[CONTRIBUTION FROM THE DIAMOND ORDNANCE FUZE LABORATORIES]

Synthesis of 2,2-Dialkylcyclopropane Nitriles[1]

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The ditosylate of 2,2-dimethyl-1,3-propanediol reacted with potassium cyanide in ethylene glycol to give 2,2-dimethylcyclopropane nitrile in 63% yield. In a similar manner, the ditosylate of 2,2-diethyl-1,3-propanediol was converted to 2,2-diethylcyclopropane nitrile. The ditosylates of 1,3-propanediol and 2-methyl-1,3-propanediol failed to yield cyclopropane derivatives when treated under comparable conditions.

In a recent publication, Brown and van Gulick[2] described the synthesis of 2,2-dimethyl-4-methoxybutyronitrile by the treatment of 2,2-dimethyl-3-methoxypropyl tosylate with potassium cyanide in refluxing ethylene glycol. An attempt to adapt this procedure to the preparation of β,β-dimethylglutaronitrile from the ditosylate of 2,2-dimethyl-1,3-propanediol unexpectedly resulted in a cyclopropane nitrile. On hydrolysis, this nitrile gave 2,2-dimethylcyclopropane carboxylic acid, as shown by comparisons of the infrared spectrum of the corresponding amide with that of the amide of an authentic sample prepared by the method of Kishner.[3] Thus the original cyclopropane nitrile was identified as 2,2-dimethylcyclopropane nitrile.

The physical properties of the acid and amide described above corresponded closely to those reported by Kishner,[3] and also by Blanc,[4] for the same compounds prepared by different methods.

A survey of the methods of synthesizing cyclopropane compounds was compiled by Feldman[5] in 1940. Subsequently Schlatter[6,7] concluded that the most satisfactory method of obtaining cyclopropane nitrile involved the halogenation of 1,3-propanediol followed by reaction with sodium cyanide. This procedure resulted in only a 25% yield of the nitrile. Thus, the reaction of the ditosylate of 2,2-dimethyl-1,3-propanediol with potassium cyanide to give a cyclopropane ring structure appeared to be of interest because of the high yield of 2,2-dimethylcyclopropane nitrile (63%) and the ease of preparation of the ditosylate.

Reactions of potassium cyanide with the ditosylates of three other 1,3-glycols were then attempted in an effort to determine the general applicability of this method of ring closure. In the first experiments, treatment of the ditosylate of 2,2-diethyl-1,3-propanediol with potassium cyanide resulted in a 66% yield of 2,2-diethylcyclopropane nitrile. The infrared spectra of the acid and amide of this compound were similar to those obtained from the dimethylcyclopropanes. Presumably, other 2,2-dialkylcyclopropane nitriles could be prepared in a similar fashion.

The ditosylates of 2-methyl-1,3-propanediol and 1,3-propanediol, however, failed to yield cyclopropane derivatives under comparable conditions. This result probably is due to the absence of geminal alkyl groups and related steric effects in these two compounds. Such effects have been studied by Ingold[8] for the reaction of α-bromo-β-alkylglutaric acid with alkali.

None of the cyclopropane compounds prepared in this investigation had infrared bands in the region 1000 to 1020 cm^{-1} which is reported by Bellamy[9] to be a characteristic absorption band for cyclopropane compounds. However, all five compounds had bands of medium intensity nearby: 2,2-dimethylcyclopropane nitrile at 1034 cm.$^{-1}$, 2,2-dimethylcyclopropane carboxylic acid at 1037 cm.$^{-1}$, 2,2-dimethylcyclopropanecarboxamide at 1036 cm.$^{-1}$, 2,2-diethylcyclopropane nitrile at 1024 cm.$^{-1}$ and 2,2-diethylcyclopropane carboxamide at 1024 cm.$^{-1}$. In all likelihood the characteristic region for cyclopropane absorption should be broadened to 1000–1040 cm.$^{-1}$. This is supported by work of Cromwell and Mohrbacher[10] who reported bands in the region 1025–1036 cm.$^{-1}$.

