were removed by trap-to-trap distillation; the reaction vessel was evacuated to 10^{-4} mm at 50°. The dark semisolid residue was triturated with cold hexane and filtered. The resulting tan solid was dissolved in hot 2:1 hexane–benzene and cooled. Two crops of *cis*-1,2-bis(difluoramino)acenaphthene (XI) were obtained, totaling 3.41 g (0.0133 mole, 38% based on unrecovered N_2F_4). Further recrystallization from benzene–hexane gave the analytical sample of XI as white needles, mp 107–108°.

Anal. Calcd for $C_{12}H_8F_4N_2$: C, 51.72; H, 3.44; N, 12.07. Found: C, 51.83; H, 3.65; N, 12.16.

The infrared spectrum of XI exhibited significant maxima at 6.68 (m), 8.30 (m, br), 10.36, 10.60 (s), 11.39 (vs), and 12.02 (m) μ. The nmr spectrum consisted of signals at τ 2.4–2.6 (6 H, multiplet, aryl hydrogens) and 5.24 (2 H, triplet, J_{HF} = 32 cps, aliphatic hydrogens).

Further concentration and cooling of the mother liquors gave a total of three crops of *trans*-1,2-bis(difluoramino)acenaphthene (XII, 4.02 g, 0.0157 mole, 46%), mp 46–48°. Two recrystallizations from hexane–benzene gave the analytical sample as white prisms, mp 49–50°.

Anal. Found: C, 51.46; H, 3.68; N, 11.90.

Compound XII showed infrared maxima at 6.69 (m), 8.52 (m), 9.70 (m), 10.66 (s), 10.89 (s), 11.37 (vs), and 12.26 (s) μ. The nmr spectrum consisted of signals at τ 2.4–2.65 (6 H, multiplets, aryl hydrogens) and 4.71 (2 H, broad triplet, J = cps, aliphatic hydrogens).

Dipole Moment Measurements.—Measurements of the electrical properties and refractive indices of solutions of IX and X in benzene were made at 30°. A General Radio Corp. Model 1610-A capacitance bridge was used for the electrical measurements and the dielectric constants of the solutions were caculated using the directions of the manufacturer.

The method used for calculating the dipole moments from the above data was that of Everard, Hill, and Sutton.[15] There were thus obtained values of 4.7 ± 0.2 D. for IX and 1.3 ± 0.3 D. for X.

Registry No.—Tetrafluorohydrazine, 10036-47-2; I, 10083-79-1; 1,2-bis(difluoramino)cyclooctane, 10076-43-4; 3,8-bis(difluoramino)cyclooctene, 10095-57-5; 3,4-bis(difluoramino)cyclooctene, 10095-58-6; VI, 10095-59-7; VII, 10095-60-0; dimer of 1-nitro-2-nitrosocyclooctane, 10102-91-7; IX, 10095-61-1; X, 10095-62-2; XI, 10095-63-3; XII, 10095-64-4; 1,4-diaminocyclooctane dihydrochloride, 10095-65-5.

Acknowledgment.—The microanalyses were performed by Mrs. P. P. Wheeler; some of the nmr spectra were provided by Dr. D. W. Moore of the Naval Ordnance Test Station, China Lake, Calif. This work was supported by the Foundational Research Program of the Naval Air Systems Command.

[15] K. B. Everard, R. A. W. Hill, and L. E. Sutton, *Trans. Faraday Soc.*, **46**, 417 (1950).

Bridgehead Substituted Bicyclo[2.1.0]pentanes

P. G. Gassman and K. T. Mansfield[1]

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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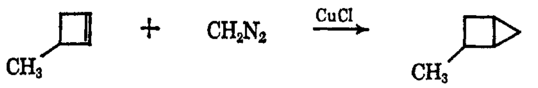
Previously unknown bridgehead substituted bicyclo[2.1.0]pentanes have been synthesized by a variety of methods including intramolecular displacement of *p*-toluenesulfonic acid from butyl *cis*-(2-tosyloxymethyl)-cyclobutanecarboxylate, methylene transfer to methyl cyclobutene-1-carboxylate, metalation of bicyclo[2.1.0]-pentane with amylsodium, and subsequent carbonation, and pyrolysis, and photolysis of the pyrazoline obtained *via* reaction of methyl cyclobutene-1-carboxylate with diazomethane. The preferred routes involve either the metalation of bicyclo[2.1.0]pentane or photolysis of the above-mentioned pyrazoline.

In connection with our continuing work on the cycloaddition reactions of acetylenes with bicyclo[2.1.0]-pentane[2] we desired a variety of bridgehead substituted derivatives of **1**. It was desired that these compounds should differ considerably in the nature of the substituent group such that both strongly electron-withdrawing and electron-inducing groups were present. Since the first preparation of bicyclo[2.1.0]pentane (**1**) was published by Criegee and Rimmelin[3] in 1957, several derivatives of **1** have been synthesized.[4] Unfortunately, methyl[4e,f] and isopropyl[4c] were the only known bridgehead substituents. In view of this lack of bridgehead substituted bicyclo[2.1.0]pentanes, it was decided to synthesize methyl bicyclo[2.1.0]-pentane-1-carboxylate (**2**). The ester function was chosen because simple chemical transformations could readily convert this group into substituents having considerably different electronic effects.

Five alternate pathways to 1-substituted bicyclo-[2.1.0]pentane were envisioned. These were (a) methylene transfer to the appropriately substituted cyclobutene, (b) intramolecular displacement of a sulfonic acid from a simple functionalized cyclobutylcarbonyl derivative, (c) metalation and subsequent carbonation of bicyclo[2.1.0]pentane, (d) pyrolytic loss of nitrogen from the pyrazoline obtained from the reaction of methyl cyclobutene-1-carboxylate with diazomethane, and (e) photolysis of the above-mentioned pyrazoline.

