than with the alcohol itself. It seemed to us that, by carrying out this reaction with tracer amounts of C^{14}-methyl alcohol, we could determine whether or not this step consisted of the standard oxo reaction, as postulated.

Experimental

The labeled methanol was prepared by the method of Brown, Nystrom and Yanko.[5] The diethyl carbitol was vacuum distilled over lithium aluminum hydride below 60°. The reaction of the first few drops of the *n*-butyl carbitol with the solid which had separated around the edge of the reaction flask was undesirably vigorous. The labeled methanol was diluted with reagent methanol and fractionated.

The preparation of the dicobalt octacarbonyl[6] went according to description but some of the oxo reactions went more slowly. In each oxo reaction, 0.1 to 0.2 g. of the copper gasket dissolved and deposited as metallic copper in the top of the autoclave.

The oxo reaction mixture was worked up by boiling the entire mixture with dilute sulfuric acid and then with an excess of potassium hydroxide to hydrolyze acetals, esters and to destroy the cobalt carbonyl. The excess potassium hydroxide was neutralized with carbon dioxide and the volatile material distilled. In the case of run 2, which started with one mole of methyl alcohol, 0.14 mole of volatile acid, not oxidizable by cold permanganate, was recovered from this mixture of potassium salts; m.p. of the sodium salt, 319.5–324.5° (uncor.). The distillate from the potassium salts was fractionated by means of a Piros–Glover spinning band column. A portion of the 78.1° distillate (b.p. 95% ethyl alcohol, 78.15°) was oxidized by permanganate using the same conditions that Phares[7] used for the oxidation of ethylamine. The resulting sodium acetate melted at 326.0–328.6°, 324.7–326.9° (uncor.). A portion of the 87.3–87.8° distillate (b.p. 71.7% 1-propanol, 87.72°), gave a 3,5-dinitrobenzoate melting at 71.6–73.0° which when mixed with a sample of *n*-propyl 3,5-dinitrobenzoate melting at 72.8–73.8°, melted at 72.2–73.4°. This propyl alcohol was oxidized to the acid by cold alkaline permanganate and converted to the sodium salt. The salt was recrystallized several times from 95% ethanol–diisopropyl ether; various samples melted from 285.5–286.8° to 286.5–287.6° (uncor.). *Anal.* Calcd. for $C_3H_5O_2Na$: C, 37.50; H, 5.25; Na, 23.93. Found: C, 37.62; H, 5.32; Na, 24.00.

The sodium salts were degraded by Phares'[8] method which uses the Schmidt reaction to change the acid to carbon dioxide and the next lower amine. The amine is then oxidized to the corresponding acid and the process repeated. There is the possibility that the oxidation of the *n*-propyl alcohol yielded some acetic acid as well as propionic acid. If this acetic acid were not removed in the recrystallization any activity of the acid carbon would have appeared in the results as activity of the 1-carbon of the propyl alcohol. The methyl carbon of this acetic acid would be discarded in the course of the analysis and would not affect the results. All degradations were on different samples, one of which was more highly purified than the other. The barium carbonate samples were counted as solids of infinite thickness. The statistical error in counting was 1% but the counter sometimes gave variations as high as 5% on the same sample. This gives a total error of at least 10% since 5% variations are common in the method of analysis.

Results and Discussion

Table I gives the relative activities of the various carbons with the 2-carbon of the ethyl alcohol of runs 1a and 2a set at 100. The actual values for these carbons were 2.9 and 6.2 millimicrocuries per milligram of carbon. In the case of the ethyl alcohol, all the activity is in the 2-carbon. These values, in conjunction with the values for methyl alcohol, indicate that no methyl alcohol is formed during the reaction and that the 1-carbon of the ethyl alcohol comes from the carbon monoxide.

TABLE I

Run		1a	1b	2a	2b
Methyl alcohol		102	102	107	107
Ethyl alcohol	1-carbon	−0.1	0.1	0.5	−0.1
	2-carbon	100	98	100	100
Acetic acid	1-carbon	0.4			
	2-carbon	98			
n-Propyl alcohol	1-carbon	0.4	0.3	0.5	−0.3
	2-carbon	54	54	52	54
	3-carbon	47	49	48	45

The second largest product, 14 mole per cent., in this variation of the oxo reaction is acetic acid. A sample of this was purified and the activity was in the 2-carbon.

