

REARRANGEMENT STUDIES WITH ^{14}C —VIII* EXTERNAL AND INTERNAL RETURNS IN THE SOLVOLYSIS OF 2-PHENYL-1- ^{14}C -ETHYL *p*-TOLUENESULFONATE

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Abstract—Acetolysis and formolysis of 2-phenyl-1- ^{14}C -ethyl *p*-toluenesulfonate (I) were interrupted when the reactions were about 50 per cent complete. All samples of 2-phenylethyl *p*-toluenesulfonate recovered from the partially solvolyzed mixtures showed some rearrangements of the ^{14}C -labeled atoms from the C-1 to the C-2 positions, indicating the occurrence of some return to covalent bonding through the intermediate ethylphenonium ion (V) or its equivalent. The fraction of V undergoing return as compared to the amount of V involved in product formation was greater for acetolysis than formolysis. The presence of lithium perchlorate gave rise to salt-promoted ionization resulting in an increase in the ^{14}C rearrangement for the reaction products; however, lithium perchlorate also reduced the relative extent of return involving V. Solvolysis of I in the presence of sodium *p*-toluene- ^{35}S -sulfonate made possible the simultaneous determinations of ^{14}C rearrangement and ^{35}S exchange in the recovered 2-phenylethyl *p*-toluenesulfonate. Considerations of such data led to the conclusion that both external and internal returns take place during acetolysis and formolysis of I.

In a previous paper¹ on isotope position rearrangements observed in the products of solvolyses of 2-phenyl-1- ^{14}C -ethyl *p*-toluenesulfonate (I), conclusions were drawn on the degrees of phenyl participation during solvolysis in different solvents. These results have been substantiated by Saunders *et al.*² from their studies on the rates of solvolysis of some deuterated 2-phenylethyl *p*-toluenesulfonates. It has also been noted¹ that a small amount of "unreacted" 2-phenylethyl *p*-toluenesulfonate recovered from the ethanolysis mixture showed rearrangement to almost the same extent as the ethanolysis product. Such rearrangements in the recovered sulfonate was tentatively attributed to the phenomenon of internal return involving an ethylphenonium *p*-toluenesulfonate ion-pair. In the present studies, acetolysis and formolysis of I were interrupted when the reactions were about 50 per cent complete, and the rearrangements of the ^{14}C -labeled atoms from the C-1 to the C-2 positions were determined for the reaction products and for the *p*-toluenesulfonate recovered from the reaction mixtures. The changes in the magnitude of these rearrangements brought about by effecting the solvolyses in the presence of added lithium perchlorate were also investigated. As an attempt to shed further light on a possible differentiation between external and internal returns, the acetolysis and formolysis of I were carried out in the presence of ^{35}S -labeled sodium *p*-toluenesulfonate, thus affording the simultaneous determinations of the rearrangement of ^{14}C -labeled atoms as well as the exchange of ^{35}S -labeled *p*-toluenesulfonate anion in the 2-phenylethyl *p*-toluenesulfonate recovered from the interrupted reactions.

* For paper VII, see A. J. Finlayson and C. C. Lee, *Canad. J. Chem.* **37**, 940 (1959).

† Holder of Canadian Industries Limited Fellowship, 1956–1958.

¹ C. C. Lee, G. P. Slater and J. W. T. Spinks, *Canad. J. Chem.* **35**, 1417 (1957).

² W. H. Saunders, Jr., S. Asperger and D. H. Edison, *J. Amer. Chem. Soc.* **80**, 2421 (1958).

RESULTS

2-Phenyl-1-¹⁴C-ethyl *p*-toluenesulfonate (I) was prepared as previously described.¹ The location of the ¹⁴C labels on the C-1 position was established by reaction of I with sodium iodide in acetone to give 2-phenyl-1-¹⁴C-ethyl iodide which was oxidized to produce nonradioactive benzoic acid. Alternatively, the 2-phenyl-1-¹⁴C-ethyl iodide so obtained was converted to the Grignard reagent followed by reaction with carbon dioxide to give hydrocinnamic acid which also oxidized to nonradioactive benzoic acid. The latter method was used for the degradation of the samples of 2-phenylethyl *p*-toluenesulfonate recovered from the interrupted solvolysis reactions because firstly, it affords a further purification of the 2-phenylethyl iodide through