Precedent for the formation of a bicyclo[2.1.0]pentane *via* methylene addition to a cyclobutene derivative was provided by the work of Chesick[4a] who treated **3** with diazomethane in the presence of cuprous chloride[5] to obtain **4** in unspecified yield (eq 1). We



3 **4**

(1)

attempted to apply the diazomethane–cuprous chloride procedure to 1-carbomethoxycyclobutene (**5**) but none of the desired bicyclo[2.1.0]pentane derivative was obtained. Since the Simmons–Smith reaction was

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[1] The Ohio State University Fellow, 1962–1963.

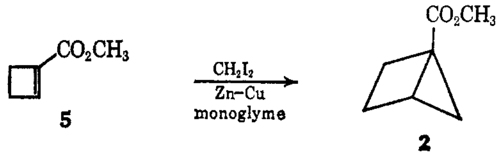
[2] P. G. Gassman and K. T. Mansfield, *Chem. Commun.*, 391 (1965).

[3] R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).

[4] For derivatives of **1** see (a) J. P. Chesick, *J. Am. Chem. Soc.*, **84**, 3250 (1962); (b) K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Letters*, 4245 (1965); (c) R. Srinivasan in "Advances in Photochemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p 106; (d) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846 (1966); (e) J. R. Chapman, *Tetrahedron Letters*, 113 (1966); (f) M. Jorgenson, *J. Am. Chem. Soc.*, **88**, 3463 (1966).

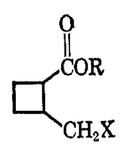
[5] W. von E. Doering and J. F. Coburn, Jr., *Tetrahedron Letters*, 991 (1965).

reported[6] to yield 9% methyl *trans*-2-methylcyclopropane-1-carboxylate *via* methylene transfer to methyl *trans*-crotonate, it was felt that a similar reaction might occur with **5**. Thus, when **5** was treated with 100% excess of methylene iodide in the presence of zinc–copper couple and monoglyme, **2** was obtained in 5% yield (eq 2). Spectroscopic data provided confirmatory evidence for the structure of **2**. The infrared spectrum of **2** showed absorptions at 3.28 and 9.98 μ.[3,7] Near-infrared spectroscopy indicated the presence of a cyclopropyl methylene group by the presence of an absorption at 1.640 μ (ϵ 0.398).[8] The nmr spectrum of **2** was also consistent with the assigned structure, showing a characteristic bicyclo[2.1.0]pentane (**1**) pattern and being devoid of absorptions owing to olefinic hydrogens. The high-field multiplet assigned to the C-5 hydrogens of **1** was shifted downfield about 0.5 ppm in **2**. Blanchard and Cairncross observed an analogous downfield shift when one of the bridgehead protons of bicyclo[1.1.0]butane was replaced by a cyano group.[9]



(2)

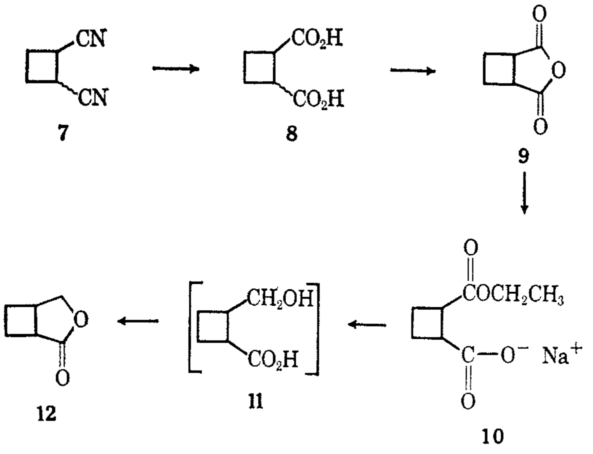
The low yield of **2** obtained in the methylene transfer reaction prompted the investigation of other synthetic routes to **2**. The elimination of *p*-toluenesulfonic acid from an appropriately substituted cyclobutane derivative appeared attractive. Thus, various approaches to compounds of type **6** were studied. Starting with



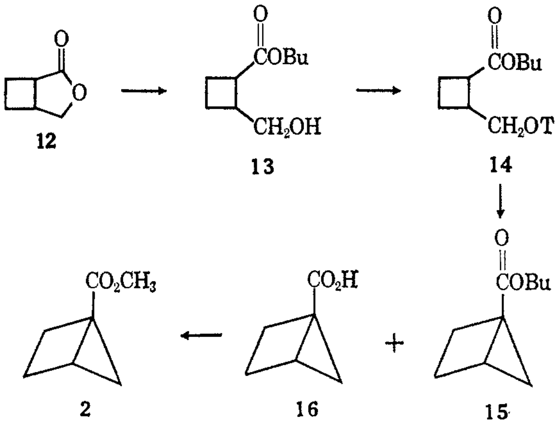
6

the commercially available mixture of *cis*- and *trans*-1,2-dicyanocyclobutane (**7**), the anhydride **9** was prepared *via* hydrolysis of **7** to **8**, followed by cyclization of **8** with acetyl chloride to yield **9** in 62% over-all yield. Opening of **9** with sodium ethoxide gave **10**, which on reduction with sodium borohydride–aluminum chloride according to the procedure of Brown and Subba Rao[10] gave hydroxy acid **11**, which under the reaction conditions cyclized to yield lactone **12** (Scheme I). Reaction of **12** with potassium *n*-butoxide in *n*-butyl alcohol provided *n*-butyl ester **13** in 80% yield. The *n*-butyl ester was chosen since it was readily separated from traces of unreacted **12**. In addition to 80% of *cis*-hydroxy ester about 10% of the *trans* isomer was formed *via* epimerization of the ester function. The tosylate (**14**) was obtained in 92% yield from **13**, *p*-toluenesulfonyl chloride, and pyridine in chloroform. When **14** was treated with sodium hydride in N,N-dimethylformamide at 60° a mixture of *n*-butyl bicyclo[2.1.0]pentane-1-carboxylate (**15**) and bicyclo[2.1.0]pentane-1-carboxylic acid (**16**) was obtained (Scheme II). The yield of **15** was 11%. The acid (**16**) was converted to its methyl ester with diazomethane. This methyl ester was identical in all respects with the sample of **2** prepared by the previously discussed methylene-transfer reaction. In view of the numerous steps involved in synthesizing **14**, the poor yield of **15** made this route unattractive for the preparation of large amounts of 1-substituted bicyclo[2.1.0]pentanes.