In the case of the propyl alcohol the 1-carbon had no activity while the 2- and 3-carbons had activities about half that of the original methyl alcohol. This could be explained by assuming that the propyl alcohol was formed by the addition of a carbon monoxide carbon to a symmetrical intermediate, probably ethylene, derived from the ethyl alcohol. Kummer and co-workers[9] studied the addition of carbon atoms in the Fischer–Tropsch reaction by adding C^{14}-labeled alcohols to the hydrogen–carbon monoxide mixture. Since this reaction, unlike the oxo reaction, does not require an initial substrate the efficiency of incorporation was lower. They found that 90% of the propane produced from the labeled ethyl alcohol was formed by the addition of a carbon monoxide carbon to the 1-carbon of the alcohol. Thus, in this reaction, the addition is to an unsymmetrical intermediate rather than to a symmetrical one as in our case.

Acknowledgment.—This problem was suggested by Dr. R. Christian Anderson and was carried out while the author was a Guest Scientist at the Brookhaven National Laboratory during 1952–1953. Dr. Manny Hillman, Washington University, St. Louis, Mo., had done important preliminary work.

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t-Butyl Cyclopropyl Ketone[1]

BY STANLEY C. BUNCE

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t-Butyl cyclopropyl ketone (I), *t*-butylcyclopropylmethylcarbinol (II), and 1,3-dicyclopropyl-2-buten-1-one (III), have been prepared, incident to investigations of rearrangements of cyclopropyl ketones.[2]

The alkylation of such aliphatic ketones as pinacolin with sodium amide in refluxing benzene[3] suggested this method for the preparation of *t*-

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(1) Presented before the Organic Division at the 125th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1953.

(2) S. C. Bunce and J. B. Cloke, THIS JOURNAL, **76**, 2244 (1954).

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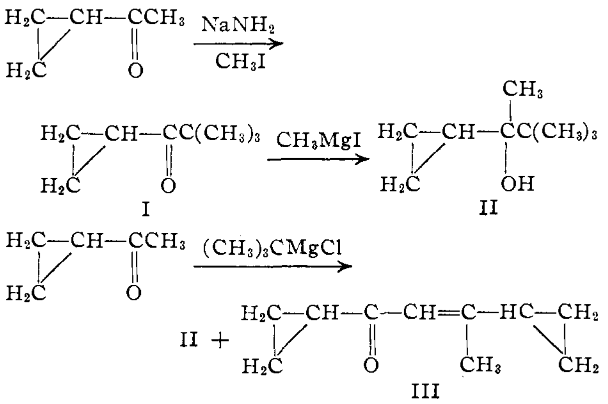

butyl cyclopropyl ketone; similar acylations have since been reported.[4] The crude product obtained by alkylation of cyclopropyl methyl ketone with three moles of sodium amide and three and two-tenths moles of methyl iodide was separated by fractionation into cyclopropyl ethyl ketone, 4%, cyclopropyl isopropyl ketone, 21%, and *t*-butyl cyclopropyl ketone, 18%. Alkylation with three and two-tenths moles of sodium amide and four moles of methyl iodide gave 42% of *t*-butyl cyclopropyl ketone. Cyclopropyl ethyl ketone and cyclopropyl isopropyl ketone had been prepared by another method[5]; the infrared spectrum of the latter and of *t*-butyl cyclopropyl ketone have already been reported[6] and confirm their structures.

t-Butylcyclopropylmethylcarbinol (II) was prepared in 57% yield by the reaction of methylmagnesium iodide with *t*-butyl cyclopropyl ketone. Its infrared spectrum includes strong absorptions at 3367 cm.$^{-1}$ (bonded hydroxyl) and at 1168 cm.$^{-1}$ (tertiary alcohol) as well as the absorptions at 3095 cm.$^{-1}$, 2976 cm.$^{-1}$, 1022 cm.$^{-1}$, and 895 cm.$^{-1}$ confirming the presence of the cyclopropyl group.[6]

