contained a considerable amount of gas chromatographic low retention time material (10–30 peaks). These materials apparently interfered with the rearrangement, since successive catalyst passes gave less and less rearrangement, even though the ratio of ketones was far from the equilibrium value and fresh ketone passed over the catalyst rearranged readily.

Using the above procedure, a number of ketones and related compounds were studied to determine the scope and mechanisms of the rearrangement reactions. The results are given in Tables I–V. In these scope experiments, no attempts were made to determine optimum temperatures or flow rates.

Analytical Procedures. After the required number of passes over the catalyst, the recovered material was removed from the receiver, dried, and without further purification analyzed by gas chromatography. The gas chromatographs used in this study were Model A-90-C, A-700 Autoprep, and 600-C Hy-Fi Wilkens Instrument and Research, Inc., instruments. Some 26 different chromatographic columns were employed, utilizing a wide variety of sizes, lengths, liquid phases, and solid supports.

When a reaction product was analyzed on the gas chromatographic column, the retention time of each separated component was obtained. Then, while the column remained under the same conditions, a standard mixture containing the starting ketone and the expected rearranged products was analyzed for the retention times of its components. If the retention time of any peak in the reaction product was about the same as that of any of the standard compounds, a standard mixture which contained approximately the same concentrations as those of the reaction product was prepared and it and the reaction product were analyzed on several columns of different polarity. A change in the polarity of the column substrate often resulted in greatly changed retention times and, in some cases, inversion of the order in which compounds eluted. The use of several columns of different polarity ensures the correct identity of the compound under study. By a study of relative areas of eluted peaks on one column in comparison with another column one was ensured of studying the same compound (peak) under study on the other column. In some cases, small amounts of known compounds were added to the reaction product to determine whether a particular peak's relative area increased in comparison to the other peaks or whether two peaks would form. If two peaks formed, the peak under study was not identical with the known compound.

The percentage compositions given in the tables were calculated from the integrated areas of the gas chromatographic peaks without correction for variation of sensitivity with compound structure. For the closely related compounds involved in this study, this procedure gives results accurate to 1% or better, as shown by analysis of known mixtures. The per cent of ketonic material in the recovered material is perhaps not quite so accurate since compounds of different types are being compared.

In a number of cases, the rearranged ketone was isolated by preparative chromatography. For these isolated samples, the gas chromatographic retention times on several columns, the nuclear magnetic resonance and infrared spectra, and the properties of derivatives were found to be identical with those of authentic samples.[19]

Reactions of Alkynes with Solid Supported Phosphoric Acid Catalyst. To test for the possible intermediacy of alkynes in the observed ketone rearrangements, 1-pentyne, 2-pentyne, and 4-methyl-2-pentyne were passed over the catalyst. Samples (15 ml) of the alkynes were used, and during the injection, a 5-ml sample of water was gradually injected from a separate syringe. The results of the 1- and 2-pentyne experiments are given in the text above, and those for 4-methyl-2-pentyne are given in Table V.

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[19] Further details of the separations and analyses are given in the Ph.D. dissertation of W. H. C., University of Arkansas, Fayetteville, Ark., 1966.

Reactions of Ketones and Related Compounds with Solid Supported Phosphoric Acid Catalyst. II. A Carbon-14 Tracer Study of the Mechanism of the Rearrangement of 3-Pentanone to 2-Pentanone[1a]

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Contribution from the Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701. *Received December 30, 1966*

Abstract: Extensive rearrangement of 3-pentanone to 2-pentanone is accomplished by repeated passage over solid supported phosphoric acid catalyst at 340–360°. 3-Pentanone-3-^{14}C rearranged almost exclusively to 2-pentanone-3-^{14}C rather than 2-pentanone-2-^{14}C, indicating that an oxygen function rearrangement mechanism must be operative.

