General Procedure for the Reaction of Dithiocarbamates with Acrylamide.—In the examples where a precipitate of the dithiocarbamate salt was present, the mixture was stirred vigorously. A 3.0-g. quantity of acrylamide[4] (0.042 mole) was added and the mixture was stirred or allowed to stand for 24 hours. Any precipitate which had separated was collected, washed with water and dried. Second crops were obtained after dilution of the filtrate with 50 ml. of ligroin (60-90°) in the chloroform experiments and 100 ml. of water in the ethanol runs. The products were then crystallized from appropriate solvents as stated in the table. The percentage yields were calculated on the crude products, but in no case was the melting range of the crude sample more than 12-15° lower than the melting point of the analytical sample prepared from it.

2-Carbamoylethyl Dithiocarbamate.—To a solution of 1.50 g. of ammonium dithiocarbamate[5] in 5 ml. of water was added 1.00 g. of acrylamide. The solution was filtered and allowed to stand for two hours. The resulting mixture was filtered of 0.73 g. of 2-carbamoylethyl dithiocarbamate (m.p. 119-120°) and an additional 0.82 g. crystallized from the filtrate (m.p. 115-118°); yield 1.55 g.; 70%. The product was recrystallized from ethanol and the analytical sample melted at 125-126°.

Anal. Calcd. for $C_4H_8N_2OS_2$: C, 29.25; H, 4.91. Found: C, 29.51; H, 5.23.

From the second filtrate there crystallized within 24 hours 0.24 g. of β,β'-thiodipropionamide, m.p. 165-170°. By recrystallization from water or ethanol, the melting point of the product obtained as colorless, lustrous plates was raised to 176-177°. The melting point of this compound has been reported as 177-178.5°.[6]

Anal. Calcd. for $C_6H_{12}N_2O_2S$: C, 40.89; H, 6.87. Found: C, 40.68; H, 6.82.

Hydrolysis of β,β'-thiodipropionamide through the use of concentrated hydrochloric acid followed by crystallization from hot water afforded β,β'-thiodipropionic acid, lustrous plates, m.p. 127-128°. The melting point of this acid has been reported as 128°.[7]

Attempts to prepare ammonium dithiocarbamate through the use of aqueous ammonia were apparently unsuccessful in agreement with the more recent literature,[5] as the only product isolated after acrylamide was added was β,β'-thiodipropionamide.

β,β'-Dithiodipropionamide.—When 6.5 ml. of triethylamine, 4.5 ml. of carbon disulfide and a 4.9 ml. of α-phenylethylamine were mixed in chloroform according to the general procedure described above, a significant temperature rise was observed. After 30 minutes, 2.84 g. of acrylamide was added and the mixture was allowed to react by the general procedure. There was obtained 4.0 g. of a light yellow product, m.p. 125-135°. By recrystallization from 95% ethanol, there was isolated 2.2 g. of β,β'-dithiodipropionamide, m.p. 167-168° (54%), microcrystalline.

Anal. Calcd. for $C_6H_{12}N_2O_2S_2$: C, 34.59; H, 5.81; S, 30.78. Found: C, 34.68; H, 5.97; S, 30.92.[8]

Hydrolysis of β,β'-dithiodipropionamide with dilute hydrochloric acid afforded β,β'-dithiodipropionic acid as plates, m.p. 154-155°. The melting point of this compound previously has been reported as 154-155°.[9]

β-(Diethylamino)-propionamide.—Diethylamine reacts with acrylamide very slowly at room temperatures. Therefore, a solution of 2.84 g. of acrylamide in 7.0 ml. of diethylamine was refluxed for two hours and then allowed to stand overnight. The mixture was filtered of a small amount of polyacrylamide and the filtrate was vacuum distilled. β-(Diethylamino)-propionamide distilled at 154-157° at 8 mm. (4.6 g., 79%). The amide is hygroscopic and cannot be dried *in vacuo* over sulfuric acid.

Anal. Calcd. for $C_7H_{16}N_2O$: C, 58.29; H, 11.18. Found: C, 56.36, 56.17, 56.48; H, 11.25, 11.12, 11.48.

For identification, a derivative of the amide was prepared with methyl iodide. The derivative was crystallized from a mixture of ethyl acetate and ethanol and melted at 93-94°.

Anal. Calcd. for $C_8H_{19}IN_2O$: C, 33.57; H, 6.69. Found: C, 33.85; H, 6.94.

β-Morpholinopropionamide.—When 4.0 g. of morpholine was added to a solution of 2.84 g. of acrylamide in 95% ethanol at room temperature, the temperature rose. The solvent was evaporated in a stream of air and the residue was crystallized from benzene; yield 4.7 g. (75%). The melting point of the purified β-morpholinopropionamide was 98-99°.

