking of the analytical method. The correction factor necessary to calibrate the g.l.p.c. was determined with a synthetic mixture of IV and V of known composition. The method of analyzing the mixture of VI and VII involved saponification to the corresponding malonic acids, decarboxylation to the substituted acetic acids, methylation with ethereal diazomethane and analysis of the resulting mixture of IV and V by g.l.p.c. Despite the length of the procedure, its application to a known mixture consisting of 70.0% of VI and 30.0% of VII gave 69.3% and 30.7% as the result.



The photolysis of methyl diazoacetate in isobutane led to a mixture of esters in 50% of the theoretical yield consisting of 25.4% of IV and 74.6% of V. A similar photolysis of diethyl diazomalonate led to a mixture of malonic esters transformed as described above into methyl butylmalonates consisting of 70.0% IV and 30.0% V. The reactivity ratios are summarized in Table I.

The relative reactivity of secondary and primary hydrogen atoms was determined using *n*-butane as substrate. The photolysis of methyl diazoacetate and ethyl diazomalonate in *n*-butane led, after analysis by a completely analogous scheme, to methyl 3-methylpentanoate (VIII) and methyl hexanoate (IX) in the ratios 60.9/39.1 and 84.8/15.2, respectively. The relative reactivities are given in Table I.

TABLE I

RELATIVE REACTIVITIES OF CARBON-HYDROGEN BONDS TOWARD CARBENES

Hydrocarbon	Ratio	CH ₂	CHCOOCH ₃	C(COOCH ₂ H) ₂
[(CH ₃) ₂ CH-] ₂	3°/1°	1.2	2.9	12.5
(CH ₃) ₃ CH	3°/1°	..	3.1	21.0
[CH ₂ CH ₂ -] ₂	2°/1°	1.0 ^a	2.3	8.4

^a Taken from ref. 6.

In reactions of methylene one had ascribed lack of discrimination to an order of reactivity so high that the free energy of activation was zero or close to it.⁷ Later, in studies of methylene generated in the gas phase, Frey and Kistiakowsky¹² found that reaction with 2° hydrogen was favored by a factor of 1.7 over reaction with 1°. This discrim-

(12) H. M. Frey and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **79**, 6373 (1957).

(8) See particularly, footnote 13 in ref. 4.

(9) H. R. Snyder and C. W. Smith, *J. Am. Chem. Soc.*, **66**, 35 (1944).

(10) H. Lindemann, A. Walter and P. Grozer, *Ber.*, **63**, 702 (1930).

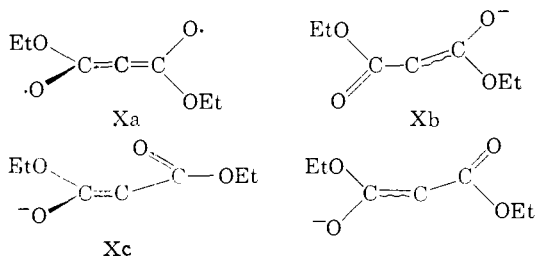
(11) The reported results⁷ (17% 2,2,3-trimethylbutane and 83% 2,3-dimethylpentane) differ only slightly and perhaps not significantly from the statistical (14.28%, 85.72%), but affect the sensitivity ratio ($3^\circ/1^\circ$) markedly: 1.23 vs. 1.00.

ination was ascribed to the cooling of initially formed "hot" methylene molecules by collision with inert gases. In solutions of the reactant, by contrast, the first collision of photochemically produced, "hot" methylene should be fruitful rather than cooling. Some hesitation about unreserved acceptance of this explanation should be generated by the recent announcement of Herzberg and Shoosmith concerning the existence of a singlet and triplet methylene.¹³ However, in considering the data in Table I, it should be noted that the ratios may be smaller than would prevail in the reactions of thermally equilibrated carbenes.

Notwithstanding, the trend to greater selectivity is clear. The presence of carbalkoxy groups has done two things: it has increased the free energy of activation for the insertion reaction so that differences in inherent reactivity of the substrate may be observed; and it has increasingly favored reaction with 3° hydrogen.