Acid-catalyzed rearrangements of straight-chain aliphatic ketones to isomeric ketones were unknown prior to the 1960 report[2] of the rearrangement of 3-pentanone to 2-pentanone in perchloric acid solution. For appreciable rearrangement to take place, sufficiently drastic conditions had to be used (*e.g.*, 72% perchloric acid, 100°, 12 hr) so that the recovered pentanone fraction amounted to only a few per cent of the starting material.[3] However, using a solid supported phosphoric acid catalyst, and starting with either 2- or 3-pentanone, good recoveries of extensively rearranged ketone are obtained.[4] This discovery made practical a detailed carbon-14 tracer study of the mechanism of the rearrangement.

The various mechanisms suggested for acid-catalyzed ketone rearrangements[4] fall into two classes, those which involve transfer of the oxygen function from one carbon to another, and those which do not. It is pos-

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[1] (a) Supported by U. S. Atomic Energy Commission Contract AT-(40-1)-3234; taken from the Ph.D. dissertation of W. H. C. and presented at the American Chemical Society Midwest Regional Meeting, Lawrence, Kan., Oct 27, 1966. (b) Monsanto Fellow, 1963–1964.

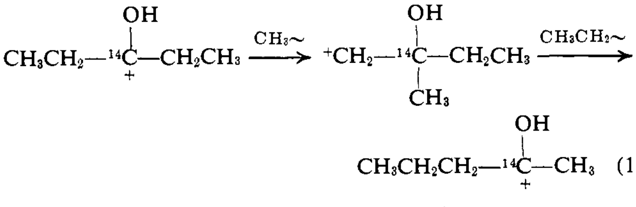
[2] A. Fry, M. Eberhardt, and I. Ookuni, *J. Org. Chem.*, 25, 1252 (1960) (the extent of the rearrangement was later shown[3] to be considerably less than originally reported).

[3] A. Fry, I. Ookuni, G. J. Karabatsos, J. D. Graham, and F. Vane, *ibid.*, 27, 1914 (1962).

[4] Paper I of this series: W. H. Corkern and A. Fry, *J. Am. Chem. Soc.*, 89, 5888 (1967).

sible to distinguish between these two types of mechanisms using carbonyl carbon-14 labeled ketones. Results corresponding to both types of mechanisms have been observed. Barton and Porter[5] found no oxygen function rearrangement in the conversion of 2,2,4,4-tetramethyl-3-pentanone-3-^{14}C to 3,3,4,4-tetramethyl-2-pentanone-2-C^{14}. Other carbon-14 tracer experiments have shown that oxygen function rearrangement does take place with benzopinacolone[6] and pinacolone.[7]

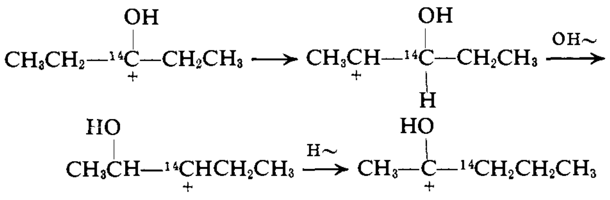
Perhaps the simplest mechanism for the rearrangement of 3-pentanone to 2-pentanone is *concerted* or *stepwise* interchange of methyl and ethyl groups in the ketone conjugate acid. No oxygen function rearrangement is involved; 3-pentanone-3-^{14}C would be converted to 2-pentanone-2-^{14}C.[8]



$$CH_3CH_2-\underset{+}{\overset{\overset{OH}{|}}{^{14}C}}-CH_2CH_3 \xrightarrow{CH_3\sim} {}^{+}CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{^{14}C}}-CH_2CH_3 \xrightarrow{CH_3CH_2\sim} CH_3CH_2CH_2-\underset{+}{\overset{\overset{OH}{|}}{^{14}C}}-CH_3 \quad (1)$$

In the *stepwise* version of this mechanism a high energy primary carbonium ion would be required. The *concerted* version would involve simultaneous shifts of the methyl and ethyl groups.