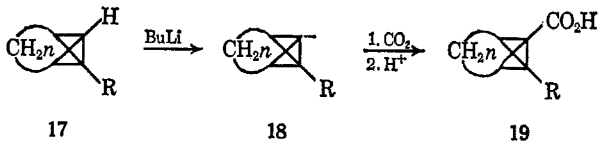
SCHEME I



SCHEME II



It is well known that cyclopropyl hydrogens are reasonably acidic.[11] In addition it has been shown that incorporation of a cyclopropane into a fused ring system increases this acidity.[12,13] Thus, the removal of protons from 1,4-bridged bicyclo[1.1.0]butanes (**17**) was readily accomplished with butyllithium to produce anion **18** which on carbonation yielded **19**[12,13] (eq 3). In less strained systems such as nortricyclane



(3)

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[6] H. E. Simmons, Jr., and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

[7] G. Chirudoglu, T. Doehaerd, and M. Duts, *Bull. Soc. Chim. Belges*, **70**, 642 (1961).

[8] P. G. Gassman, *Chem. Ind.* (London), 740 (1962); H. Weitkamp and F. Korte, *Tetrahedron*, **20**, 2125 (1964); P. G. Gassman and F. V. Zalar, *J. Org. Chem.*, **31**, 166 (1966); H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *ibid.*, **31**, 295 (1966).

[9] E. P. Blanchard, Jr., and A. Cairncross, *J. Am. Chem. Soc.*, **88**, 487 (1966).

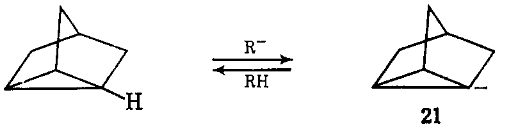
[10] H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 2582 (1956).

[11] A. I. Shatenshtein, *Advan. Phys. Org. Chem.*, **1**, 176 (1963).

[12] J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).

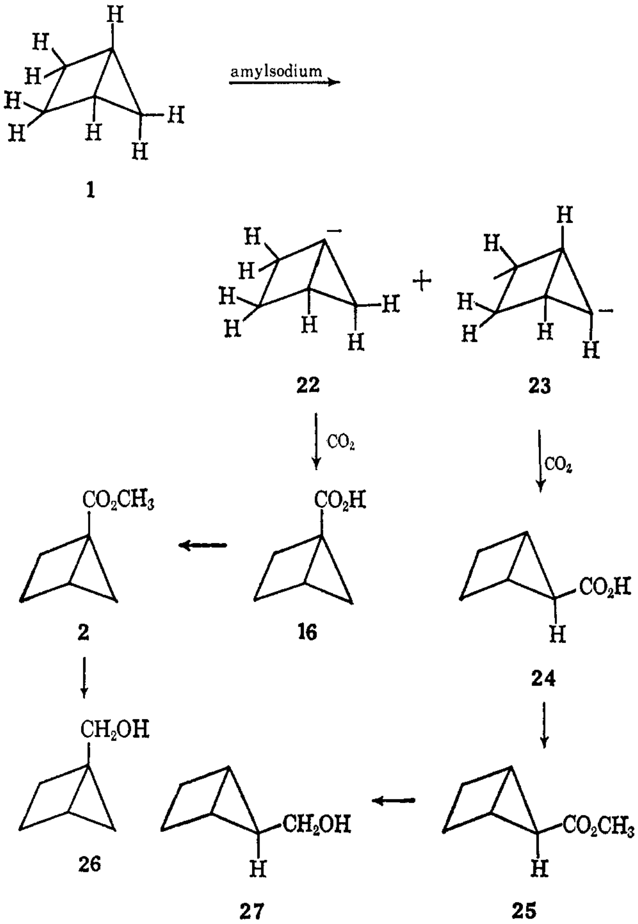
[13] G. L. Closs and R. B. Larrabee, *Tetrahedron Letters*, 287 (1965).

(20) amylsodium was necessary to facilitate a shift of the equilibrium to **21** in a reasonable period of time[14,15] (eq 4). Bicyclo[2.1.0]pentane (**1**) lies between bicyclo[1.1.0]butane (**17**) and nortricyclane (**20**) in strain energy. Thus, it might be anticipated that the acidity of its bridgehead protons would be less than that of **17** and slightly more than that of **20**. Attempts to convert **1** to its anion with butyllithium and subsequent carbonation failed to produce detectable amounts of **16**. However, when **1** was allowed to shake with amylsodium in heptane for 8 days a mixture of anions **22** and **23** were formed. Carbonation of the anions gave **16** and **24**. These were converted to methyl esters **2** and **25**, respectively, with diazomethane. Although these methyl esters could be separated by analytical vpc, they were not cleanly separated on preparative vpc. When the mixture of **2** and **25** was reduced with lithium aluminum hydride a mixture of **26** and **27** was obtained (see Scheme III). Preparative vpc readily separated this mixture of carbinols. The chromatographed samples were dissolved in ether, dried over anhydrous magnesium sulfate, and then distilled. This gave an over-all yield of 18% **26** and 21% **27** from bicyclo[2.1.0]pentane. The structure of **26** was substantiated by its near-infrared absorption at 1.653 μ (ϵ 0.318) and its characteristic nmr spectrum which consisted of a one-proton singlet at τ 5.86, and AB quartet (J = 11.8 cps) centered at 6.40 (CH_2OH), a two-proton doublet at 9.34, a two-proton multiplet centered at *ca.* 8.0, and a three-proton multiplet centered at *ca.* 8.6. In addition the precursor of **26** was shown to have vpc retention times identical with those of **2** on three different columns.