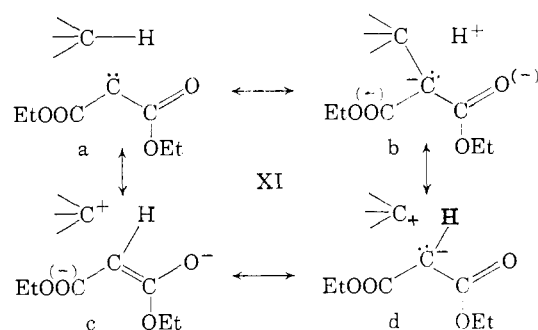
Increase in the free energy of activation reflects an increase in the stabilization of the carbene. Either as a triplet or a singlet (at this point in the development of one's knowledge, no definitive distinction can be made between the two possible electronic structures of the reacting agencies in these liquid phase photodecompositions) a linear structure would derive stabilization by delocalization of electrons (Xa) without extensive charge separation. A singlet, trigonal structure could derive stabilization either by overlap of the sp² orbital of the central carbon with the 2p orbital of the carbonyl groups (Xb: in this case the carbonyl oxygen atoms are not in the plane of the three-carbon system) or the third sp² orbital could be empty (at the expense of one-third of the energy required to promote an electron from 2s to 2p) and the overlap would be of the usual 2p-2p sort (Xc).

The description of the transition states assumes that the carbene is not reacting as a diradical, is on its way toward becoming a tetrahedral carbon atom and is forming the new carbon-carbon and carbon-hydrogen bond simultaneously. Among the seven resonance structures (XI) used to describe this state,⁸ three (XIc and d) in particular make clear how negative substitution in the carbene leads to a favoring of 3° hydrogen over 2° (in turn favored over 1°) for the reason that the order of stability of carbonium ions is 3° > 2° > 1°.



This explanation of the experimental facts is offered as a self-consistent one which tends to support the proposed transition state. However, there are other consistent explanations, so that the one favored here should not be considered as uniquely established.

(13) G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959).



Experimental

Diethyl Diazomalonate (I).—Prepared according to Snyder and Smith⁹ without isolating the intermediary isonitroso ester, diethyl aminomalonate was converted to the hydrochloride by dissolving the ester in ether (400 ml. per mole) and passing in dry hydrogen chloride. After two crystallizations from ethanol of the crude product (148 g. (56%) from 173 g. of diethyl malonate), m.p. 159–163° dec., diethyl aminomalonate hydrochloride was obtained, m.p. 167° dec.

Anal. Calcd. for C₇H₁₃ClNO₄: C, 39.9; H, 6.1; N, 6.7. Found: C, 39.8; H, 6.3; N, 6.8.

The diazo compound was prepared according to Lindemann and co-workers¹⁰ by successively treating 105 g. (0.5 mole) of the crude diethyl aminomalonate hydrochloride in 125 ml. of water with an 8-ml. portion of a solution of 53 g. of sodium nitrite in 70 ml. of water, an 8-ml. portion of 2 *N* sulfuric acid and extracting with 8 ml. of ether until the reagents had been consumed. The ether extracts were dried over magnesium sulfate and concentrated *in vacuo* at room temperature under nitrogen. Distillation *in vacuo* gave 14.3 g. (0.125 mole calcd. as ethyl diazoacetate) of a first fraction, b.p. 35–84° (1 mm.), and 26.9 g. (0.145 mole, 29% of theory) of diethyl diazomalonate, b.p. 84–85° (1 mm.). Recrystallized twice from pentane at –20°, this material melted at 7–8°, *n*_D²⁰ 1.4630.

Anal. Calcd. for C₇H₁₀N₂O₄: C, 45.2; H, 5.4; N, 15.1. Found: C, 45.4; H, 5.5; N, 15.2.

The first fraction (1.0 g.) in 20 ml. of ether was treated with ethereal hydrogen bromide sufficient to decolorize the yellow color. Excess trimethylamine was added. After 2 hr. at room temperature, the mixture was filtered to give (51%) of carboethoxymethyltrimethylammonium bromide which melted at 162–163° after two recrystallizations from absolute methanol and did not depress the m.p. of authentic material prepared in 92% yield from authentic ethyl diazoacetate.

Anal. Calcd. for C₇H₁₆BrNO₂: C, 37.2; H, 7.1; Br, 35.3; N, 6.2. Found: C, 37.3; H, 7.0; Br, 35.3; N, 6.4.