The preparation of *t*-butylcyclopropylmethylcarbinol had first been attempted by the reaction of *t*-butylmagnesium chloride with cyclopropyl methyl ketone. A small amount of the carbinol (9%) was separated by distillation from a higher-boiling, unsaturated fraction, whose structure, III was indicated by its oxidation by alkaline permanganate to cyclopropyl methyl ketone (80%) and cyclopropanecarboxylic acid (20%). Grignard reagents have been reported to lead to condensation reactions of this type,[7] and 1,3-dicyclopropyl-2-buten-1-one (III) has been prepared also by condensation of cyclopropyl methyl ketone catalyzed by aluminum *t*-butoxide.[8] Distillation at atmospheric pressure in the presence of moisture converted the compound in part to cyclopropyl methyl ketone, and hydrolysis of this type must explain its slow reaction with sodium hypochlorite and potassium iodide to give iodoform (38%) and cyclopropanecarboxylic acid (30%). Indeed, it was not possible to obtain III free from a small proportion of the ketol, 1,3-dicyclopropylbutan-3-ol-1-one. Infrared absorptions at 3105 cm.$^{-1}$, 3021 cm.$^{-1}$, 1022 cm.$^{-1}$, and 896 cm.$^{-1}$ are characteristic of the cyclopropyl group;[6] absorptions at 3546 cm.$^{-1}$ (hydroxyl), 1672 cm.$^{-1}$ (carbonyl) and at 1592 cm.$^{-1}$ (ethylenic unsaturation) are also present.

Experimental[9]

Alkylation of Cyclopropyl Methyl Ketone.—Sodium amide (3.6 moles) was prepared by the addition of sodium to liquid ammonia, the excess ammonia was replaced by benzene, and 100 g. (1.2 moles) of cyclopropyl methyl ketone, b.p. 111–112°, in 400 ml. of benzene was added during three hours. After refluxing for one hour, 537 g. (3.8 moles) of methyl iodide in benzene was added and the mixture was refluxed for three hours. After filtration and extraction of the salt with benzene, the combined solutions, dried and distilled several times through a 100-cm. vacuum-jacketed column packed with glass helices, gave 5.0 g., b.p. 108–129°; 5.5 g. cyclopropyl ethyl ketone, b.p. 129–137°; 10.0 g., b.p. 137–140.5°; 28.0 g. cyclopropyl isopropyl ketone, b.p. 140.5–141.5°, $n^{20}\mathrm{D}$ 1.4290 (lit.[5] b.p. 141°, $n^{20}\mathrm{D}$ 1.4299); 13.5 g., b.p. 142–147.5°; 26.5 g. cyclopropyl *t*-butyl ketone, b.p. 147.5–149.5°. A second alkylation used 101 g. (1.2 moles) of cyclopropyl methyl ketone in benzene, to which was added one-third of a total of 3.8 moles of sodium amide prepared as before and suspended in benzene. One third of a total of 683 g. (4.8 moles) of methyl iodide dissolved in an equal volume of benzene was then added, and the mixture was refluxed for one hour; the successive additions were made similarly. The crude product gave, after fractionation, 23.0 g., b.p. 81–148°; 63.0 g., b.p. 148–149°, collected in successive fractions of constant refractive index; 14.0 g., b.p. 150–164°; 11.0 g., b.p. 105–130° at 25 mm.; 14.0 g. residue.

A pure sample of cyclopropyl *t*-butyl ketone, b.p. 148.8°, $n^{20}\mathrm{D}$ 1.4318,[10] d_4^{20} 0.8662, was used for the determination of the infrared spectrum. The MR_{D} found was 37.74; that calculated from atomic refractivities including an exaltation of 0.6 for the cyclopropyl group[11] was 37.55.

Anal. Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.18. Found: C, 76.0; H, 11.13.

The 2,4-dinitrophenylhydrazone, after separation from 2,4-dinitrophenylhydrazine by extraction with chloroform, was recrystallized from alcohol and melted 153.4–153.8°.

Anal. Calcd. for $C_{14}H_{18}O_4N_4$: N, 18.30. Found: N, 18.16.

***t*-Butylcyclopropylmethylcarbinol.**—The Grignard reagent prepared from 14.2 g. (0.10 mole) of methyl iodide and 2.4 g. (0.10 mole) of magnesium turnings was allowed to react with an ether solution of 12.6 g. (0.10 mole) of cyclopropyl *t*-butyl ketone at reflux for ten hours. After treatment with ice and dilute hydrochloric acid, the ether solution was washed, dried with sodium sulfate, and distilled; 8.0 g. of methylcyclopropyl-*t*-butylcarbinol, b.p. 64–67° at 20 mm. was obtained, a center cut had $n^{20}\mathrm{D}$ 1.4491.