Experimental

Ditosylate of 2,2-Dimethyl-1,3-propanediol.—A solution containing 286 g. (1.5 moles) of *p*-toluenesulfonyl chloride in 500 ml. of pyridine was held below 0°, and 52 g. (0.5 mole) of 2,2-dimethyl-1,3-propanediol in 100 ml. of pyridine was added. The mixture was stirred at 0° for 2 additional hours and then allowed to stand overnight at room temperature. The reaction mixture was poured into 1 liter of water and ice and the solid collected by filtering. The product was washed with water, dilute sulfuric acid, dilute sodium carbonate and again with water. There was obtained 194 g. of the ditosylate (94% yield) which, after two recrystallizations from a mixture of acetone and water, melted at 121–123°; reported 116–120° by Brown and van Gulick.[2]

Anal. Calcd. for $C_{19}H_{24}S_2O_6$: C, 55.3; H, 5.9; S, 15.5. Found: C, 55.4; H, 5.9; S, 14.9.

2,2-Dimethylcyclopropane Nitrile.—A mixture of 206 g. (0.5 mole) of the ditosylate of 2,2-dimethyl-1,3-propanediol and 97.6 g. (1.5 moles) of potassium cyanide in one liter of ethylene glycol was heated. The solids dissolved on warming and the reaction mixture turned dark when its temperature reached 70 to 90°. The distillation product, produced at 175°, consisted of a mixture of two liquids. Distillation of this mixture continued until a vapor temperature of 198° was reached. One-hundred-fifty ml. of a colorless two-phase system was obtained in about 2 hr. The top phase was separated and the lower phase, ethylene glycol, was extracted three times with 100 ml. of *n*-pentane which was combined with the top phase. The pentane was then removed by distillation and the final product, obtained in 63% yield, was a clear liquid with a very sharp boiling point, 154.5–155.5°, $n^{23}{}_D$ 1.4261, and $d^{24.6}{}_{20}$ 0.8536. It slowly re-

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[1] Presented at the Atlantic City Meeting of the American Chemical Society, September, 1956.

[2] R. F. Brown and N. M. van Gulick, THIS JOURNAL, **77**, 1089 (1955).

[3] N. Kishner, *J. Russ. Phys. Chem. Soc.*, **45**, 957 (1913).

[4] G. Blanc, *Compt. rend.*, **145**, 79 (1907).

[5] Julian Feldman, Master of Arts Thesis, 1940, Brooklyn College, Brooklyn, New York.

[6] M. J. Schlatter, THIS JOURNAL, **63**, 1733 (1941).

[7] M. J. Schlatter, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 221.

[8] C. K. Ingold, *J. Chem. Soc.*, **121**, 2676 (1922).

[9] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1954, pp. 27–28.

[10] N. H. Cromwell and R. J. Mohrbacher, Abstracts 130th Meeting Am. Chem. Soc., page 5-O (Sept. 1956).

duced a 2% potassium permanganate solution, indicating the presence of some unsaturated material.

Anal. Calcd. for C_6H_9N: C, 75.7; H, 9.5; N, 14.7. Found: C, 75.5; H, 9.7; N, 14.6.

2,2-Dimethylcyclopropane Carboxylic Acid.—The nitrile was hydrolyzed by refluxing with aqueous potassium hydroxide for 48 hr. The colorless acid was collected, b.p. 83–84° (5 mm.), 198–201° (1 atm.), n^{20}_D 1.4405 (78% yield); reported for 2,2-dimethylcyclopropane carboxylic acid, b.p. 100° (10 mm.), b.p. 198° (751 mm.),[4] n_D 1.4385.[3] This acid slowly reduced a 2% potassium permanganate solution, indicating the presence of some unsaturated material.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.1; H, 8.8. Found: C, 63.3, 62.8; H, 8.9, 9.0.

2,2-Dimethylcyclopropane Carboxamide.—The acid was converted into the amide *via* the acid chloride, by action of liquid ammonia upon the latter compound. The amide, after recrystallization from ethyl acetate, gave white needles, m.p. 177–177.5°; reported[4] m.p. 177°, yield 44%.

This amide did not reduce a dilute solution of potassium permanganate in acetone.

Anal. Calcd. for $C_6H_{11}NO$: C, 63.7; H, 9.8. Found: C, 63.7; H, 9.8.

A sample of this amide was hydrolyzed back to the acid using aqueous potassium hydroxide; this acid, n^{20}_D 1.4398, did not decolorize dilute potassium permanganate.