TABLE I. RESULTS FROM PARTIAL SOLVOLYSIS OF 2-PHENYL-1-¹⁴C-ETHYL *p*-TOLUENESULFONATE

Reaction	Added salt ^c	% Rearrangement in product		% Rearrangement in recovered sulfonate		Rearrangement ratio (rearrangement in recovered sulfonate/rearrangement in product)		% ³⁵ S in Recovered sulfonate	
		Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
Acetolysis ^a	None	4.8	4.4	2.0	1.9	0.41	0.43		
	0.05 M LiClO ₄	5.4	5.3	2.1	2.1	0.39	0.40		
	0.5 M LiClO ₄	11.9	11.1	2.6	2.1	0.22	0.19		
Formolysis ^b	0.5 M NaOTs- ³⁵ S	5.0	4.9	2.5	2.6	0.50	0.53	7.7	7.4
	None	43.0	43.6	2.7	2.6	0.06	0.06		
	0.05 M LiClO ₄	44.7	46.1	2.7	2.8	0.06	0.06		
	0.5 M LiClO ₄	50.7	50.0	2.9	2.7	0.06	0.05		
	0.5 M NaOTs- ³⁵ S	44.5	41.6	4.6	4.9	0.10	0.12	6.5	6.0

^a 0.5 Mole of 2-phenyl-1-¹⁴C-ethyl *p*-toluenesulfonate and 0.5 mole of potassium acetate per liter of acetic acid.

^b 0.5 Mole of 2-phenyl-1-¹⁴C-ethyl *p*-toluenesulfonate and 0.5 mole of potassium formate per liter of formic acid.

^c Besides potassium acetate or potassium formate.

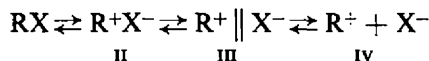
the formation of hydrocinnamic acid, and secondly, the hydrocinnamic acid oxidizes much more readily than 2-phenylethyl iodide.

Acetolysis and formolysis of 0.5 M solutions of I were carried out at reflux temperature in the presence of equimolar quantities of potassium acetate and potassium formate, respectively. In some experiments, other salts added included 0.1 or 1.0 molar equivalent of lithium perchlorate or 1.0 molar equivalent of sodium *p*-toluene-³⁵S-sulfonate. The acetolyses were interrupted after 30 min of refluxing and the formolyses after 20 minutes of refluxing. Under these conditions, 2-phenylethyl *p*-toluenesulfonate (I_r) recovered from the reaction mixtures ranged between 50 and 60 per cent and between 40 and 50 per cent, respectively, for the acetolyses and formolyses. Samples of the recovered sulfonate, I_r, were degraded to benzoic acid as indicated earlier. The products of solvolysis, 2-phenylethyl acetate or 2-phenylethyl formate, were also oxidized to benzoic acid with potassium permanganate. In each case, the radioactivity in the benzoic acid was a measure of the rearrangement of the ¹⁴C-labeled atoms from the C-1 to the C-2 positions of the 2-phenylethyl group. For example, for run no. 1 in the acetolysis with no added salt other than potassium acetate, the radioactivity, on a molar basis, for the hydrocinnamic acid derived from I was 14,394 c.p.m. The benzoic acid derived from the recovered sulfonate I_r and from the reaction product contained, respectively, 294 and 687 c.p.m. of radioactivity on a molar basis. Thus the rearrangement in the recovered 2-phenylethyl *p*-toluenesulfonate was $294/14394 \times 100 = 2.0\%$, and the rearrangement in the reaction product, 2-phenylethyl acetate, was $687/14394 \times 100 = 4.8\%$. The extents of such rearrangements for all solvolysis runs are summarized in Table I.

For the solvolyses in the presence of sodium *p*-toluene-³⁵S-sulfonate, besides determinations of ¹⁴C rearrangements, the exchange or incorporation of ³⁵S into the recovered 2-phenylethyl *p*-toluenesulfonate (I_r) were measured. Thus for acetolysis run no. 1 carried out in the presence of an equimolar amount of ³⁵S-labeled sodium *p*-toluenesulfonate, the specific activity of the barium sulfate derived from the added sodium *p*-toluene-³⁵S-sulfonate and from the recovered sulfonate I_r were, respectively, 3456 and 266 c.p.m. The ³⁵S incorporated into the recovered 2-phenylethyl *p*-toluenesulfonate, therefore, equals $266/3456 \times 100 = 7.7\%$. The results on the ³⁵S incorporation into I_r from both acetolysis and formolysis are also included in Table 1.

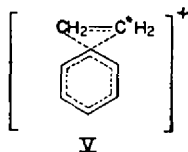
DISCUSSIONS

The possible processes for return from ionic intermediates to covalent bonding during solvolysis have been extensively discussed by Winstein *et al.*^{3,4} The following sequence of ionization-dissociation has been postulated:



The species represented by II is termed an intimate ion-pair, III a solvent separated ion-pair and IV dissociated ions. In the intimate ion-pair, no solvent molecule intervenes between the ions. In the solvent separated ion-pair, the solvation shells of the ions are believed to overlap.⁵ Return to covalent bonding can occur from II, III or IV. It was suggested³ that return from II be called "internal return", and return from III or IV "external return". More specifically, return from III may be termed "external ion-pair return" and return from IV "external ion return". It is of interest to bear these postulated processes in mind in the discussion of the present results.