1,3-Dicyclopropyl-2-buten-1-one and Methylcyclopropyl-*t*-butylcarbinol.—To the Grignard reagent prepared from 92 g. (1.0 mole) of *t*-butyl chloride, and 24 g. (1.0 mole) of magnesium was added 84 g. (1.0 mole) of cyclopropyl methyl ketone in ether. The mixture was refluxed while stirring for two hours, then poured into sulfuric acid and ice. The ether layer was separated, washed with water, dried with potassium carbonate, and distilled. The fraction boiling 40–115° contained cyclopropyl methyl ketone and other products not separated; the residue when distilled through a Vigreux column gave 7 g. of *t*-butylcyclopropylmethylcarbinol, b.p. 55–57° (12 mm.), and 25.5 g. of 1,3-dicyclopropyl-2-buten-1-one, b.p. 105–107° (12 mm.). A second reaction, conducted similarly but with improved stirring, gave, from 60 g. (0.71 mole) of the ketone and a 5% excess of the Grignard reagent, 9 g. of the tertiary alcohol, and 7 g. of the unsaturated ketone, at the same boiling points.

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(9) Boiling points are uncorrected. Melting points are corrected (S. C. Bunce, *Anal. Chem.*, **25**, 825 (1953)). Analyses for carbon and hydrogen are by Clark Microanalytical Laboratory, Urbana, Ill.

(10) The refractive index reported in (6) is in error.

(11) V. R. Slabey, THIS JOURNAL, **76**, 3603 (1954).

4.5 g. (0.03 mole) of 1,3-dicyclopropyl-2-butene-1-one in 150 ml. of water was oxidized at room temperature by adding 8.4 g. (0.06 mole) of potassium permanganate during three hours. Excess permanganate was removed with sodium bisulfite, manganese dioxide was separated, and the alkaline filtrate was acidified and continuously extracted with ether for two days. Cyclopropanecarboxylic acid, 0.5 g., was separated from the ether solution by extraction with alkali; the residual ether solution on evaporation gave 2.0 g. of cyclopropyl methyl ketone. A 4.5 g. (0.03 mole) portion of the unsaturated ketone mixed with 16 g. of potassium iodide and 250 ml. of 5% sodium hypochlorite gave, after sixteen hours, 8.0 g. of iodoform. The alkaline filtrate was acidified and extracted with ether, and after separation from iodine, 1.5 g. of cyclopropanecarboxylic acid, b.p. 175–185°, was obtained.

A sample of 1,3-dicyclopropyl-2-buten-1-one, b.p. 104° at 12 mm., $n^{20}\text{D}$ 1.4872, d_4^{20} 1.001, was used for infrared absorption measurements and for preparation of the semicarbazone which, when recrystallized from dilute alcohol, melted 142.9-143.4°.

Anal. Calcd. for $C_{11}H_{17}ON_3$: N, 20.27. Found: N, 19.45.

A pure sample of methylcyclopropyl-*t*-butylcarbinol, b.p. 85° at 45 mm., $n^{20}\text{D}$ 1.4495, d_4^{20} 0.886, was used for the determination of the infrared spectrum. The MR_D found was 43.09; that calculated from atomic refractivities including the exaltation of 0.6 was 43.69.

Anal. Calcd. for $C_9H_{18}O$: C, 76.0; H, 12.76. Found: C, 75.5, 75.5; H, 12.48, 12.52.

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Difluoromethyl Phenyl Ether

BY REGINALD F. CLARK AND J. H. SIMONS

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Ethyl difluoromethyl ether has been made and is reported to be unstable.[1,2]

We wish to report the preparation of difluoromethyl phenyl ether by the reaction of potassium phenoxide with dibromodifluoromethane in anhydrous acetone. It has been found to be stable.

Difluoromethyl phenyl ether is a colorless liquid with a very pungent odor, soluble in ethyl ether, ethyl alcohol, benzene and insoluble in water. In the presence of sulfuric acid, the difluoromethyl phenyl ether decomposes to tars and liberates hydrogen fluoride. Upon refluxing the difluoromethyl phenyl ether with ethyl ether and sodium, the ether splits to form sodium phenoxide and sodium fluoride.