Photolysis of Crude Diethyl Diazomalonate in Cyclohexane.—Crude undistilled diazomalononic ester (9.3 g.) in 450 ml. of cyclohexane was irradiated in the usual manner with two General Electric R. S. Sunlamps (unfiltered mercury arc in Pyrex) at 15° for 44 hr. Distillation of excess solvent in a 1-ft. Vigreux column gave a residue which was saponified by refluxing for 2 hr. with 10 g. of potassium hydroxide in 110 ml. of 95% ethanol. When diluted with water, extracted with ether, acidified with 6 *N* sulfuric acid and extracted further with ether, the reaction mixture yielded an ether solution of acidic material. Concentration *in vacuo* and standing gave crystalline material which was separated by triturating with pentane and filtering; 3.24 g. (35%), m.p. 160–162° dec. Recrystallization from 98% formic acid afforded cyclohexylmalonic acid, m.p. 174.5–175.5° (reported¹⁴ m.p. 176–178° with dec.).

Distillation of the pentane left a residue (1.57 g.) which was esterified with diazomethane. Evaporative distillation gave 1.39 g. of liquid, 89% of which was methyl cyclohexylacetate, analyzed by g.l.p.c. and identified by infrared spectrum.

Gas-Liquid Partition Chromatographic (g.l.p.c.) Analysis.—A Perkin-Elmer model 154 Vapor Fractometer with a

(14) E. Hope and W. H. Perkin, Jr., *J. Chem. Soc.*, **95**, 1360 (1909).

2-m. stainless steel di-*n*-decyl phthalate column (Type A) was employed with hydrogen at 15–20 lb. p.s.i. gauge pressure as the carrier gas. Quantitative estimation of areas was made by tracing the curves on filing cards, cutting out the pertinent section and weighing. In most instances, a correction factor (c.f.) needed to multiply the observed composition to obtain the true composition was determined by calibration with known mixtures.

Photolysis of Diethyl Diazomalonate (I) in 2,3-Dimethylbutane.—A solution of 13.0 g. (0.07 mole) of diazomalonate ester in 550 ml. (5.4 mols) of 2,3-dimethylbutane (Phillips Petroleum Co.; pure grade, > 99%) was irradiated according to the previously described procedure for diazoacetic ester.⁴ The crude malonic esters remaining after distillation of the solvent were refluxed 3 hr. with 125 g. of 10% ethanolic potassium hydroxide. Removal of the ethanol left a solid residue which was dissolved in 50 ml. of water and acidified. Ether extraction afforded the crude malonic acids which were decarboxylated by heating at 160–180°. The resulting monocarboxylic acids were dissolved in ether and extracted with 6 *N* sodium hydroxide. After two ether extractions, the aqueous solution of sodium salts was acidified to liberate the free acids, which were then converted by excess ethereal diazomethane to the methyl esters; 4.09 g. (37.2% of theory), b.p. 56–63° (15 mm.).

G.l.p.c. separation of the liquid esters at 133° gave two fractions, of which the first (67.6%) was isolated and shown to have the same infrared spectrum as methyl 3,3,4-trimethylpentanoate (c.f. 1.03)⁴ and the second (32.4%) had the same infrared spectrum as authentic methyl 4,5-dimethylhexanoate (c.f. 0.97).⁴

Calculation of Reactivity Ratio.—The reactivity ratio of different groups (or types of hydrogen atoms), $\alpha_{i/a}$, is defined as the ratio of the rate of reaction (of the carbene) with the group *i* to that with group *a* taken as standard. The reactivity ratio is therefore equal to $f_i n_a / n_i f_a$ where *f* is the fraction of total product and *n* the number of each type of group.

Photolyses in Isobutane. (a) **Authentic Materials.**—Methyl 2,2-dimethylbutanoate, b.p. 133° (760 mm.), was prepared according to Homeyer, *et al.*¹⁵ Diethyl *t*-butylmalonate was prepared from *t*-butylacetic acid by the procedure of Bush¹⁶; b.p. 102–103° at 11 mm. Methyl 4-methylpentanoate, b.p. 146° (760 mm.), and diethyl isobutylmalonate were prepared by a standard malonic ester synthesis. A mixture of 61.9% of methyl *t*-butylacetate

(15) A. H. Homeyer, F. C. Whitmore and W. H. Wallingford, *J. Am. Chem. Soc.*, **55**, 4209 (1933).

(16) M. T. Bush, *ibid.*, **61**, 637 (1939).

and 38.1% of methyl 4-methylpentanoate was analyzed by g.l.p.c. at 100°; three determinations gave relative compositions of 61.9 and 38.1%, 61.6 and 38.4%, and 61.3 and 38.7%. Correction factors (c.f.) of 1.005 and 0.992, respectively, were derived and applied in the analytical procedure.

