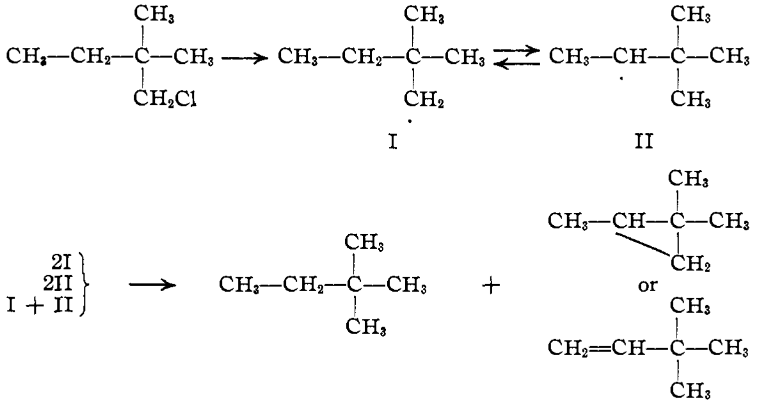
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Common Basis of Intramolecular Rearrangements. VIII.[1] The Formation of Cyclopropanes from Monohalides and Sodium. II.[1] The Formation of 1,1,2-Trimethylcyclopropane from 1-Chloro-2,2-dimethylbutane

BY FRANK C. WHITMORE AND THOMAS P. CARNEY

The reaction of neopentyl chloride with sodium to give neopentane and 1,1-dimethylcyclopropane is a new type of reaction.[1] We have now found another example of this process involving the simplest homolog of neopentyl chloride, 1-chloro-2,2-dimethylbutane. This chloride with sodium gives neohexane (2,2-dimethylbutane), 1,1,2-trimethylcyclopropane, and *t*-butylethylene in percentage yields of 29, 13 and 8. All attempts to find 1-methyl-1-ethylcyclopropane failed. Only a small amount of the coupled product 3,3,6,6-tetramethyloctane appeared. No product due to a rearrangement of a methyl or ethyl group could be detected. This is further evidence that the rearrangements accompanying the dehydration of *t*-amylcarbinol to give 2-methyl- and 3-methyl-2-pentenes[2] do not occur by a free radical mechanism.[1] The products of the present reaction and the absence of 1-methyl-1-ethylcyclopropane indicate the following changes



The mechanism is probably bimolecular.[1] Neohexane is formed from the free radicals of both neohexyl and pinacolyl. It is highly significant that the free pinacolyl radical gives no olefin other than *t*-butylethylene, whereas the dehydration of pinacolyl alcohol gives very little of this olefin but mainly the rearranged products tetramethylethylene and 1,1-methylisopropylethylene.[3]

We believe that the key to the free radical reactions observed by us lies in the work of Smith and Taylor on the action of free methyl radicals on hydrocarbons,[4] and in the earlier work of Rice and others on free radicals.[5]

Experimental

The Reaction of 1.02 Moles of 1-Chloro-2,2-dimethylbutane with 1.0 Mole of Sodium.—The apparatus consisted of a 500-cc. three-necked flask fitted with a thermometer extending below the liquid level, and a reflux condenser to the outlet of which was attached a Gilman trap through a dry-ice–acetone trap. The third neck of the flask through which the sodium was added was closed with a rubber stopper.

To the flask was added 122 g., 1.02 moles, of 1-chloro-2,2-dimethylbutane, b. p. 116.1° at 735 mm., $n^{20}\mathrm{D}$ 1.4200, and, after cooling the flask to 10° by means of an ice-bath, 5 g. of sodium cut into about 3-mm. cubes. No reaction took place. When the mixture was allowed to come to room temperature, a vigorous reaction occurred. Cooling was necessary. The temperature rose to 92°. By alternately raising and lowering the ice-bath around the reaction flask the reaction was kept under control. Over a period of five hours a total of 23 g., 1 mole, of sodium was added. The temperature was maintained at 55–70°. The reaction mixture was allowed to stand for twelve hours. The material boiling 40–120° was stripped off through a packed column with the liquid collected in the dry-ice–acetone trap. Fractionation of the material through a packed column of 80 theoretical plates gave the following results: Cuts 1–6, wt. 4.8 g., $n^{20}\mathrm{D}$ 1.3760, b. p. 41–42° at 760 mm.; 7–13, 5.9 g., 1.3744–1.3697, 42–49.5° at 760 mm.; 14–39, 20.7 g., 1.3689, 50.5–51° at 760 mm.; 40–60, 14.0 g., 1.3695–1.3872, 51–56.5° at 760 mm.; 61–68, 5.3 g., 1.3880, 57–58° at 760 mm.; 69–74, 4.7 g., 1.3884–1.4179, 58–117° at 760 mm.; 75–83, 8.1 g., 1.4192, 118° at 760 mm. Cuts 56–60, and cut 69 were refractionated through a packed micro-column of 20 theoretical plates. The following results were obtained: cuts 84–85, 0.95 g., 1.3854–1.3870, 52–54° at 730 mm.; 86–88, 2.4 g., 1.3876–1.3878, 55° at 730 mm. Cuts

