orthosilicate have been investigated. It has been used to prepare silica gel free from strong electrolytes and some of the properties of such gel have been studied.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

SOME 1,2-DIALKYL CYCLOPENTANE DERIVATIVES[1,2]

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As cyclic hydrocarbons are found in some petroleums it is important to know more of the chemistry of this class. The derivatives of cyclopentane have not been extensively studied; it seemed desirable to synthesize more of them so as to extend our knowledge of the properties of the members of this group. The particular line chosen was the 1,2-dialkyl cyclopentanes. The reaction chosen for the preparation of these hydrocarbons led quite unexpectedly to the formation of the corresponding unsaturated hydrocarbons. Due to the expiration of the grant, time was not available for the reduction of the latter to the saturated derivatives, and it was deemed best to publish the results obtained.

The necessary intermediate for the study was α-ethyl-cyclopentanone. This compound is supposed to have been obtained by Best and Thorpe[5] by the hydrolysis of 2-cyano-2-methyl-cyclopentane-one-1. They described it as boiling at 149° at 756 mm. and gave the melting point of its semicarbazone as 177°. This compound prepared by our method boils at 160–161° (755 mm.) corr. and its semicarbazone melts at 189° corr. We started with ethyl adipate (I), which was made to undergo an internal acetoacetic ester condensation to form the ethyl ester of α-carbethoxy-cyclopentanone (II). The sodium compound of this[6] reacted with ethyl iodide to give the ethyl derivative (III), which by the ketone splitting left α-ethyl-cyclopentanone (IV). By the Grignard reaction this ketone was converted to the tertiary alcohol (V). This was transformed into the iodide. It was intended to remove the iodine by reduction to obtain the 1,2-alkyl-ethyl-cyclo-pentane (VI). When this was attempted an unsaturated hydrocarbon was obtained.

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[1] In memory of Ira Remsen.

[2] This paper presents the results of an investigation of cyclopentane derivatives listed as Project 15 of the American Petroleum Institute. Financial assistance has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Co. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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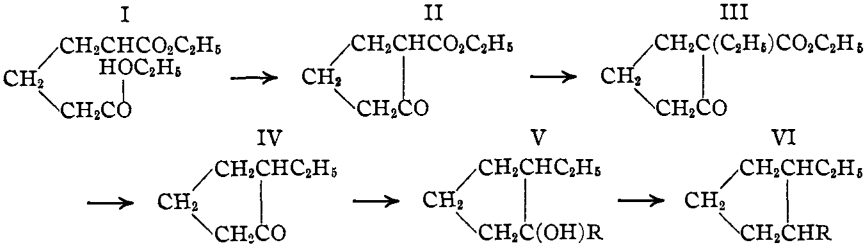
[5] Best and Thorpe, *J. Chem. Soc.*, **95**, 713 (1909).

[6] Rysselberge, *Bull. sci. acad. roy. Belg.*, [5] **12**, 171 (1926).



In the preparation of α-methyl-α-carbethoxy cyclopentanone, Bouveault[7] treated one mole of α-carbethoxy-cyclopentanone with one equivalent of sodium dissolved in absolute alcohol and added methyl iodide to the cooled mixture. Whereas the method was generally satisfactory for the methyl derivative, it sometimes miscarried, giving almost exclusively ethyl-α-methyl adipate. For higher alkyl groups such as the *iso*propyl, no reaction occurred unless heating in a sealed tube was resorted to. In this case a large amount of ethyl-α-*iso*propyl adipate was obtained. Indeed Bouveault was unable to prepare the *iso*propyl keto ester in a state of purity. It was prepared, however, by Kötz and Schüler[8] by treating α-carbethoxy-cyclopentanone with a finely divided alloy of sodium and potassium and refluxing the mixed salt thus formed for seventy hours with *iso*propyl iodide.

We have been able to prepare the various alkyl derivatives of α-carbethoxy-cyclopentanone in a reasonable time by adding the alkyl iodide to the sodium salt of the keto ester suspended in an aromatic hydrocarbon and refluxing. It was found that as the size of the alkyl group increases it is necessary to use a higher boiling solvent and to heat for a longer time. Thus an 82% yield of methyl derivative was obtained in three hours using benzene as solvent, 74% of ethyl keto ester in six hours in toluene and 59% of *iso*propyl in twelve hours in xylene.