The oxygen function rearrangement mechanisms may be illustrated by the (concerted or stepwise) OH migration version, wherein 3-pentanone-3-^{14}C would be converted to 2-pentanone-3-^{14}C.[9]



$$CH_3CH_2-\underset{+}{\overset{\overset{OH}{|}}{^{14}C}}-CH_2CH_3 \longrightarrow CH_3\underset{+}{C}H-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{^{14}C}}-CH_2CH_3 \xrightarrow{OH\sim} CH_3\underset{+}{\overset{\overset{HO}{|}}{C}}H-{}^{14}CHCH_2CH_3 \xrightarrow{H\sim} CH_3-\underset{+}{\overset{\overset{HO}{|}}{C}}-{}^{14}CH_2CH_2CH_3 \quad (2)$$

Other oxygen function rearrangement mechanisms involve concerted or stepwise epoxide conjugate acid formation,[10] reversible pinacol formation,[11] and reversible alkyne formation.[4]

In the present research, 3-pentanone-3-^{14}C was subjected to the action of the solid supported phosphoric acid catalyst, and the reaction products were separated, degraded, and assayed for carbon-14.

2-Pentanone and 3-pentanone have such similar physical properties that separation by distillation or preparative gas chromatography is impractical. The iodoform reaction originally used[2] to determine the amount of 2-pentanone in a mixture of the two ketones was later shown to be unsatisfactory in that 3-pentanone also gives iodoform under our usual reaction conditions.[3] For that reason, the mixture of 2- and 3-pentanone isolated by preparative gas chromatography from the reaction product was oxidized with peroxybenzoic acid. Ethyl propionate was obtained from the 3-pentanone and propyl acetate from the 2-pentanone. A careful search was made for methyl butyrate, the isomeric ester which might be expected from the oxidation of 2-pentanone, but none was found; the propyl group migrates to oxygen with much greater facility than the methyl group, in accordance with the observations of Hawthorne, Emmons, and McCallum.[12] The ethyl propionate and propyl acetate were separated easily by preparative gas chromatography. The two esters were then separately degraded to the corresponding anilides and 3,5-dinitrobenzoate esters, which were assayed for carbon-14 content.

The critical question is the location of the carbon-14 in the 2-pentanone obtained from the rearrangement of 3-pentanone-3-^{14}C; if the mechanism involves oxygen function rearrangement, the label should appear in the propyl 3,5-dinitrobenzoate; if not, it should appear in the acetanilide. The rearrangement and degradative scheme is shown in Chart I.

In order for meaningful results to be obtained from the tracer experiments, it was necessary that all of the carbon-14 in the starting 3-pentanone be located at the 3 position, and that no radioactive 2-pentanone impurity be present. A sample of the 3-pentanone-3-^{14}C was diluted with inactive 2-pentanone, and the mixture was subjected to the degradative procedures outlined in Chart I. The results are shown in Table I. Clearly, all of the 3-pentanone activity was contained in the carbonyl group since the ethyl 3,5-dinitrobenzoate was completely inactive, and the starting material contained no active 2-pentanone impurity since the acetanilide and propyl 3,5-dinitrobenzoate contain no significant activity.

Table I. Activity Results from Degradation of a Mixture of 2-Pentanone and the Starting 3-Pentanone-3-^{14}C

Compound	Activity, mcurie/mole
Ethyl propionate	0.1332 ± 0.0002
Propionanilide	0.1332 ± 0.0006
Ethyl 3,5-dinitrobenzoate	0.000
Acetanilide	0.00039 ± 0.00004
Propyl 3,5-dinitrobenzoate	0.00039 ± 0.00004

3-Pentanone-3-^{14}C was subjected to the action of the solid supported phosphoric acid catalyst in three separate experiments, the results of which are shown in Table II.

In all three experiments, approximately 99% of the carbon-14 activity which started out in the 3 position of 3-pentanone ended up in the 3 position of 2-pentanone (approximately 99% of the activity was contained in the propyl 3,5-dinitrobenzoate). Clearly mechanism 2 or some other oxygen function rearrangement mechanism is the only important path for the reaction.

None of the oxygen function rearrangement mechanisms[4,9–11] is ruled out by these results, although on other grounds[4] it appears that OH migration (mechanism 2) or epoxide conjugate acid formation is most likely.

It is interesting to note that replacement of the four α-hydrogens in 3-pentanone by methyl groups results in

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[5] S. Barton and C. R. Porter, *J. Chem. Soc.*, 2483 (1956).