(b) **Methyl Diazoacetate.**—Irradiation of 10.0 g. of methyl diazoacetate in 1000 ml. of isobutane gave 6.48 g. of product, b.p. 114–117° at 760 mm., which was shown by g.l.p.c. (100°) to consist of 25.4% of methyl *t*-butylacetate and 74.6% of methyl 4-methylpentanoate. The pure compounds were separated by g.l.p.c. and were identified by their infrared spectra.

(c) **Ethyl Diazomalonate.**—The product from irradiating 8.0 g. of ethyl diazomalonate in 1000 ml. of isobutane was saponified with 120 g. of refluxing ethanolic potassium hydroxide. The crude acids were decarboxylated and methylated with ethereal diazomethane giving 2.74 g. of mixed esters, b.p. 150–180°. Separation by g.l.p.c., identification by infrared spectrum and analysis by g.l.p.c. showed the mixture to consist of 70.0% of methyl *t*-butylacetate (c.f. 1.01) and 30.0% of methyl 4-methylhexanoate (c.f. 0.99).

(d) **Validation of Analytical Procedure.**—A synthetic mixture of 2.120 g. (70.0%) of diethyl *t*-butylmalonate and 0.910 g. (30.0%) of diethyl isobutylmalonate was treated in the same manner as above, then saponified, decarboxylated, methylated and analyzed by g.l.p.c. at 100°. The mixture, after applying the correction factor, appeared to consist of 69.3% of methyl *t*-butylacetate and 30.7% of methyl isobutylacetate.

Photolyses in *n*-Butane. (a) **Authentic Materials.**—Methyl *n*-hexanoate (IX) was obtained from commercial hexanoic acid and excess ethereal diazomethane: b.p. 152° (760 mm.), n_D^{25} 1.4038. Methyl 3-methylpentanoate (VIII) was prepared from *sec*-butyl chloride by a standard malonic ester synthesis: b.p. 142° (760 mm.), n_D^{25} 1.4050. Triplicate analyses by g.l.p.c. at 100° of a synthetic mixture of 69.0% of VIII and 31.0% of IX indicated 69.8, 69.8 and 69.5% of VIII, corresponding to c.f. of 0.990 for VIII and 1.022 for IX.

(b) **Methyl Diazoacetate.**—The reaction of 9.5 g. of methyl diazoacetate afforded 6.02 g. (49%) of mixed esters consisting of 60.9% of VIII and 39.1% of IX. The pure products were separated by g.l.p.c. and identified by their infrared spectra.

(c) **Ethyl Diazomalonate.**—The product from 15.0 g. of I was worked in the usual manner to give 2.06 g. of mixed esters, b.p. 75–154°, consisting of 84.8% of VIII and 15.2% of IX (determined by g.l.p.c. with hydrogen at 15 lb. p.s.i. (gauge) and 75°).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

Ionic Reactions in Bicyclic Systems. III. Solvolysis of Bicycloöctanyl and Bicycloöctenyl *p*-Toluenesulfonates¹

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First-order rate constants for acetolysis and ethanolysis of (a) *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (I), (b) bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII) and (c) *exo*(*axial*)-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) have been determined. Rate constants for the solvolysis of VII in 80% aqueous acetone and acetolysis of *endo*(*equatorial*)-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (XVI) have also been determined. Ionization of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-toluenesulfonate (I), which results in complete rearrangement to the bicyclo[3.2.1]oct-3-en-2-yl system, is anchimerically assisted. Solvolysis of bicyclo[2.2.2]octan-2-yl *p*-toluenesulfonate (VII) and *axial*-bicyclo[3.2.1]octan-2-yl *p*-toluenesulfonate (VIII) is accompanied by internal return which results in the interconversion (equilibration) of the two isomers during solvolysis. The reactivities of these isomers are consistent with the idea that ionization results in the formation of a common bridged ("non-classical") carbonium ion; *i.e.*, anchimeric acceleration is indicated.

Introduction

In the first paper in this series³ it was shown that acetolysis of *endo*-bicyclo[2.2.2]oct-5-en-2-yl *p*-

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(2) Wisconsin Alumni Research Foundation Fellow 1956–1958; National Science Foundation Fellow 1958–1960.

toluenesulfonate (I) gives *axial*-bicyclo[3.2.1]oct-3-en-2-yl acetate (IX). Deamination of *endo*-5-aminobicyclo[2.2.2]oct-2-ene also results in complete rearrangement to the bicyclo[3.2.1]oct-3-en-2-yl system.^{3,4} On the other hand, solvolysis

(3) H. L. Goering, R. W. Greiner and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1391 (1961).