20 **21** (4)

Scheme III

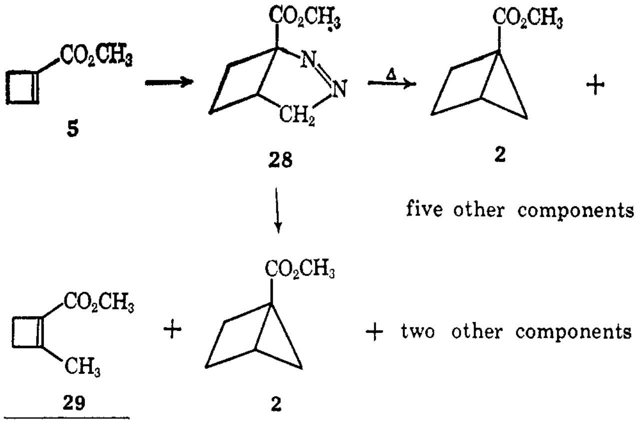


The nmr spectrum of **26** may serve to clarify the assignment of the nmr peaks in the parent hydrocarbon. Chesick has reported[4a] that the spectrum of **1** consisted of three groupings of peaks centered at τ 7.9, 8.6, and 9.5 which he assigned to the bridgehead, cyclobutyl methylene, and cyclopropyl methylene hydrogens, respectively. Since the nmr spectrum of **27** showed only one high-field proton resonance, it would appear that the assignment of the cyclopropylmethylene group was correct. However, **26** showed a two-proton multiplet at τ 7.9 and a three-proton multiplet at 8.6. It would appear that the two-proton multiplet at τ 7.9 was not due to the bridgehead protons as suggested by Chesick but rather to either the *endo*- or *exo*- cyclobutyl protons. This would mean that the absorption at τ 8.6 was due to the bridgehead protons plus either the *exo* or the *endo* protons.

The structure of **27** was proven by a comparison of its nmr spectrum with that of an authentic sample.[4,16] This route offered an attractive preparative route to both **26** and **27**.

Having prepared 1-carbomethoxycyclobutene (**5**) in an early part of this study, we decided to investigate its conversion to a pyrazoline which might be pyrolyzed or photolyzed to yield **2**. When **5** was allowed to stand at room temperature for 3 days with excess diazomethane, a 90% yield of **28** was obtained. Pyrolysis of **28** gave 85% of volatile products. Vapor phase chromatography indicated at least six components. The ester **2** accounted for 30% of the mixture; the other products were not identified. The photolysis of **28** was considerably cleaner than the pyrolysis. When a 450-w Hanovia source with a pyrex filter was used, we obtained 43% of **2** and a 19% yield of **29**. Two other products, which were not identified, were present in *ca.* 7 and 12% yields (see Scheme IV).

Scheme IV



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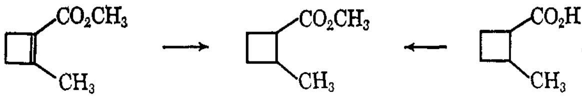
[14] R. A. Finnegan and R. S. McNees, *J. Org. Chem.*, **29**, 3234 (1964).

[15] It should be noted that potassium *t*-butoxide in *t*-butyl alcohol will also remove these acidic protons. However, the position of the equilibrium is unfavorable for subsequent alkylation or carbonation: P. G. Gassman and F. V. Zalar, *J. Am. Chem. Soc.*, **80**, 3070 (1966).

[16] We wish to thank Professor K. Wiberg for providing us with a nmr spectrum of authentic **27**.

The structural assignment of **29** was based on its nmr and ultraviolet spectra combined with its catalytic hydrogenation to methyl *cis*-2-methylcyclobutanecarboxylate (**30**). Reaction of the known[17] acid (**13**) with diazomethane provided an authentic sample of **30** which was identical with our hydrogenation product (eq 5). The formation of **29** under the photolytic conditions described above indicated to us that the pyrazoline formed from **5** had added diazomethane as shown in structure **28**. This is consistent with the nmr data (see the Experimental Section).



(5)

29 **30** **31**

The synthetic sequences outlined above provide a ready source of 1-substituted bicyclo[2.1.0]pentanes. Further reactions of these derivatives of **1** will be the topic of subsequent publications.

Experimental Section

Melting points were taken on a Thomas-Hoover Unimelt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord, Model 137; near-infrared and ultraviolet spectra were determined on a Cary Model 14 recording spectrometer, and nmr spectra were obtained on a Varian A-60 spectrometer employing 10–30% solutions in carbon tetrachloride or deuteriochloroform with tetramethylsilane as an internal standard. An Aerograph Hi-Fi or F & M Model 810 gas chromatograph was used for analytical vpc work while preparative separations were carried out on an Aerograph Auto-Prep, Model 700. Microanalyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark, or by Dr. Alfred Bernhardt, Max-Planck-Institute, Mülheim (Ruhr), Hohenweg, Germany.

Simmons-Smith Reaction with 5.—In a 50-ml, round-bottomed flask containing a small magnetic stirring bar was placed 7.5 g of granular zinc-copper couple,[18] a small amount of hydroquinone, and 25 ml of ether. To this stirred, refluxing mixture was added a mixture of 26.78 g of methylene iodide, 6.25 g (0.0558 mole) of methyl cyclobutenecarboxylate[19] (97% pure by vpc), and 13 ml of monoglyme over a period of 1 hr. After stirring at room temperature for 24 hr another 8.93 g of methylene iodide, 4 ml of monoglyme, and 2.5 g of couple were added. Stirring was continued for another 16 hr.

After 40 hr the volatile substances in the flask were removed by vacuum transfer at 0.1 mm. Removal of ether under reduced pressure and distillation through a 12-cm Vigreux column yielded four fractions (1.271 g) of material boiling between 45 and 59° (17 mm). Analytical vpc indicated the presence of approximately 5.3% of **2** based on starting **5**.