---

[1] VII, Whitmore and co-workers, THIS JOURNAL, **63**, 124 (1941).

[2] Unpublished results from this Laboratory.

[3] Whitmore, *et al.*, THIS JOURNAL, **55**, 3721 (1933); **56**, 1395 (1934).

[4] Smith and Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

[5] Rice and Rice, "The Aliphatic Free Radicals," The Johns Hopkins Press, 1935; Meinert, THIS JOURNAL, **55**, 979 (1933); Whaley, Ph.D. Thesis, Johns Hopkins Univ., 1932, *cf.* Rice and Rice, p. 62; Simons, McNamee and Hurd, *J. Phys. Chem.*, **36**, 939 (1932); Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934); Leermakers, *ibid.*, **56**, 1537, 1899 (1934).

7–13 were redistilled through the same micro column; 89–91, 1.9 g., 1.3764–1.3768, 41° at 730 mm.; 92–96, 2.2 g., 1.3756–1.3696, 42–47° at 730 mm.; 97–98, 1.4 g., 1.3689, 50° at 730 mm. Cuts 40–55 were refractionated through the micro column: cut 99, 0.62 g., 1.3679, 49° at 730 mm.; 100–103, 2.1 g., 1.3688–1.3689, 50° at 730 mm.; 104–111, 5.3 g., 1.3694–1.3869, 51–55° at 730 mm.; 112–115, 2.3 g., 1.3874–1.3878, 55° at 730 mm.

The residual solid of the original reaction mixture was washed with ten 100-cc. portions of dry ether. The weight of the solid residue was 65 g. The ether was stripped off the extract through a packed column, and the residue fractionated through a column of 12 theoretical plates. Cuts 116–120, 7.3 g., 1.4230–1.4232, 125° at 140 mm. were obtained.

Identification of Products.—The physical properties of cuts 1–6, and 89–91 correspond to those of *t*-butylethylene. The combined cuts were ozonized by the method of Whitmore and Church.[6] Formaldehyde was found in the water layer of the decomposed reaction mixture, and was identified by its dimetol derivative, m. p. 189–190°. Trimethylacetaldehyde was isolated from the oil layer, and identified by its 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 210–211°. The original olefin, therefore, 6.68 g., 0.0795 mole, 7.8% yield, was *t*-butylethylene.

Cuts 14–39, 97–98 and 100–103, wt. 24.2 g., 0.28 mole, 27.1% yield, were identified by their physical properties as neohexane.

Cuts 75–83, 8.09 g., 0.067 mole, 6.5% yield, were identified from their physical properties as unreacted 1-chloro-2,2-dimethylbutane.

Cuts 116–120, 7.3 g., 4.29% yield, are probably impure 3,3,6,6-tetramethyloctane, b. p. 125° at 140 mm., $n^{20}\mathrm{D}$ 1.423.

Cuts 61–68, 86–88, and 112–115, wt. 10.3 g., 11.8% were identified as 1,1,2-trimethylcyclopropane by comparing the physical properties with those of a known sample of this compound prepared in this Laboratory and by eliminating all possible cyclic and olefinic isomers on the basis of the incompatibility of their physical properties with those of the compound recovered from the reaction.