[6] A. Fry, W. L. Carrick, and C. T. Adams, *J. Am. Chem. Soc.*, **80**, 4743 (1958); G. Shulman and A. Fry, unpublished data.

[7] C. T. Davis and A. Fry, *Chem. Ind.* (London), 277 (1960); K. Bhatia, Ph.D. Dissertation, University of Arkansas, Fayetteville, Ark., 1965.

[8] This is a simplified interpretation of the mechanism given by T. E. Zalesskaya, *Zh. Obshch. Khim.*, **16**, 1813 (1946).

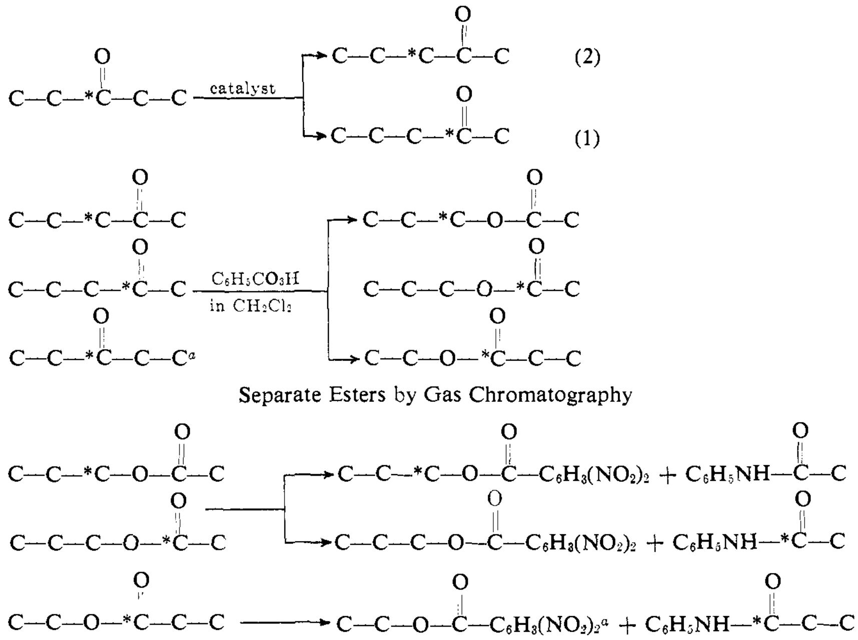
[9] S. Barton, F. Morton, and C. R. Porter, *Nature*, **169**, 373 (1952).

[10] H. D. Zook, W. Smith, and J. Greene, *J. Am. Chem. Soc.*, **79**, 4436 (1957).

[11] T. S. Rothrock and A. Fry, *ibid.*, **80**, 4349 (1958).

[12] M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *ibid.*, 80, 6393 (1958).

Chart I. Scheme for the Rearrangement of 3-Pentanone-3-^{14}C and the Degradation of a Mixture of 2- and 3-Pentanone



[a] 2-Pentanone-2-^{14}C formed by mechanism 1 might revert to 3-pentanone-2-^{14}C by mechanism 2, leading to activity in the ethyl 3,5-dinitrobenzoate; practically none was found there, so that degradative path is not outlined in detail.

reaction[5] by some version of mechanism 1 (in a different reaction system). This is readily understandable in that the stepwise version of mechanism 1 would involve a low energy tertiary carbonium ion with 2,2,4,4-tetramethyl-3-pentanone and a high energy primary carbonium ion with 3-pentanone itself.

Table II. Activity Results from the Degradation of Derivatives of the 2-Pentanone Recovered from Treatment of 3-Pentanone-3-^{14}C with Solid Supported Phosphoric Acid

Sample	Activity, mcurie/mole I	II	III
Propionanilide[a]	0.1332 ± 0.0006	0.0878 ± 0.0001	0.0878 ± 0.0001
Acetanilide[b]	0.00152 ± 0.00006	0.00097 ± 0.00003	0.00086 ± 0.00001
Propyl 3,5-dinitrobenzoate[b]	0.1309 ± 0.0006	0.0891 ± 0.0003	0.0889 ± 0.0004

[a] From the 3-pentanone-3-^{14}C starting material used. [b] From the 2-pentanone recovered from the rearrangement.