The major impurities were methyl cyclobutanecarboxylate and methyl 1-bromocyclobutanecarboxylate, identified by comparison with the authentic samples. The product from several such experiments was separated on a 10-ft column of 20% SE 30 on Chromosorb W at 90°, dried, and redistilled. The near-infrared spectrum of a pure sample, bp 78° (43 mm), n^{20}_{D} 1.4573, showed absorption at 1.640 μ (ϵ 0.398). The nmr of this material showed a sharp singlet at τ 6.40 (three protons) and multiplets at 7.85, 8.50, and 8.94 which integrated for a total of seven protons. The infrared spectrum showed apparent cyclopropyl absorptions at 3.23 and 9.98 μ,[3,7] and no absorption in the 5.9–6.5-μ region.

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.50; H, 8.05.

***cis*-Cyclobutane-1,2-dicarboxylic Anhydride** (**9**).—To 68.1 g (0.47 mole) of crude **8**, obtained by hydrolysis of 50 g of **7** with 6 *N* hydrochloric acid,[20] in a 1-l., round-bottomed flask equipped with a magnetic stirring bar and condenser, was added 220 ml of acetyl chloride and the mixture was refluxed for 15 hr. Acetyl chloride and acetic acid were distilled off at atmospheric pressure. The brown residue which crystallized on cooling was dissolved in hot benzene and transferred to a 250-ml Claisen flask. After distillation of the benzene at atmospheric pressure the residue was rapidly distilled into a solids receiver at 20 mm to give 40 g of white crystals, bp *ca.* 170°. Recrystallization from benzene gave 37.3 g of **9**, mp 76.5–77.4° (lit.[21] mp 76–77°). A mixture melting point with an authentic sample was undepressed.

Ethyl Sodium *cis*-Cyclobutane-1,2-dicarboxylate (**10**).—Sodium ethoxide, prepared by treating 4.869 g (0.211 g-atom) of sodium metal with 50 ml of anhydrous[22] ethanol, was added to 26.71 g (0.211 mole) of **9** in 50 ml of anhydrous ethanol. The resulting mixture was evaporated to dryness *in vacuo* and the white, crystalline residue (38.0 g) was dried at 65° in a vacuum oven. Owing to its highly hydroscopic nature, no sample was submitted for analysis.

***cis*-(2-Hydroxymethyl)cyclobutanecarboxylic Acid Lactone** (**12**).—A mixture of 8.15 g of sodium borohydride, 38.0 g (0.211 mole) of ethyl sodium *cis*-cyclobutane-1,2-dicarboxylate, and 300 ml of dry diglyme[23] was stirred for 30 min in a three-necked, 500-ml, round-bottomed flask equipped with a mechanical stirrer, a dropping funnel and a condenser. In small portions 9.38 g (0.0703 mole) of anhydrous aluminum trichloride was added to 30 ml of dry diglyme at −10°, and the resulting mixture was slowly added to the reaction vessel through the dropping funnel. Stirring was continued another 0.5 hr after which the mixture was heated to 140° for 90 min with stirring. The cooled reaction mixture was slowly poured over a mixture of 400 g of ice and 40 ml of concentrated hydrochloric acid. The acidic solution was stirred for 0.5 hr, then saturated with salt and continuously extracted with ether for 2 days. The ethereal solution was dried over anhydrous magnesium sulfate and concentrated *in vacuo* to afford a yellow oil. Distillation through a 30-cm Vigreux column gave 17.28 g (73.2%) of **12**, bp 74° (1.15 mm). The compound showed strong infrared absorption at 5.67 μ, characteristic of γ-lactones.[24] An analytical sample, n^{20}_{D} 1.4683, was obtained by preparative vpc on an SE-30 column.

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 63.88; H, 7.21.

Butyl *cis*-(2-Hydroxymethyl)cyclobutanecarboxylate (**13**).—Potassium *n*-butoxide was prepared by adding 1.22 g of potassium to 50 ml of anhydrous *n*-butyl alcohol (Baker Analyzed reagent). To the swirled solution was slowly added 25.95 g (0.232 mole) of **12**. After 15 min the brownish orange solution was poured over 30 g of ice and neutralized with cold hydrochloric acid. Extraction with four 75-ml portions of ether, followed by drying over anhydrous magnesium sulfate and removal of the ether and *n*-butyl alcohol under reduced pressure, left a mixture of starting material and product. Distillation *in vacuo* afforded *ca.* 7 g of starting lactone, 13.4 g of **13**, bp 92° (0.20 mm), n^{20}_{D} 1.4540, and 1.74 g of the *trans* isomer of **13**, bp *ca.* 150° (0.13 mm).

The infrared spectra of the *cis* and *trans* isomers were virtually identical. The nmr spectrum of **13** consisted of a two-proton triplet (J = 6.5 cps, $COOCH_2$) at τ 5.98, a singlet at

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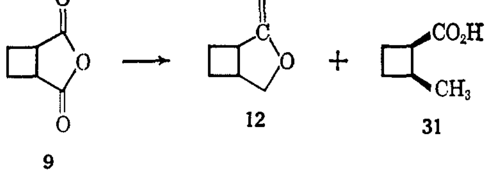
[17] R. McCrindle, K. H. Overton, and R. A. Raphael [*Proc. Chem. Soc.*, 313 (1961); *J. Chem. Soc.*, 4798 (1962)] report that catalytic hydrogenation of **9** yields **31** as the only isolable product. In our hands the major product was the lactone, **12**, while **31** was a minor product.



9 **12** **31**

[18] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

[19] A. Campbell and N. H. Reardon, *J. Chem. Soc.*, 3002 (1953).

[20] E. C. Coyner and W. S. Hillman, *J. Am. Chem. Soc.*, **71**, 324 (1949).

[21] W. H. Perkin, Jr., *J. Chem. Soc.*, **65**, 583 (1894).