2,2-Dimethyl-1-isobutenylcyclopropane.—This synthesis was performed by a modification of methods described by Kishner[3] and Smith and Rogier.[11] To a mixture of 127.4 g. (0.92 mole) of phorone in 250 ml. of absolute ethanol, cooled in an ice-bath, there was added 93.3 g. (1.84 moles) of hydrazine hydrate in small amounts with stirring. After the reaction mixture had cooled, it was heated on a water-bath for an hour. The excess hydrate and ethanol were removed under 15 mm. pressure and a temperature of 80°.

The crude pyrazoline obtained from the above reaction was mixed with 6.2 g. of 5% platinum on asbestos and 14.0 g. of powdered potassium hydroxide, after which it was heated in an oil-bath. At a bath temperature of 175°, 2,2-dimethyl-1-isobutenylcyclopropane began to distil from the reaction mixture with evolution of nitrogen. The temperature of the bath was raised to 200° over a period of 2 hr. by which time the distillation had ceased. Upon redistillation, 69 g. (55% over-all yield) was obtained, b.p. 130–132°.

2,2-Dimethylcyclopropane Carboxylic Acid and its Amide.—A mixture of 25 g. (0.2 mole) of the above hydrocarbon and 63.2 g. (0.4 mole) of potassium permanganate in one liter of water was stirred at room temperature for 4 hr. The manganese dioxide was removed by filtration and the filtrate was made acid to litmus with dilute sulfuric acid. The acid was extracted with ether, and distillation of the ether solution gave 3.7 g. (8.1% yield) of 2,2-dimethylcyclopropane carboxylic acid, b.p. 95–98° (12 mm.). The infrared spectrum showed this material to be somewhat impure.

The amide of this sample was prepared by treating the acid with thionyl chloride and aqueous ammonium hydroxide according to the method of Shriner and Fuson.[12] The amide melted at 177° with sublimation. The spectrum of this amide was the same as that of the amide prepared from the acid originally obtained from the reaction of the 2,2-dimethyl-1,3-propanediol ditosylate and potassium cyanide.

Ditosylate of 2,2-Diethyl-1,3-propanediol.—To 66.1 g. (0.5 mole) of 2,2-diethyl-1,3-propanediol there was added 286 g. (1.5 moles) of *p*-toluenesulfonyl chloride in 600 ml. of pyridine. This synthesis was carried out in the same fashion as that used previously for 2,2-dimethyl-1,3-propanediol. The product was crystallized from acetone yielding 152.1 g. (69% yield), m.p. 109–110°.

Anal. Calcd. for $C_{21}H_{28}O_6S_2$: C, 57.2; H, 6.4. Found: C, 57.2; H, 6.5.

2,2-Diethylcyclopropane Nitrile.—This reaction was conducted in a fashion similar to that described previously for the ditosylate of 2,2-dimethyl-1,3-propanediol. A solution of 152 g. (0.34 mole) of the above ditosylate, 65.1 g. (1.0 mole) of potassium cyanide and a liter of ethylene glycol was heated. A codistillation took place at a vapor temperature of 188° giving a two-phase distillate. The lower phase was extracted with *n*-pentane, and the pentane extract was combined with the upper phase. The combined solution was washed with water, dried with calcium sulfate and distilled. It yielded 28.4 g. (66% yield) of 2,2-diethylcyclopropane nitrile, n^{20}_D 1.4422, b.p. 76–77° (8 mm.). The infrared spectrum was similar to that obtained with 2,2-dimethylcyclopropane nitrile.

Anal. Calcd. for $C_8H_{13}N$: C, 78.0; H, 10.6. Found: C, 77.8; H, 10.8.

2,2-Diethylcyclopropane Carboxylic Acid and Amide.—Thirty-five and five-tenths grams of 2,2-diethylcyclopropane nitrile was hydrolyzed by refluxing in an alcoholic solution of potassium hydroxide for 4.5 days. The resulting mixture was filtered and yielded 25 g. of the crude amide (61% yield), m.p. 133–135°. Recrystallization from a mixture of ethyl alcohol and water raised the melting point to 136–137° with sublimation. The amide did not react with dilute potassium permanganate solution in acetone.

Anal. Calcd. for $C_8H_{15}NO$: C, 68.04; H, 10.7. Found: C, 67.9; H, 10.6.

The filtrate from the above-described filtration of the amide was extracted with ether and acidified. The acid was extracted with ether. The ether extract was distilled, yielding 7.5 g. (18.2% yield) of 2,2-diethylcyclopropane carboxylic acid, b.p. 109–112° (6 mm.), $n^{25.5}_D$ 1.4488.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found: C, 67.6; H, 9.8.