Unless the activity in the acetanilide is due to impurities, and we doubt that it is, about 1% of the rearrangement of 3-pentanone to 2-pentanone takes place by mechanism 1 or its equivalent. This conclusion is supported by the fact that a small amount of activity was found in the ethyl 3,5-dinitrobenzoate obtained by degradation of the 3-pentanone recovered from the rearrangement.

Experimental Section

Activity Determinations. All of the compounds were converted to carbon dioxide by a Pregl microcombustion method. The carbon dioxide was collected in an ionization chamber, and the activity was determined using a vibrating reed electrometer. All of the reported activities are averages of at least two determinations on the same sample, and the average deviation of these measurements is given. The over-all reproducibility of the experiments can be judged by the duplicate experiments given in Table II. Generally the errors are no larger than 0.5–1.0%.

Degradation of a Mixture of 2-Pentanone and the Starting 3-Pentanone-3-^{14}C. The 3-pentanone-3-^{14}C used was obtained from Nuclear Research Chemicals, Inc., at a specific activity of 0.9 mcurie/mole. About 0.5 mcurie of this material was diluted with approximately 200 g of 99.9% pure (by gas chromatographic analysis) inactive 3-pentanone which had been purified previously by preparative gas chromatography on a 10 ft × $^3/_8$ in. column of 20% silicone fluid nitrile on 60–80 mesh Firebrick using a Wilkens Instrument and Research, Inc., Model A-700 Autoprep. The 2,4-dinitrophenylhydrazone, mp 158° (lit.[13] mp 156°), and the semicarbazone, mp 139° (lit.[13] mp 139°), of the diluted 3-pentanone were prepared and assayed for radioactivity. The values obtained were 0.1534 ± 0.0008 and 0.1546 ± 0.0001, respectively. A sample of the 3-pentanone-3-^{14}C was diluted with inactive 2-pentanone, and the mixture was degraded by the procedure given in Chart I and described in detail below. The results are given in Table I. It is to be noted that the activities of the 3-pentanone-3-^{14}C 2,4-dinitrophenylhydrazone and semicarbazone are considerably higher than the other derivatives, ethyl propionate and propionanilide. It appears that the starting ketone contains some radioactive impurities which are not removed by the preparation of the usual ketone derivatives. It seems likely that these impurities are also ketones and, being present in only tracer concentrations, are to a considerable extent coprecipitated with the semicarbazone and the 2,4-dinitrophenylhydrazone. The agreement between the activities of ethyl propionate and propionanilide probably indicates complete separation of the radioactive impurities, since the two compounds have the same activity even though several chemical transformations occur before propionanilide was obtained from ethyl propionate.

In spite of the fact that the starting 3-pentanone-3-^{14}C contained radioactive impurities, it should be noted that all of the 3-pentanone activity was contained in the carbonyl group since the ethyl 3,5-dinitrobenzoate contains no activity, and that there was no active

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[13] I. Heilbron, "Dictionary of Organic Compounds," Vol. II, 2nd ed, Oxford University Press, New York, N. Y., 1953, p 186.

2-pentanone impurity since the 2-pentanone derivatives contain no activity. Establishment of these two facts was essential before any significant results could be obtained from the experiments.