[22] L. F. Fieser, "Experiments in Organic Chemistry," Revised 3rd ed, D. C. Heath and Co., Boston, Mass., 1957, p 286.

[23] Distillation of commercial diglyme at 60 mm from calcium hydride followed by distillation from lithium aluminum hydride was necessary to obtain material sufficiently dry. Use of anhydrous diglyme which had been stored for an appreciable length of time drastically reduced the yield of **12**.

[24] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958, p 186.

6.18 (OH), a doublet (J = 5 cps, CH_2OH) at 6.49, a two-proton multiplet at 7.21 (tertiary cyclobutyl protons), four-proton multiplets at 8.05 and 8.55 (cyclobutyl and butyl methylenes), and a three-proton triplet (J = 6 cps, CH_2CH_3) at τ 9.09. The only significant difference in the position of the peaks of the *trans* isomer was the position of the hydroxyl proton which appeared at τ 6.00, thus partially overlapping the ester α-methylene.

Anal. Calcd for $C_{10}H_{18}O_3$ (*cis* isomer): C, 64.49; H, 9.74. Found: C, 64.84; H, 9.78.

Butyl *cis*-(2-Tosyloxymethyl)cyclobutanecarboxylate (14).—A mixture of 9.23 g of **13** and 14.10 g of *p*-toluenesulfonyl chloride in 125 ml of chloroform was cooled to −5°. To the stirred solution was added dropwise 5.85 g of pyridine and the mixture was stirred for 24 hr at room temperature. The chloroform solution was then washed with 60-ml portions of 1 *N* hydrochloric acid, 0.5 *N* hydrochloric acid, water, and 5% sodium bicarbonate, and distilled water. After drying over anhydrous magnesium sulfate the chloroform was removed under reduced pressure to leave about 20 g of yellow oil which would not crystallize even at −20°. The oil was placed in a short-path distillation flask. Distillation at 60° (0.009 mm) removed all volatile impurities leaving 15.57 g (92.4%) of **14** as a yellow, viscous liquid. An analytical sample obtained by molecular distillation of *ca.* 0.05 g of this material for 3 days at 60° (0.005 mm) was also yellow and there was no significant difference between its infrared spectrum and that of the undistilled material.

Anal. Calcd for $C_{17}H_{24}O_5S$: C, 59.99; H, 7.11. Found: C, 60.04; H, 7.35.

Butyl Bicyclo[2.1.0]pentane-1-carboxylate (15).—Under a dry nitrogen atmosphere 1.42 g of 51.6% sodium hydride in mineral oil was placed in a magnetically stirred, 100-ml, round-bottomed flask equipped with a short side arm capped with a rubber septum. After installation of a gas inlet tube, constant-pressure dropping funnel, and condenser, the mineral oil was removed by two washings of the sodium hydride with 20-ml portions of hexane which were introduced and withdrawn from the flask through the rubber septum with a hypodermic transfer syringe. Then 40 ml of N,N-dimethylformamide freshly distilled *in vacuo* from calcium hydride and stored briefly over Linde 13X molecular sieves was injected. After heating the stirred mixture to 60° under nitrogen, 3.62 g (0.0106 mole) of **14** dissolved in 40 ml of dry dimethylformamide was added dropwise over a period of 5 hr. After an additional 3 hr of heating and stirring, the cooled suspension was poured slowly into 50 ml of an ice-cold, saturated ammonium chloride solution. Following addition of 10 g of ice the stirred mixture was slowly allowed to warm up to room temperature over 0.5 hr. Extraction with four 50-ml portions of ether, followed by drying over anhydrous magnesium sulfate and removal of the solvent under reduced pressure left *ca.* 6 g of a dimethylformamide solution of starting material and reaction products. This residue was triturated with three 20-ml portions of hexane and the combined hexane extracts were washed with three 10-ml portions of distilled water, dried over anhydrous magnesium sulfate, and concentrated. Distillation through a 12-cm Vigreux column yielded 150 mg of material, bp 75–76° (2.7 mm), 238 mg, bp 120–130° (2.7 mm), and 179 mg of material, bp 150–170° (0.01 mm). Analytical vpc revealed that 95% of the first fraction and 16% of the second fraction was **15** for a total yield of 11.4%. The other components were not investigated thoroughly, although two of them were identified as **12** and **13** by comparison of vpc retention times with those of authentic samples on several different columns.

The product was purified by preparative vpc on 10-ft of 20% SE-30 on Chromosorb W. Its infrared spectrum, which was strikingly similar to that of **2**, showed apparent cyclopropane absorptions at 3.23 and 9.94 $\mu^{3,7}$ and no absorption in the 5.9–6.5-μ region.

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.09; H, 9.51.

Acidification with hydrochloric acid of the previously extracted basic aqueous solution obtained above was followed by extraction with three 50-ml portions of ether and drying of the combined ether extracts over anhydrous magnesium sulfate. Treatment of the solution with ethereal diazomethane and removal of the ether under reduced pressure yielded mostly dimethylformamide. This material was dissolved in 15 ml of hexane, washed with several portions of distilled water, dried, and concentrated. Distillation gave only *ca.* 10 mg of **2**, identified by its infrared spectrum and vpc retention time on several different columns. In other experiments in which the exclusion of moisture was not so successful, the ratio of **2** to **15** was much higher.