Experimental

Starting Materials.—Dibromodifluoromethane was obtained from the Dow Chemical Co. and fractionated. The potassium phenoxide was prepared from phenol and potassium hydroxide.

Preparation.—Dibromodifluoromethane, 118 g. (0.56 mole), was bubbled through a mixture of 400 ml. of anhydrous acetone and 74 g. (0.56 mole) of potassium phenoxide with stirring, at a rate to keep the temperature below 50°. After the addition of the dibromodifluoromethane was started, the solution turned red and finally dark brown.

After completion of the reaction, the Dewar-type condenser was removed and a mixture of acetone and excess dibromodifluoromethane was distilled from the solution. After removal of 300 ml. of acetone, an equal volume of water was added and the mixture was steam distilled. The difluoromethyl phenyl ether layer was separated from the aqueous layer, dried over anhydrous magnesium sulfate and fractionated at reduced pressure through a 50-cm. column, 8 mm. i.d. packed with 1/16 in. glass helices. The difluoromethyl phenyl ether distilled at 66-67° at 30 mm., 139-140° at 763 mm., d^{25}_4 1.171, $n^{25}\text{D}$ 1.4460. The amount of difluoromethyl phenyl ether collected was 13.2 g.

To the excess dibromodifluoromethane and the acetone distilled from the original solution, 2 liters of cold water was added and the dibromodifluoromethane which separated was collected, dried and used for subsequent experiments. The amount of dibromodifluoromethane recovered was 50 g. The yield of difluoromethyl phenyl ether based on the dibromodifluoromethane used was 28.3%.

When phenol and potassium hydroxide were substituted for anhydrous potassium phenoxide, the yield was 16.3%.

Anal.[3] Calcd. for $C_6H_5OCF_2H$: C, 58.33; H, 4.20. Found: C, 58.37; H, 4.48.

The molar refractivity calculated from the density and refractive index is 32.58; the value calculated from the sum of atomic refractivities is 32.35.

Degradation.—To 5 g. of difluoromethyl phenyl ether was added 10 ml. of 50% sulfuric acid. A violet semi-solid mass was formed and hydrogen fluoride liberated. The acidity was neutralized with sodium hydroxide. A residue remained which was removed by filtration and which was not readily identified. The filtrate, however, after acidification and extraction with ethyl ether, yielded 1.1 g. of phenol.

To a flask containing 2 g. of sodium metal in 20 ml. of anhydrous ethyl ether was added 5 g. of difluoromethyl phenyl ether. The mixture was refluxed for 12 hours after which the excess sodium was slowly decomposed by adding ethyl ether saturated with water. After acidifying the mixture with 20% hydrochloric acid, the ether layer was separated, dried and distilled, yielding 2.1 g. of unreacted difluoromethyl phenyl ether and 1.6 g. of phenol. The dilute hydrochloric acid layer contained a large amount of fluoride ion.

The authors wish to acknowledge the sponsorship of the Minnesota Mining and Mfg. Co. for part of the work reported in this paper.

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(3) Analysis by Clark Microanalytical Lab., Urbana, Ill.

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Ultraviolet Absorption Spectra of Derivatives of 2,3,5- and 2,4,5-Trihydroxyacetophenone[1]

BY D. D. CLARKE AND F. F. NORD

RECEIVED MAY 10, 1955

In the course of structural studies[1a] in our laboratory, it became necessary to synthesize certain trihydroxybenzene derivatives as model compounds for comparison of ultraviolet absorption spectra. The syntheses of some intermediates and the absorption spectra of the acetophenones are reported here.

2,3,5-Trimethoxybenzaldehyde[2] was chosen as the starting material for building up an α-substituted propionic acid side chain from the aldehyde group. This aldehyde I was converted to the nitrile II.[3] The variable yield obtained in the preparation of I made it difficult to prepare a sufficient quantity of this intermediate to carry out the projected steps in the synthesis of the desired side chain.

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(1) Condensed from a portion of the dissertation of D.D.C. submitted to the Graduate School of Fordham University in partial fulfillment of the requirements for the Ph.D. degree.

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