Preparation of 1,1,2-Trimethylcyclopropane by the Cyclization of 2-Methyl-2,4-dibromopentane.—The method of Zelinsky and Zelikoff was used.[7] The dibromide was prepared in 42% yield by heating 2-methyl-2,4-pentanediol to 60° for twelve hours with aqueous hydrobromic acid. The starting glycol[8] was obtained in almost theoretical yields by the catalytic hydrogenation of diacetone alcohol. The method of Hass and McBee[9] was used in the cyclization.

The apparatus consisted of a three-necked flask fitted with a mercury-sealed stirrer, a dropping funnel and a small air condenser to the outlet of which were attached two dry-ice–acetone traps in series. To the flask were added 100 g. of dry, recrystallized acetamide, 17.2 g. of sodium carbonate, 5.6 g. of sodium iodide and 52 g. of zinc dust. The reaction flask was heated by means of an air-bath. The bath was raised to 155° and 162 g., 0.66 mole, of 2-methyl-2,4-dibromopentane was added with stirring over a period of six hours. The low boiling products were collected in the dry-ice–acetone traps and fractionated from sodium through a 25-plate packed column. After two refractionations, 8.0 g. of material, b. p. 54–54.5° at 735 mm., $n^{20}\mathrm{D}$ 1.3876–1.3878, was obtained.

The corrected properties of the 1,1,2-trimethylcyclopropane obtained both from the Wurtz reaction and from the dibromide, together with the properties of the other isomeric compounds possible from this reaction are tabulated:

Compound	B. p., °C. at 760 mm.	d^{20}	$n^{20}\mathrm{D}$
1,1,2-trimethyl cyclopropane—from Wurtz reaction	56.5–57.0 (735 mm.)	0.6967	1.3880
—from dibromide	55.5–56.5 (735 mm.)	.6941	1.3876
3-Methyl-1-pentane	53.6	.6700	1.3855
4-Methyl-1-pentene	53.8	.6647	1.3825
cis-4-Methyl-2-pentene	58	.6704	1.3885
2,3-Dimethyl-1-butene	55.8	.6825	1.3915
3,3-Dimethyl-1-butene	41.2	.6519	1.3766
2,3-Dimethyl-2-butene	73.3	.7054	1.4116

The reaction of aqueous potassium permanganate on the 1,1,2-trimethylcyclopropane prepared from the dibromide and from the neohexyl chloride, and on a sample of 4-methyl-1-pentene was observed. When 0.2 cc. of a solution of one part of permanganate in 5000 parts of water was added to one cc. of the cyclopropane product from the Wurtz reaction, the permanganate was discolored only after shaking for ten minutes. The material obtained from the dibromide took up the permanganate rather rapidly at first, then acted just as the Wurtz product did, indicating that this material might be contaminated with a small amount of olefin. This would account for the lower index and density observed for the compound from this source. The 4-methyl-1-pentene decolorized the permanganate rapidly, and in large volumes. It has, therefore, been shown that the compound identified as 1,1,2-trimethylcyclopropane differs markedly from a possible olefinic isomer. The indication in the literature[7,10] that it reacts with permanganate much like an olefin is incorrect.

Summary

1. Neohexyl chloride, 1-chloro-2,2-dimethylbutane, reacts with sodium to give mainly 1,1,2-trimethylcyclopropane, *t*-butylethylene and neohexane.

2. A small yield of the coupled product 3,3,6,6-tetramethyloctane was formed.

---

[6] Whitmore and Church, This Journal, **54**, 3710 (1932).

[7] Zelinsky and Zelikoff, *Ber.*, **34**, 2862 (1901).

[8] This product is now available commercially from Commercial Solvents Corp.

[9] McBee, Hass and Tarrant, Abstracts of the 97th Meeting, Am. Chem. Soc., Organic Section, p. 29 (1939).

[10] Ostling, *J. Chem. Soc.*, **101**, 457 (1912).

3. No rearranged product could be found.
4. Further evidence has been advanced that the rearrangements studied in this Laboratory do not take place by a free radical mechanism.

STATE COLLEGE, PENNSYLVANIA RECEIVED MAY 5, 1941

[CONTRIBUTION FROM THE RESEARCH DIVISION OF COMMERCIAL SOLVENTS CORPORATION]

Some Nitro and Amino Acetals Derived from Polyhydric Nitro Alcohols

BY MURRAY SENKUS

Introduction

Polyhydric alcohols which have hydroxyl groups on carbon atoms removed by one carbon atom or on adjacent carbon atoms are characterized by the ease with which they form acetals. Ethylene glycol, propylene glycol, trimethylene glycol, glycerol and erythritol are a few common polyhydric alcohols of the above types which can be converted readily to acetals.