Ditosylate of 1,3-Propanediol.—This synthesis also was conducted in a fashion similar to that described previously for the ditosylate of 2,2-dimethyl-1,3-propanediol. Thirty-eight g. (0.5 mole) of propanediol-1,3 was added to 286 g. (1.5 moles) of *p*-toluenesulfonyl chloride in 600 ml. of pyridine, and the product was recrystallized from acetone and water yielding 106 g. (55% yield), m.p. 94°; reported[13] 94°.

Reaction of Potassium Cyanide with the Ditosylate of 1,3-Propanediol.—This reaction was carried out in the same fashion as that described for the ditosylate of 2,2-dimethyl-1,3-propanediol. A solution of 152.1 g. (0.39 mole) of the ditosylate of propanediol-1,3, 77.4 g. (1.19 moles) of potassium cyanide and 750 g. of ethylene glycol was heated and distillation began at 199°. The distillation was stopped when 100 ml. of distillate was collected and found to contain only ethylene glycol.

2-Methylpropanediol-1,3.—To a slurry of 50.4 g. (1.33 moles) of lithium aluminum hydride in 1.5 liters of anhydrous ether, there was added, over a period of 2 hr., 231.9 g. (1.33 moles) of ethyl methylmalonate, b.p. 82–84° (13 mm.), which had been prepared by a method described in "Organic Syntheses."[14] After the addition was completed, the mixture was refluxed for an additional hour. Upon cooling, 25 ml. of 1-propanol was added followed by 250 ml. of saturated sodium chloride solution. After the salts were removed by filtration and the ether by evaporation, the solution was distilled through a two-foot-long vacuum Vigreux column, yielding 41.7 g. (46.3% yield) of 2-methylpropanediol-1,3, b.p. 106–109° (16 mm.), n^{25}_D 1.4433; reported[15] b.p. 107–109° (12 mm.); reported[16] n^{4}_D 1.4499.

Ditosylate of 2-Methylpropanediol-1,3.—This synthesis was conducted in a fashion similar to that described for the ditosylate of 2,2-dimethyl-1,3-propanediol. To 45.06 g. (0.5 mole) of 2-methylpropanediol there was added 286 g. (1.5 moles) of *p*-toluenesulfonyl chloride in 600 ml. of pyridine. When the reaction mixture was poured into ice-water, there was obtained an oil which was difficult to crystallize. Recrystallization from methanol four times, and from ether and pentane twice, did not produce a material of sharp or constant melting point. Yield after six recrystallizations: 83.66 g. (42% yield) of white crystals, m.p. 78–83°. The infrared spectrum showed this material to be similar to the other ditosylates and free of hydroxyl groups.

Anal. Calcd. for $C_{18}H_{22}S_2O_6$: C, 54.3; H, 5.6. Found: C, 54.6; H, 5.8.

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(11) L. I. Smith and E. R. Rogier, THIS JOURNAL, **73**, 3841 (1951).

(12) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, New York, N. Y., 1948.

(13) I. Heilbron, "Dictionary of Organic Compounds," Revised Edition, Oxford Press, New York, N. Y., 1953.

(14) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943.

(15) J. Brewster, THIS JOURNAL, **73**, 368 (1951).

(16) R. Plummerer, *Ber.*, **75B**, 867 (1942).

Reaction of Potassium Cyanide with the Ditosylate of 2-Methylpropanediol.—This reaction was also carried out in the same fashion as that described for the ditosylate of 2,2-dimethyl-1,3-propanediol. A solution of 83.6 g. (0.22 mole) of the ditosylate of 2-methylpropanediol and 43.0 g. (0.66 mole) of potassium cyanide in 600 ml. of ethylene glycol was heated. There was no distillate below the boiling point of ethylene glycol. Extraction of the 175 ml. of distillate with *n*-pentane, and evaporation of the pentane, yielded no product.