Rearrangement of 3-Pentanone-3-^{14}C over Solid Supported Phosphoric Acid Catalyst. 3-Pentanone-3-^{14}C (50 ml) was passed ten times over 61 g of catalyst at 340° (injection rate of 65 ml/hr) according to the procedure previously described,[4] yielding 30 ml of product. Gas chromatographic analysis of the product on a 15 ft × $^1/_8$ in. column of 2% β,β'-oxydipropionitrile on 60–80 mesh Firebrick at 45° indicated the presence of 16.4% 2-pentanone, 41% 3-pentanone, and 42.6% waste material. The other 20 ml of the starting material was accounted for by char on the catalyst bed and material which was condensed in an isopropyl alcohol–Dry Ice trap which was connected to the side arm of the receiver. The 2- and 3-pentanone fraction was separated from the rest of the reaction mixture by gas chromatography on a 12 ft × $^3/_8$ in. column of 30% Carbowax 4000 on 60–80 mesh Firebrick. Samples (0.8 ml) of the product were injected while the column was at 120°. The material which eluted first was discarded, the 2- and 3-pentanone mixture was collected, and then the temperature of the column was raised to 170° until the rest of the waste material eluted. The column was then cooled back down to 120° for another injection. Another 50-ml sample of the 3-pentanone-3-^{14}C was rearranged and separated in the same way, and the 2- and 3-pentanone mixture obtained was combined with that from the first sample. The combined mixture, 21.6 g, contained 5.8% impurities, 28.1% 2-pentanone, and 66.1% 3-pentanone, and was degraded as sample I. After a further dilution of the 3-pentanone-3-^{14}C with inactive 3-pentanone, two more samples were rearranged at 360°, and the pentanone fraction was collected as before. The ketone mixture from sample II, 21.9 g, contained 6.2% impurities, 34% 2-pentanone, and 59.8% 3-pentanone; that from sample III, 21.2 g, contained 7.3% impurities, 34.4% 2-pentanone, and 58.3% 3-pentanone.

Peroxybenzoic Acid Oxidation[14] of the 2- and 3-Pentanone-*X*-^{14}C Mixture. The three samples prepared above were separately degraded. Details are given for sample I. The 2- and 3-pentanone-*X*-^{14}C mixture (21.6 g, 0.251 mole) was added to a solution, contained in a 1-l. round-bottomed flask, which consisted of 719 ml of methylene chloride and 55.51 g (0.402 mole) of peroxybenzoic acid (preliminary experiments with nonradioactive ketones indicated a 1.6:1 molar ratio of the peroxy acid to ketone was necessary to ensure complete oxidation of the ketones). The flask was fitted with a water condenser and placed in an oil bath at 41.5 ± 0.5°. After 120 hr of reaction time, the product was distilled using a short Vigreux column and the fraction boiling at 85–115° was collected.

Chromatographic analysis indicated the presence of ethyl propionate-*X*-^{14}C, propyl acetate-*X*-^{14}C, and small amounts of methylene chloride, chloroform, and some unidentified compounds. Preliminary experiments with inactive materials indicated that 2-pentanone is oxidized only to propyl acetate and not to methyl butyrate under these conditions.[12] No trace of methyl butyrate could be detected when the oxidation reaction products were compared with authentic samples of propyl acetate and methyl butyrate on three gas chromatographic columns: 10 ft × 0.25 in., 20% 1,2,3-tris(2-cyanoethoxy)propane on 60–80 mesh Firebrick; 10 ft × 0.25 in., 20% Carbowax 4000 on 60–80 mesh Firebrick; and 20 ft × $^3/_8$ in., 30% Zonyl E-7 on 60–70 mesh Chromosorb P, DMCS treated and acid washed.

Gas Chromatographic Separation of Ethyl Propionate-*X*-^{14}C and Propyl Acetate-*X*-^{14}C. The reaction product, bp 85–115°, was initially separated by gas chromatography using 0.3-ml sample injections on a 20 ft × $^3/_8$ in. column of 20% 1,2,3-tris(2-cyanoethoxy)propane on 60–80 mesh Firebrick. The separation yielded 11.3 g of 99% pure ethyl propionate-*X*-^{14}C and 3.8 g of 97.5% pure propyl acetate-*X*-^{14}C. Pure ethyl propionate-*X*-^{14}C (99%, 8.3 g) was obtained after the ester was further purified at 95° using 0.3-ml sample injections on a new (noncontaminated) column of the above type. Further purification of propyl acetate-*X*-^{14}C was accomplished at 95° using 0.2-ml sample injections on the Zonyl E-7 column mentioned above. This purification resulted in 3.1 g of 99.9% pure propyl acetate-*X*-^{14}C. The infrared spectra of these two esters, ethyl propionate-*X*-^{14}C and propyl acetate-*X*-^{14}C, were found to be identical with the spectra of authentic samples.