Recent work on the nitroparaffin–aldehyde condensation has made available several nitro glycols for the first time.[1] *tris*-(Hydroxymethyl)-nitromethane, a condensation product of nitromethane and formaldehyde, had already been known.[2] These nitro hydroxy compounds have hydroxyl groups on carbon atoms removed by one carbon atom. Preliminary work showed that these nitro polyhydric alcohols also react with aldehydes in the presence of inorganic acids to form acetals. In view of the possible application of these materials in industry, a number of cyclic acetals of the three commercially available nitro polyhydric compounds, namely, *tris*-(hydroxymethyl)-nitromethane, 2-nitro-2-methyl-1,3-propanediol and 2-nitro-2-ethyl-1,3-propanediol were prepared and are reported herein. The reduction of these nitro acetals to the corresponding amino acetals and the conversion of some of these amino acetals to alkylidenimino acetals and alkylamino acetals are also described.

Experimental

Formaldehyde acetals of 2-nitro-2-methyl-1,3-propanediol and 2-nitro-2-ethyl-1,3-propanediol were prepared by heating a mixture of nitro glycol (1 mole), 36% (by weight) aqueous formaldehyde (1 mole) and 1 g. of *p*-toluenesulfonic acid in a Claisen flask until 66–68 ml. of distillate (vapor temperature 96–103°) had been obtained. The residue was cooled and washed with 200 ml. of 2% sodium bicarbonate solution. The material solidified during the washing. The mixture was filtered and the product was washed with 100 ml. of cold water. The acetals were purified by recrystallization from 50% aqueous methanol.

Other acetals were prepared by refluxing mixtures of an aldehyde (1 mole), nitro hydroxy compound (1 mole), 200 ml. of benzene and 0.2 g. of *p*-toluenesulfonic acid in a flask connected to a modified Dean and Stark moisture trap[3] which was connected to a reflux condenser. After water had ceased separating in the trap, heating was arrested and the mixtures were cooled. They were washed with 500 ml. of 2% sodium bicarbonate solution and 500 ml. of water. The benzene was removed by distillation and the products were purified by rectification *in vacuo* or by recrystallization from methanol or petroleum ether.

The reactions required from two to three hours and conversions of nitro hydroxy compounds to acetals averaged about 90% of theoretical.

The nitro acetals prepared are white crystalline solids or colorless liquids. They are entirely stable at room temperature, however they decompose slowly when heated to 150°. They are unaffected by dilute alkali and boiling water, but are rapidly hydrolyzed by hot mineral acids. The formaldehyde acetals are appreciably soluble in hot water but insoluble in cold water. All nitro acetals described herein are soluble in ether, methanol, acetone and benzene. They are entirely odorless.

The procedure for the reduction of the nitro acetals was the same in all cases. One hundred grams of nitro acetal dissolved in 300 ml. of methanol was hydrogenated for two to three hours at 60 to 75° at 1000 to 1500 lb. pressure in the presence of 5 g. of Raney nickel catalyst. The conversions of nitro acetals to amino acetals averaged about 90%.

The amino acetals are white crystalline solids or colorless liquids. Their thermal stability is comparable to that of the amino alcohols. Hot mineral acids convert them to aldehydes and salts of the corresponding amino polyhydric alcohols. The amino acetals, except those derived from α-ethylhexaldehyde and lauraldehyde, are soluble in water. All amino acetals are soluble in ether, methanol, acetone and benzene. The amino acetals derived from formaldehyde possess a faint amine-like odor. The remaining amino acetals are odorless.

5-Methylenimino-5-ethyl-1,3-dioxane was prepared by heating a mixture of 36% (by weight) aqueous formaldehyde (1 mole) and 5-amino-5-ethyl-1,3-dioxane (1 mole) until all of the water had been removed from the product. The crude material was purified by recrystallizing from ether. The other two alkylidenimino acetals were pre-

---

[1] Vanderbilt and Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

[2] Henry, *Compt. rend.*, **120**, 1265 (1895).

[3] Dean and Stark, *Ind. Eng. Chem.*, **12**, 486 (1920).