With reference to the results tabulated in Table 1, the fact that there is rearrangement of the ¹⁴C-labeled atoms from the C-1 to C-2 positions in every sample of 2-phenylethyl *p*-toluenesulfonate (I_r) recovered from partially solvolyzed reaction mixtures definitely indicated some return to covalent bonding involving an intermediate ethylphenonium ion (V) or its equivalent. That the rearrangements in



most of the recovered samples of sulfonate I_r are of the order of 2 per cent is merely a matter of coincidence. It did not arise from the use of a rearranged starting material since degradation of the starting material, I, has shown that it has no activity on carbon-2. Because anchimeric assistance through phenyl participation and anchimerically unassisted solvolysis both contribute to the acetolysis and formolysis of I^{1,2,6} and because S_N2 displacement by the conjugate base of the solvent may also be important, as a qualitative indication of the magnitude of the return process from ionic intermediates, a rearrangement ratio, obtained from division of the percentage

³ S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *J. Amer. Chem. Soc.* **78**, 328 (1956).

⁴ S. Winstein and G. C. Robinson, *J. Amer. Chem. Soc.* **80**, 169 (1958).

⁵ E. Grunwald, *Analyt. Chem.* **26**, 1696 (1954).

⁶ S. Winstein and R. Heck, *J. Amer. Chem. Soc.* **78**, 4801 (1956).

rearrangement in the recovered sulfonate I_r by the percentage rearrangement in the corresponding reaction product, is more significant than the percentage rearrangement in I_r as such. These rearrangement ratios are tabulated in Table I.

For the acetolysis and formolysis of I with no added salt other than potassium acetate or potassium formate, the extent of isotope position rearrangement in the recovered sulfonate, I_r , was slightly higher for formolysis than for acetolysis. However, the rearrangement ratio for acetolysis averaged 0.42 while this ratio for formolysis was only 0.06. These ratios indicate that in the acetolysis, the return process or processes involving the ethylphenonium ion (V) averaged 42 per cent as much as the formation of reaction product, 2-phenylethyl acetate, through V. On the other hand, the return process or processes through V during formolysis was only 6 per cent as much as the formation of 2-phenylethyl formate through V. This is what one would expect since the increase in ionizing power of formic acid over acetic acid would tend to facilitate further solvolysis and relatively retard the return step.^{4,7}

With added lithium perchlorate, it is evident that salt-promoted ionization^{3,4} occurred as the extent of isotope position rearrangements in the reaction products increased with increasing amounts of this added salt. The contribution from such an increase in ionization with phenyl participation to the overall solvolysis would account for at least in part, if not entirely, the increase in acetolysis rate of 2-phenylethyl *p*-toluenesulfonate attributed to the "normal salt effect" of added lithium perchlorate.⁸ The presence of lithium perchlorate is expected to reduce the extent of the return process or processes, possibly through irreversible formation of a carbonium perchlorate ion-pair which will only give rise to reaction product and thereby preventing some of the carbonium ions from possible returns to covalent bonding.^{4,7} In the acetolysis, the presence of an equimolar quantity of lithium perchlorate decreased the rearrangement ratio from about 0.4 to about 0.2, in agreement with expectation.

The data discussed so far do not differentiate the types of return processes involved because the arguments presented can be applied to both external and internal returns. For the solvolysis of I in the presence of sodium *p*-toluene- ^{35}S -sulfonate, a more detailed dissection of the return processes is possible. The incorporation of ^{35}S in the recovered sulfonate I_r may be accounted for by the exchange for added *p*-toluenesulfonate anion in the return from ionic intermediates to covalent bonding, or by a bimolecular displacement reaction between added *p*-toluenesulfonate anion and I, or both. The ^{14}C rearrangement in the recovered sulfonate I_r must arise from return involving ionic intermediates; the bimolecular displacement between *p*-toluenesulfonate anion and I will not contribute to ^{14}C rearrangement in I_r . For the present system, especially in the acetolysis, it is very likely that some of the ^{35}S found in I_r was derived from such a bimolecular displacement since considerable bimolecular reaction between 2-phenylethyl *p*-toluenesulfonate and acetate anion was noted during acetolysis.⁹ Even if one were allowed to neglect the incorporation of ^{35}S into I_r through bimolecular displacement, the presence of ^{35}S in I_r is not a definitive criterion for a differentiation between external and internal returns because it may be possible to have exchange of *p*-toluenesulfonate anion with ionic intermediates II, III

⁷ A. Streitwieser, Jr., *Chem. Rev.* **56**, 571 (1956).

⁸ A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.* **78**, 2767 (1956).