The yields of substituted cyclopentanols obtained by the action of various Grignard reagents on α-ethyl-cyclopentanone were found to be very low, due perhaps to the steric effect of the ethyl radical in the α-position to the carbonyl group. In each case much of the ketone was recovered unchanged and much high boiling material was found. Thus, with ethyl magnesium bromide, the yield of 1,2-diethyl-cyclopentanol-1 (V) was 27%, with propyl magnesium bromide the yield of 1-propyl-2-ethylcyclo-ethyl-cyclopentanol-1 was only 8.5% and with *iso*propyl magnesium bromide no alcohol was obtained. In an attempt to prepare 1,2-diethyl-cyclopentane from 1,2-diethylcyclopentanol-1, the latter compound was converted to the iodide and this reduced with zinc and hydrochloric

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[7] Bouveault, *Bull. soc. chim.*, [3] **21,** 1019 (1899). Bouveault and Locquin, *ibid.*, [4] **3,** 432 (1908).

[8] Kötz and Schüler, *Ann.*, **350,** 222 (1906).

acid. The resulting hydrocarbon was, however, shown to be unsaturated, having the formula C_9H_{16}. In its physical constants it resembled rather closely the unsaturated hydrocarbon C_9H_{16} prepared by Kishner[9] by the dehydration of diethyl-cyclobutylcarbinol. This hydrocarbon was designated by Kishner as 1,2-diethyl-cyclopentene-1, although evidence for this structure appears to be lacking.

Experimental Part

α-Carbethoxy-cyclopentanone.—The directions of von Rysselberge[6] were used.

α-Methyl-α-carbethoxy-cyclopentanone.—To 20.7 g. of sodium, finely divided by shaking in hot xylene, suspended in 400 cc. of benzene, 140 g. of α-carbethoxy-cyclopentanone was added with cooling and the mixture allowed to stand overnight. To the sodium salt thus formed, 131 g. of methyl iodide was added and the mixture refluxed for three hours. The sodium iodide was then filtered off and the benzene solution fractionated. The yield of material boiling at 106–107° (17 mm.) corr. was 125 g., or 82%. The semicarbazone melted at 152–153° corr.

α-Ethyl-α-carbethoxy-cyclopentenone.—This was prepared in the same way as the methyl derivative except that toluene was used as solvent instead of benzene. The proportions used were 29.6 g. of sodium, 200 g. of α-carbethoxy-cyclopentanone, 500 cc. of toluene and 210 g. of ethyl iodide. The yield of material boiling at 100° (7 mm.) corr. was 174 g., or 74%; $d_4^0 = 1.0531$, $d_4^{25} = 1.0310$.

Anal. Calcd. for $C_{10}H_{16}O_3$: C, 65.17; H, 8.76. Found: C, 64.68; H, 8.74.

Semicarbazone.—The semicarbazone of α-ethyl-α-carbethoxy-cyclopentanone melts at 148–149° corr.

Anal. Calcd. for $C_{11}H_{19}O_3N_3$: C, 54.73; H, 7.94. Found: C, 55.13; H, 8.00.

α-*Iso*propyl-α-carbethoxy-cyclopentanone.—To the sodium salt prepared by treating 14.7 g. of sodium suspended in 300 cc. of xylene with 100 g. of α-carbethoxy-cyclopentanone was added 100 g. of *iso*propyl iodide. The mixture was refluxed for twelve hours, the sodium iodide filtered off and the xylene removed by distillation. The yield of *iso*propyl keto ester boiling at 136–137 (34 mm.) corr. was 75 g., or 59%. The semicarbazone melted at 141–142° corr., which agrees with Bouveault's observations.

α-Ethyl-cyclopentanone.—A mixture of 100 g. of α-ethyl-α-carbethoxy-cyclopentanone, 200 cc. of water and 100 cc. of concd. sulfuric acid was refluxed for five hours. After cooling the mixture was extracted with ether and the ethereal extract washed with sodium bicarbonate solution. After removal of the ether, 39 g. of crude ketone, b. p. 161–164°, was obtained. The pure ketone boils at 160–161° (755 mm.) corr.; $d_4^0 = 0.9469$; $d_4^{25} = 0.9260$.

