might occur, although no actual experience of the latter kind is known.

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Tracer Studies with Radioactive Carbon. The Exchange between Acetic Anhydride and Sodium Acetate

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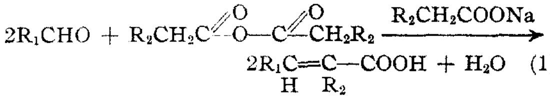
In connection with some tracer studies in these Laboratories it was desired to develop a rapid method for the synthesis from labelled carbon dioxide of an unsaturated acid containing C* only in the carboxyl group. The Perkin synthesis, in which the unsaturated acid is formed by reaction of an aldehyde with an acid anhydride in the presence of a salt (Equation (1)), seemed well suited to our needs.



$$2R_1CHO + R_2CH_2\overset{O}{\overset{/\!/}{C}}\text{—}O\text{—}\overset{O}{\overset{/\!/}{C}}\text{—}CH_2R_2 \xrightarrow{R_2CH_2COONa} 2R_1\underset{H}{C}{=}\underset{R_2}{C}\text{—}COOH + H_2O \qquad (1)$$

Since we wished to obtain the unsaturated acid with the highest possible specific radioactivity, it was desirable to measure the rate of exchange between the salt and the anhydride. Michael[1] and more recently Breslow and Hauser[2] have shown that within several hours at 100° the exchange reaction between sodium acetate and butyric anhydride has come to equilibrium. We have found that the exchange between acetic anhydride and labelled sodium acetate *at room temperature* is surprisingly rapid.

Experimental

Labelled sodium acetate was prepared by shaking 10^{-3} mole of C^*O_2[3] with 5 cc. of 1 *M* CH_3MgI in ether at room temperature for ~ten minutes. After hydrolysis with dilute sulfuric acid the ether was removed by evaporation. Excess solid silver sulfate was added to precipitate silver iodide and the acetic acid distilled off *in vacuo*. The yield was ~95% based upon carbon dioxide. The acetic acid distillate was carefully neutralized with sodium hydroxide solution and evaporated to dryness. A small amount of dilute acetic acid was added and the solution again evaporated to dryness to free the sodium acetate from traces of base. This preparation was thoroughly dried at 100° *in vacuo* until a vacuum of better than 10^{-5} mm. of mercury could be maintained over the solid without pumping.

The dry labelled sodium acetate was shaken with acetic anhydride[4] for twenty minutes at room temperature and the anhydride distilled off at room temperature *in vacuo*. The anhydride was converted into sodium acetate and counted as such.[5] The results of this and a similar experiment employing C^{14} are summarized in Table I.

TABLE I

EXCHANGE BETWEEN NaAc* AND $(Ac)_2O$ AT ROOM TEMPERATURE

Expt.	Equivalents of NaAc	Equivalents of Ac_2O	Time of exchange, min.	Per cent. of random distribution of Ac^{*-}
1	$2\cdot10^{-3}$	$95\cdot10^{-3}$	20	55
2	$1\cdot10^{-3}$	$4.8\cdot10^{-3}$	30	62

In view of the fact that sodium acetate is very insoluble in acetic anhydride it was surprising to find such rapid exchange at room temperature in this two-phase system.

A similar result was obtained with sodium butyrate and acetic anhydride. 4.7 grams of carefully dried sodium butyrate[6] was shaken with 17.6 cc. of acetic anhydride for ~forty minutes at room temperature, after which the anhydride was distilled off at room temperature *in vacuo*.

When the distillate was fractionally distilled it was found that 4.6 cc. had a boiling point above that of acetic anhydride. The acetic and butyric acid content of the high boiling fraction was determined by means of a Duclaux distillation. This fraction consisted of 72% butyric and 28% acetic acid. Thus 18.7% of the acid equivalent in the total anhydride fraction is butyric acid. For random distribution of butyrate between the sodium salt and the anhydride one would expect 10.3% for the above experiment. The marked tendency of butyrate to concentrate in the anhydride at room temperature is in keeping with the results of Michael[1] and Breslow and Hauser.[2]

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[1] Michael, *J. prakt. Chem.*, **60**, 364 (1899).

[2] Breslow and Hauser, THIS JOURNAL, **61**, 786 (1939).

[3] $C^{11}O_2$ was employed in the first experiment and $C^{14}O_2$ in the second.

[4] Distilled from phosphorus pentoxide into a glass receiver which had been thoroughly baked at 200° for several days. The fraction boiling between 138–139° was used.

[5] A description of the production and measurement of C^{11} and C^{14} may be found elsewhere: Ruben, Kamen and Hassid, THIS JOURNAL, **62**, 3443 (1940); Ruben and Kamen, *Phys. Rev.*, **59**, 349 (1941).

[6] Previously evaporated to dryness in the presence of excess butyric acid and then kept at 100° in high vacuum (10^{-5} mm.) for several hours.

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Preparation of β-(2-Methyl-6-oxo-1-cyclohexen-1-yl)-propionic Acid

BY ERWIN SCHWENK AND EDITH BLOCH

Unsaturated cyclic ketoesters of the type of 3-carbomethoxy-2-methyl-6-oxo-1-cyclohexene (I) contain the same atomic grouping as α,β-dialkylglutaconic acids and like the latter can be alkylated with alkyl halides and sodium ethoxide,[1] but apparently only simple alkyl halides have been studied.[2]

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[1] Richter-Taylor, "The Chemistry of the Carbon Compounds," 3rd English ed., Vol. II, p. 139.

[2] See, for instance, Koetz, *et al.*, *Ann.*, **400**, 83 (1913); E. Bergmann and A. Weizmann, *J. Org. Chem.*, **4**, 266 (1939).