Preparation[15] of Propionanilide-*X*-^{14}C. A Grignard reagent was prepared from 1 g of magnesium and 5 g of ethyl bromide. While the reaction mixture was cooled in an ice–water bath, 4 g of aniline dissolved in 30 ml of ether was added. After the evolution of ethane was complete, 2 ml of ethyl propionate-*X*-^{14}C dissolved in 20 ml of ether was added. The mixture was refluxed for 10 min, cooled, and poured into 100 ml of dilute hydrochloric acid solution. The solid which remained in the flask was dissolved in dilute hydrochloric acid solution and was added to the ethereal material. The ethereal solution was separated and washed twice with 15-ml portions of dilute hydrochloric acid solution and then once with 15 ml of water. After the ether was evaporated, the crude propionanilide (derived from 3-pentanone-*X*-^{14}C) was recrystallized twice from water and once from heptane. The anilide (0.8 g), mp 106.5° (lit.[16] mp 105–106°), was obtained. The crystals were dried under vacuum over calcium chloride for 2 days and then the carbon-14 activity was determined. The propionanilide activity values for the three samples were 0.1366 ± 0.0008, 0.0932 ± 0.0006, and 0.0913 ± 0.0010 mcurie/mole. For some unknown reason, these activity values for the recovered 3-pentanone are a few per cent higher than for the starting material, but these numbers are not needed or used in the primary argument.

Preparation[17] of Ethyl 3,5-Dinitrobenzoate-*X*-^{14}C. 3,5-Dinitrobenzoic acid (1.5 g) was mixed with 2 ml of ethyl propionate-*X*-^{14}C and three drops of concentrated sulfuric acid. This mixture was refluxed for 15 min and then two additional drops of concentrated sulfuric acid were added. After refluxing for an additional 2 hr, the solution was cooled, and 30 ml of ether was added. The ethereal solution was washed twice with 15-ml portions of 5% sodium carbonate solution and then with 10 ml of water. The ether was evaporated to produce the crude ester crystals. These crystals were dissolved in 30 ml of hot 95% ethanol, and the resulting solution was filtered. Hot water (10 ml) was then added and the ethyl 3,5-dinitrobenzoate (derived from 3-pentanone-*X*-^{14}C) was allowed to crystallize. The precipitate was collected by suction filtration and recrystallized again from an ethanol–water mixture and finally from heptane. This produced 0.9 g of ethyl 3,5-dinitrobenzoate, mp 92.5° (lit.[18] mp 92.7°), which was then dried under vacuum over calcium chloride for 2 days before being analyzed for its carbon-14 content. The ethyl 3,5-dinitrobenzoate activity values for the three samples were 0.00035 ± 0.00008, 0.00035 ± 0.00004, and 0.00032 ± 0.00004 mcurie/mole. Essentially none of the activity in the recovered 3-pentanone was anywhere but in the carbonyl group.

Preparation of Acetanilide-*X*^{14}C and Propyl 3,5-Dinitrobenzoate. Degradation of propyl acetate-*X*-^{14}C was accomplished using the same procedures employed in the degradation of ethyl propionate-*X*-^{14}C. After purification of the derivatives using the same recrystallizing solvents, 0.45 g of acetanilide-*X*-^{14}C (derived from 2-pentanone-*X*-^{14}C), mp 114° (lit.[19] mp 113–114°), and 0.49 g of propyl 3,5-dinitrobenzoate-*X*-^{14}C (derived from 2-pentanone-*X*-^{14}C), mp 72.5° (lit.[18] mp 73°), were obtained and used in the activity determinations. The activity values for these compounds are reported in Table II.

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[14] S. L. Friess and R. Pinson, Jr., *J. Am. Chem. Soc.*, 74, 1302 (1952).

[15] D. V. N. Hardy, *J. Chem. Soc.*, 398 (1936).

[16] Reference 13, Vol IV, p 239.

[17] W. B. Renfrow and A. Chaney, *J. Am. Chem. Soc.*, **68**, 150 (1946).

[18] Reference 13, Vol II, p 368.

[19] Reference 13, Vol I, p 6.