Anal. Calcd. for $C_7H_{14}N_2O_2$: C, 53.14; H, 8.92. Found: C, 53.37; H, 9.12.

β,β'-Thiodipropionamide from Hydrogen Sulfide.—A solution of 0.71 g. of acrylamide and 0.05 g. of sodium sulfide nonahydrate in ethanol was treated with excess hydrogen sulfide. The flask containing the reaction solution was stoppered and the mixture was allowed to stand overnight. The alcohol was evaporated in an air stream and the residue was crystallized from a mixture of benzene and ethanol; yield 0.61 g. (69%). The melting point of the product was 176-177° and this melting point was not lowered when a sample was mixed with the product from triethylammonium dithiocarbamate and acrylamide.

Anal. Calcd. for $C_6H_{12}N_2O_2S$: C, 40.89; H, 6.87. Found: C, 41.16; H, 7.13.

β-(Benzylthio)-propionamide.—To a solution of 0.1 g. of potassium hydroxide and 2.5 g. of benzyl mercaptan in 95% ethanol was added 1.42 g. of acrylamide. The temperature of the solution rose to 35° and the solution was then warmed externally to 55°. After being allowed to cool, the solution was neutralized with acetic acid and concentrated in an air stream. There was obtained 3.22 g. of β-(benzylthio)-propionamide as plates, m.p. 110-111°, after recrystallization from benzene; yield 83%.

Anal. Calcd. for $C_{10}H_{13}NOS$: C, 61.50; H, 6.70. Found: C, 61.62; H, 6.77.

2-Carbamoylethyl Thiolacetate.—To 1.42 g. of acrylamide in warm benzene (50°) was added 2.0 g. of thiolacetic acid. The resulting solution was allowed to cool and stand overnight. From the mixture was separated by filtration 2.36 g. of 2-carbamoylethyl thiolacetate as lustrous plates, m.p. 76-77° (80%). By recrystallization from benzene, the melting point was raised to 82-83°.

Anal. Calcd. for $C_5H_9NO_2S$: C, 40.80; H, 6.16. Found: Found: C, 40.64; H, 6.45.

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The Reaction of Labeled Methanol with Carbon Monoxide and Hydrogen[1]

BY G. RICHARD BURNS

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Wender, Orchin and co-workers,[2,3] in their studies of the oxo reaction, have reported a variation in which an alcohol rather than an unsaturated compound is heated under pressure with hydrogen and carbon monoxide in the presence of cobalt carbonyl. Methyl alcohol gives, among other products, 40 mole per cent. of ethyl alcohol and 5 of *n*-propyl alcohol. Ziesecke[4] has also carried out this reaction with similar results and has postulated that the *n*-propyl alcohol was formed by the reaction of carbon monoxide with ethylene, resulting from the dehydration of the ethyl alcohol, rather

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[4] Generously supplied by the American Cyanamid Company.

[5] R. A. Mathes, "Inorganic Syntheses," Vol. 3, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 48.

[6] G. M. Bennett and L. V. D. Scorah, *J. Chem. Soc.*, 196 (1927).

[7] J. M. Lovén, *Ber.*, **29**, 1137 (1896).

[8] Sulfur analysis by the Geller Laboratories, Hackensack, N. J.

[9] R. Andreasch, *Monatsh.*, **6**, 836 (1885).

[1] Research carried out under the auspices of the U. S. Atomic Energy Commission. Presented before the Division of Organic Chemistry at the September 1953 Meeting of the American Chemical Society.

[2] I. Wender, R. Levine and M. Orchin, THIS JOURNAL, **71**, 4160 (1949).

[3] I. Wender, R. A. Friedel and M. Orchin, *Science*, **113**, 206 (1951).

[4] K. H. Ziesecke, *Brennstoff Chem.*, **33**, 385 (1952).

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.

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[5] W. G. Brown, R. F. Nystrom and W. H. Yanko, THIS JOURNAL, **70**, 441 (1948).

[6] I. Wender, H. Greenfield and M. Orchin, *ibid.*, **73**, 2656 (1951).

[7] E. F. Phares, *Arch. Biochem. Biophys.*, **33**, 179 (1951).

[8] E. F. Phares, *ibid.*, **33**, 173 (1951).

[9] J. T. Kummer, H. H. Podgurski, W. B. Spencer and P. H. Emmett, THIS JOURNAL, **73**, 564 (1951).

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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).

[3] A. Haller and E. Bauer, *Compt. rend.*, **150**, 582 (1910).