Anal. Calcd. for $C_7H_{12}O$: C, 74.93; H, 10.70. Found: C, 74.76; H, 10.71.

The semicarbazone melts at 189° corr.

Anal. Calcd. for $C_8H_{15}N_3O$: C, 56.76; H, 8.94. Found: C, 56.95; H, 9.29.

1,2-Diethyl-cyclopentanol-1.—To the cooled Grignard reagent prepared from 28.8 g. of magnesium and 160 g. of ethyl bromide, 120 g. of α-ethyl-cyclopentanone was slowly added with stirring. After several hours the mixture was decomposed with dilute acetic acid, extracted with ether and the ether solution washed with sodium bicarbonate solution. After removal of the ether, the resulting liquid was fractionated *in vacuo*. The lower boiling fraction was found to be unchanged ketone. The fraction

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[9] Kishner, *J. Russ. Phys.-Chem. Soc.*, **43**, 1149–1157 (1911).

boiling at 100–102° at 49 mm. was 41 g. This on redistillation boiled at 101–102° corr. at 46 mm. and proved to be the desired diethyl-cyclopentanol; yield, 27%. There was a higher boiling fraction which was not investigated; $d_4^0 = 0.9250$; $d_4^{25} = 0.9041$.

Anal. Calcd. for $C_9H_{18}O$: C, 75.98; H, 12.77. Found: C, 75.79; H, 13.24.

1-Propyl-2-ethyl-cyclopentanol-1.—To the cooled Grignard reagent from 28.8 g. of magnesium and 200 g. of *n*-propyl bromide, 100 g. of α-ethyl-cyclopentanone was added slowly with stirring. After four hours at room temperature, the mixture was decomposed with dilute acetic acid, extracted with ether and the ether layer washed with sodium bicarbonate solution. After removal of the ether, the mixture was fractionated several times *in vacuo*. A large low boiling fraction proved to be unchanged ketone. The fraction boiling at 112–115° at 48 mm. was 14 g. On redistillation, the pure alcohol boiling at 115–116° at 42 mm. corr. was obtained; yield, 8.5%; $d_4^0 = 0.9156$; $d_4^{25} = 0.8949$.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.81. Found: C, 76.77; H, 13.12.

1,2-Diethyl-cyclopentene, C_9H_{16}.—1,2-Diethyl-cyclopentanol-1, 48 g., was saturated in the cold with hydrogen iodide. The resulting mixture was dissolved in 310 cc. of alcohol and 40 cc. of water and 50 g. of zinc dust was added. After refluxing for two hours, 70 cc. of concd. hydrochloric acid was added and the refluxing continued for four hours. At the conclusion of this time, the mixture was cooled, extracted with ether and the ether solution washed with sodium bicarbonate solution. After removal of the ether, 25 g. of a liquid boiling at 147–149° at 761 mm. corr. was obtained. On redistillation the pure hydrocarbon, boiling at 148–149° corr. at 761 mm. resulted; $d_4^0 = 0.9331$; $d_4^{25} = 0.8136$.

Anal. Calcd. for C_9H_{16}: C, 87.00; H, 13.00. Found: C, 86.84; H, 13.14. *Mol. wt.* (Freezing point in benzene): calcd., 124. Found: 125.

This hydrocarbon was highly unsaturated, reducing bromine and permanganate instantaneously.

The boiling point of the hydrocarbon described by Kishner as 1,2-diethyl-cyclopentene-1 was 151–152° (751 mm.); $d_4^{20} = 0.8124$.

Summary

α-Methyl-, α-ethyl- and α-*iso*propyl-α-carbethoxy-cyclopentanones have been prepared by an improved method. From α-ethyl cyclopentanone the 1,2-diethyl- and the 1-propyl-2-ethyl-cyclopentanol-1 have been obtained. On conversion into the iodide and treatment with zinc and acetic acid, the unsaturated hydrocarbon was obtained rather than the desired dialkyl cyclopentane.

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