Reaction of Bicyclo[2.1.0]heptane (1) with Amylsodium.—In a drybox under a dry argon atmosphere, a solution of 11.03 g (0.162 mole) of **1** in 400 ml of dry, olefin-free hexane was added to a suspension of *ca.* 20 g of amylsodium in heptane (Orgmet Co., Hampstead, N. H.) in a bottle with a screw cap. The cap was sealed with paraffin and the bottle was mechanically shaken for 8 days. The mixture was then carbonated by slowly pouring into a stirred hexane slurry of powdered Dry Ice. The mixture was stirred with exclusion of moisture until the dark color of the sodium alkyls had disappeared and only pale yellow solids remained. Then 5 ml of ethanol was added to destroy traces of metallic sodium, and the mixture was stirred for 1 hr. After addition of 200 ml of water, the aqueous phase was separated, washed with four 50-ml portions of ether, and carefully acidified with concentrated hydrochloric acid in an ice bath. The solution was then saturated with salt and extracted with four 100-ml portions of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give 23.15 g of crude acid mixture. This mixture was dissolved in 40 ml of anhydrous ether and added dropwise to a stirred slurry of 9.0 g of lithium aluminum hydride in 150 ml of dry ether. The mixture was refluxed slowly for 14 hr, then quenched by dropwise addition of 36.0 g of water. After 1 additional hr of reflux the salts were filtered off and triturated with four 100-ml portions of ether. The combined ether fractions were dried over anhydrous magnesium sulfate, filtered, and concentrated. Distillation of the residue gave 11.40 g of alcohols, bp 83–94° (25 mm). Vpc on a 4.5-ft 15% β,β'-oxidipropionitrile on firebrick column at 72° revealed four components in the ratio 44:25:30:1. The three major components were separated 0.7 ml at a time with almost quantitative collection efficiency on a 10 ft × $^3/_8$ in. column of 25% β,β'-oxidipropionitrile on firebrick at 100°. The purified components were taken up in ether, dried over anhydrous magnesium sulfate, filtered, and distilled.

The first component was shown to be *n*-hexyl alcohol by comparison with an authentic sample.

The second substance, 2.83 g (18% from starting bicyclo[2.1.0]pentane) was identified as 1-(hydroxymethyl)bicyclo[2.1.0]pentane (**26**), bp 83° (30 mm). Its infrared spectrum showed absorption at 3.30 μ (cyclopropyl methylene) with no evidence of unsaturation. The compound absorbed at 1.653 μ (ϵ 0.318) in the near-infrared. The nmr spectrum consisted of a one-proton singlet at τ 5.86, an AB quartet (J = 11.8 cps) centered at 6.40, a two-proton doublet at 9.34, a two-proton multiplet centered at 7.95, and a three-proton multiplet centered at 8.6.

Anal. Calcd for $C_6H_{10}O$: C, 73.43; H, 10.27. Found: C, 73.23; H, 10.43.

The third major component of the mixture, 3.27 g (20.6%), bp 83° (23 mm), was shown to be *exo*-5-(hydroxymethyl)bicyclo[2.1.0]pentane[4,16] (**27**) by comparison of its nmr with that of an authentic sample. The compound showed infrared absorption at 3.32 μ and no evidence of unsaturation. The nmr spectrum consisted of a one-proton singlet at τ 5.74 (OH), and a two proton doublet (J = 7 cps) at 6.80 (CH_2OH) coupling with a one-proton triplet at 8.80. The other six protons appeared as two complex multiplets centered at τ 7.9 and 8.6.

In another experiment 5.5 g of a crude mixture of **16** and **24** from carbonation was taken up in ether, cooled, and treated with cold ethereal diazomethane until nitrogen evolution ceased. Excess diazomethane was destroyed with acetic acid. The ether solution was then washed with 5% sodium bicarbonate and water, dried over anhydrous magnesium sulfate, filtered, and concentrated. Distillation of the residue gave 2.90 g of product, bp *ca.* 90° (60 mm). Vpc examination, using 10 ft of 15% butanediol succinate on firebrick at 105° revealed four major components in the ratio 16:36:46:2. The first two components were methyl hexanoate and **2** identified by vpc retention times on three different columns of widely differing polarity. The third component was **25** since lithium aluminum hydride reduced it to the corresponding *exo*-carbinol, **27**.

Methyl 2,3-Diazabicyclo[3.2.0]hept-2-ene-1-carboxylate (28). A mixture of 7.64 g (0.068 mole) of freshly prepared methyl cyclobutene-1-carboxylate, 94% pure by vpc on a 10-ft 15% butanediol succinate column at 100°, and *ca.* 0.15 mole of diazomethane in 300 ml of ether was allowed to stand at room temperature for 3 days.[25] The almost colorless solution was boiled briefly to expel the last traces of diazomethene, dried over anhydrous magnesium sulfate, and filtered. After removal of the solvent on a rotary evaporator, the residue was distilled through a short column to yield 8.97 g (0.058 mole) of methyl 2,3-diazabicyclo[3.2.0]hept-2-ene-1-carboxylate: bp 66° (0.20 mm), n^{26}_{D} 1.4750, λ_{max} 322 mμ (ϵ 216).[25] The product showed infrared absorptions at 5.75 (saturated ester) and 6.51 μ (N=N) and no evidence of olefinic absorption. The nmr spectrum consisted of a partially overlapping one-proton singlet at τ 5.44 and a one-proton doublet at 5.52, a three-proton singlet at 6.42, and three complex multiplets centered at 7.27, 7.88, and 8.63, with relative areas of 2:2:1.

Anal. Calcd for $C_7H_{10}O_2N_2$: C, 54.53; H, 6.54; N, 18.17. Found: C, 54.56; H, 6.57; N, 18.34.

Pyrolysis of Methyl 2,3-Diazabicyclo[3.2.0]hept-2-ene-1-carboxylate (28).—A 1.54-g (0.010 mole) sample of **28** was pyrolyzed at 155° (90 mm) and the volatile products were collected in a cooled receiver. After 2 hr 1.12 g (89%) of colorless liquid, bp *ca.* 110°, had been collected and only a small black residue remained in the pyrolysis flask. A component with the same vpc retention time as authentic **2** accounted for about 30% of the six-component mixture. No column gave sufficient separation to allow preparative separation and the mixture was not further characterized.