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[CONTRIBUTION FROM THE MCPHERSON CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Reaction of *t*-Butylethylene and 1-Hexene with Bromine in Methanol[1a]

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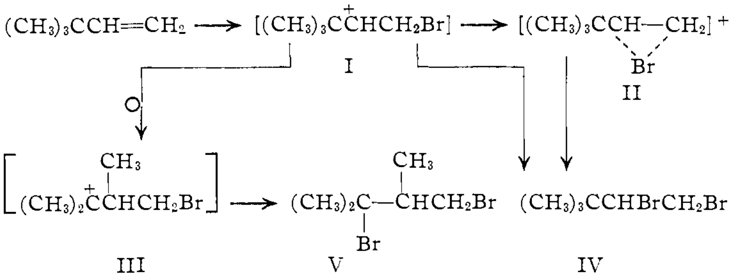
The addition of bromine in methanol to *t*-butylethylene produces 1,2-dibromo-3,3-dimethylbutane (IV) and 2-bromo-1-methoxy-3,3-dimethylbutane (VI) in roughly equal amounts. The addition of bromine in methanol to 1-hexene produces about 31% of 1,2-dibromohexane and 59% of a mixture of 1-bromo-2-methoxyhexane and 2-bromo-1-methoxyhexane in the ratio four-to-one, respectively. The mechanism of these reactions is discussed.

The work herein described was undertaken to obtain qualitative evidence about the mechanism of addition of bromine to *t*-butylethylene in particular and to olefins in general. The interest in this work was aroused by the report that the rate of bromination of *t*-butylethylene was only slightly less than that of *n*-butylethylene[2] (0.70 to 1.05).

The rate-determining step undoubtedly involves the formation of a positively-charged bromine-containing intermediate since the rates are first order with respect to olefin and bromine.[2] If the first-formed intermediate is the carbonium ion I, the further reaction of I with the reaction medium might involve attachment of bromine directly to the internal carbon of I. Alternatively, compound I might rearrange to the cyclic bromonium ion II or to skeletally rearranged III. Both I and II would yield the dibromide IV, whereas III would yield the 1,3-dibromide V.



Although the British authors recognized that the further reaction of I would be expected to be slow[3] because of the neopentyl character of the intermediate, they did not go into any further discussion of how I forms final product nor did they prove the structure of the dibromide formed.

In our analysis of this problem we believed that if Compound I were formed directly, it would rearrange rapidly to II which would then be expected to react further at the terminal less hindered carbon to yield IV.[4] The noteworthy feature of this over-all reaction path is that *both bromine atoms enter the final molecule by attack at the terminal carbon*.[5,6]

In order to test this hypothesis, we have studied the reaction of *t*-butylethylene and of *n*-butylethylene with solutions of bromine in methanol, a reagent which adds bromo and methoxy groups to an olefin.[7]

The addition of a solution of bromine in methanol to *t*-butylethylene yielded about 45% of 1,2-dibromo-3,3-dimethylbutane (IV) and 44% of 2-bromo-1-methoxy-3,3-dimethylbutane (VI). The structure of IV was proved by debromination with zinc to yield *t*-butylethylene. The structure of VI was proved by dehydrobromination with sodium amide in liquid ammonia to an unsaturated ether VII, which on treatment with 2,4-dinitrophenylhydrazine reagent afforded the 2,4-dinitrophenylhydrazone of *t*-butylacetaldehyde in high yield. This result supports the hypothesis that both addenda enter the molecule by attack at the terminal carbon, although the first-formed species may be either I or II.

Although the accuracy of our experimental work does not exclude the possibility that small amounts of skeletally rearranged substances were formed, certainly the quantities were very small, if any. This finding is of interest in light of the fact that addition of hydro-

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[1a] This work was supported by a grant from the National Science Foundation. (b) Thiel College, Greenville, Pennsylvania.

[2] P. W. Robertson, J. K. Heyes and B. E. Swedlund, *J. Chem. Soc.*, 1014 (1952). In this paper steric factors are ruled out on what seems to us inadequate grounds.

[3] However, if the formation of the bromine-containing intermediate I is the rate-determining step, the rate of further reaction of I would not affect the over-all rate.

[4] The stereochemistry of addition of bromine to *cis*- and *trans*-olefins demands an intermediate of type II. However, with *t*-butylethylene it is conceivable that an intermediate of type I could form first and then go into a type II intermediate.

[5] See M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 243.

[6] See also S. Winstein and L. Goodman, THIS JOURNAL, **76**, 4373 (1954), for an example of non-Markownikow addition of the elements of bromine and methoxyl to α,α-dimethylallyl alcohol.

[7] P. D. Bartlett and D. S. Tarbell, *ibid.*, **58**, 466 (1936).