Photolysis of Methyl 2,3-Diazabicyclo[3.2.0]hept-2-ene-1-carboxylate (28).—A solution of 3.38 g (0.022 mole) of **28** in 900 ml of dry pentane was irradiated with a 450-w Hanovia lamp in a Pyrex vessel until the pyrazoline absorption at 322 mμ could no longer be detected (5.5 hr). The solvent was then removed on a rotary evaporator and the residue was distilled through a short column to give 2.67 g (82.5%) of colorless liquid, bp 72–77° (34 mm). This consisted of four main components by vpc [10-ft 15% diethylene glycol succinate (DEGS) on Chromosorb P, 115°] in the ratio 9:15:23:53. The third and fourth components were separated from the first two on a 15 ft × $^3/_8$ in. column of 25% DEGS on Chromosorb P at 120°. The major component was shown to be **2** by direct comparison with an authentic sample.

The third component, bp 78° (40 mm), n^{20}_{D} 1.4612, λ_{max} 227 mμ (ϵ 12,300), was identified as methyl 2-methylcyclobutene-1-carboxylate (**29**). Its infrared spectrum showed stong absorptions at 5.81 (conjugated ester) and 6.00 μ (C=C).[26] The nmr spectrum of **29** consisted of a three-proton singlet at τ 6.36, a four-proton multiplet centered at 7.6 (ring methylenes), and an apparent octuplet (three protons, J = 1 cps) at 8.02.[27]

Anal. Calcd for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.47; H, 7.96.

Reduction of *cis*-Cyclobutane-1,2-dicarboxylic Anhydride (9).[17]—A solution of 1.26 g (0.010 mole) of **9** in 70 ml of reagent ethyl acetate was hydrogenated over 0.630 g of prereduced platinum oxide at 26° (745 mm). After 12 hr 601 ml (0.024 mole) of hydrogen had been consumed and the rate of hydrogen uptake had slowed to less than 1 ml/hr. The solution was filtered through Celite, and the solvent was removed at reduced pressure. The residue was taken up in ether and treated with cold, ethereal diazomethane until a yellow color persisted. Excess diazomethane was removed by brief boiling, and the ether was distilled off. Distillation of the residue gave 132 mg of pure methyl *cis*-2-methylcyclobutane-1-carboxylate (**30**), bp 62° (30 mm), and 556 mg of a 1:5 mixture of **30** and **12**, bp 96–101° (8 mm). Lactone **12** was collected by preparative vpc (SE 30 column) and identified by comparison with an authentic sample. The nmr spectrum of **30** consisted of a three-proton singlet at τ 6.39, a three-proton doublet (J = 6.5 cps, $CHCH_3$) at 8.99, and a broad six-proton envelope extending from 6.54 to 8.58.

Reduction of Methyl 2-Methylcyclobutene-1-carboxylate (29).—A solution of 126 mg (0.001 mole) of **29** in 10 ml of acetone was hydrogenated over 20 mg of prereduced 5% palladium on carbon. Hydrogen uptake ceased abruptly after 22 min with 25.3 ml (1.01 equiv) of hydrogen being consumed. After an additional 10 min the solution was filtered through Celite and concentrated to give 111 mg of **30**, identical with an authentic sample by infrared spectroscopy and vpc retention times on two different columns.

Registry No.—**9**, 7687-27-6; **12**, 7687-28-7; **13**, *trans* isomer, 7695-32-1; **13**, *cis* isomer, 7687-29-8; **14**, 7687-30-1; **15**, 7690-92-8; **26**, 7687-31-2; **27**, 7687-32-3; **28**, 7687-33-4; **29**, 7687-34-5; **30**, 7687-35-6.

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[25] T. V. Van Auken and K. L. Rinehart, *J. Am. Chem. Soc.*, **84**, 3736 (1962).

[26] Reference 24, p 36.

[27] It is well known (J. D. Roberts, "Nuclear Magnetic Resonance, Applications to Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, pp 54, 103) that the nmr spectrum of cyclobutene consists of two singlets. Similarly J. Shabtai and E. Gel-Av [*J. Org. Chem.*, **28**, 2893 (1963)] have shown that the methylene protons of 1-methylcyclobutene are unsplit. However, we have observed that the methylene protons of **5** appear as a typical A_2X_2 pattern of two triplets (J = 3 cps) with fine structure, centered at τ 7.30 and 7.56. The vinyl proton appeared as a multiplet at τ 3.23.

The Reaction of 2,3,4-Trimethylpentane in Concentrated Sulfuric Acid

G. M. KRAMER

Central Basic Research Laboratory, Esso Research and Engineering Company, Linden, New Jersey

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The effect of acidity on the reaction of 2,3,4-trimethylpentane in sulfuric acid has been investigated using tritiated acid. The reaction after an induction period appears to follow a second-order dependence on proton activity. The initial reaction leads to the formation of butyl ions and butylene in the acid. The product distributions provide evidence for an initially homogeneous reaction which acquires considerable heterogeneous character as reaction proceeds.

The behavior of paraffins in concentrated sulfuric acid has been studied extensively and is known to be quite complex. Difficulties in interpreting results arise for many reasons. Among these are the facts that the systems are heterogeneous, that an initiation process appears necessary for reaction, that the distinction between initiation and reaction rates as well as the dependence of each upon acid strength is not well understood, and that the nature of the reaction intermediates is not universally agreed upon.

This paper is primarily concerned with the relationship between reaction rate and acid strength. This investigation has been carried out with tracer techniques using tritiated acid. The relationship obtained is similar to that found by Beeck, Otvos, Stevenson, and Wagner[1] for hydrogen-exchange reactions of isobutane in sulfuric acid, but different from one reported by Roebuck and Evering,[2] with a different paraffin. In addition, some qualitative and quantitative information pointing to paraffin oxidation as an initiating step and evidence for the occurrence of reaction at two sites (bulk acid and interface) have been obtained.

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[1] O. Beeck, J. W. Otvos, D. P. Stevenson, and C. D. Wagner, *J. Chem. Phys.*, **17**, 418 (1949).

[2] A. K. Roebuck and B. L. Evering, *J. Am. Chem. Soc.*, **75**, 1631 (1953).