⁹ S. Winstein, C. R. Lindgren, H. Marshall, and L. L. Ingram, *J. Amer. Chem. Soc.* **75**, 147 (1953).

or IV. On the other hand, if the results were to show an absence of ^{35}S in I_r while I_r still shows ^{14}C rearrangement, then such observations would be decisive evidence for internal return, namely return from intimate ion-pair II. However, such results were not observed.

Considering the actual experimental data given in Table 1, the interpretation of the amount of ^{35}S in I_r in conjunction with the magnitude of ^{14}C rearrangement in I_r can lead to some interesting conclusions. Take, for example, formolysis runs. No. 1 and 2 in the presence of an equimolar quantity of sodium *p*-toluene- ^{35}S -sulfonate, the ^{14}C rearrangements in I_r were 4.6 per cent and 4.9 per cent, respectively. If this rearrangement were to arise entirely from return involving carbonium ion V and the added *p*-toluene- ^{35}S -sulfonate anion, the incorporation of ^{35}S into I_r would have to be $2 \times 4.6 = 9.2\%$ ¹⁰ and $2 \times 4.9 = 9.8\%$ ¹⁰ of the ^{35}S -labeled sulfonate added. However, allowance should be made for the dilution of the added *p*-toluene- ^{35}S -sulfonate anions by the *p*-toluenesulfonate anions formed during the reaction. Under the experimental condition employed, an estimated correction factor of 0.8 would have to be applied for reactions interrupted at 50 per cent completion. The expected incorporation of ^{35}S into I_r for the two formolysis runs would be $0.8 \times 9.2 = 7.4\%$ and $0.8 \times 9.8 = 7.8\%$ if only external return were operative and if bimolecular displacement between I and *p*-toluene- ^{35}S -sulfonate anion were negligible. Actually, the percentage ^{35}S incorporated in I_r was less, namely, 6.5 per cent and 6.0 per cent for the two runs, indicating that at least some of the *p*-toluenesulfonate anions involved in the return to give isotopically rearranged I_r were derived from an intramolecular process. In other words, there is definitely some internal return from an intimate ion-pair in the formolysis of I.

To account for the incorporating of ^{35}S in I_r from formolysis, one may assume the occurrence of only bimolecular displacement between *p*-toluene- ^{35}S -sulfonate anion and I without postulating any external return. However, very probably, this is not the case as external return may be regarded as playing a definite role from the following considerations. Comparing the ^{14}C rearrangements in the reaction product and in the recovered I_r from formolysis runs with and without added sodium *p*-toluene- ^{35}S -sulfonate, it can be seen that the extent of salt-promoted ionization due to added sodium *p*-toluenesulfonate is small, if any. However, the extent of rearrangements in the recovered I_r is increased considerably by the presence of sodium *p*-toluenesulfonate. Thus the rearrangement ratios rose from 0.06 to an average of 0.11 for formolysis without and with added sodium *p*-toluenesulfonate. These ratios indicate that the presence of added *p*-toluenesulfonate anion increased the fraction of carbonium ions (V) undergoing return to covalent bonding. Such an effect is reminiscent of the "mass-law effect" of added common ions¹¹ and thus is indicative of the occurrence of external return. One may, therefore, reasonably conclude that in the formolysis of I, both internal return and external ion return take place.

For the acetolysis of I in the presence of an equimolar quantity of sodium *p*-toluene- ^{35}S -sulfonate, the results are not as clear cut as those from formolysis. The fact that the percentage ^{35}S in the recovered sulfonate I_r was more than twice the percentage ^{14}C rearrangement in I_r (see Table 1) appears to indicate that it may not

¹⁰ If a bimolecular displacement between I and *p*-toluene- ^{35}S -sulfonate anion occurs, the ^{35}S incorporation would have to be still higher.

¹¹ L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.* 979 (1940).

be necessary to postulate the occurrence of internal return in the acetolysis. However, a substantial part of the ^{35}S in I_r recovered from acetolysis may be derived from bimolecular displacement between *p*-toluene- ^{35}S -sulfonate and I, though the present data cannot show what fraction of the ^{35}S in I_r should be attributed to this source. Actually, one should expect, by analogy with formolysis, that both internal and external returns may be involved in the acetolysis of I.

Considerable kinetic data on the acetolysis of 2-phenylethyl *p*-toluenesulfonate have been reported by Winstein *et al.*^{6,8,9} It is of interest to note that in the acetolysis of certain systems, these workers observed a "special salt effect" characterized by a rather large increase in rate with the addition of small amounts of lithium perchlorate and that such a special salt effect was not observed in the acetolysis of 2-phenylethyl *p*-toluenesulfonate.⁸ The occurrence of this special salt effect has been attributed to a suppression of external ion-pair return, or the suppression of return from solvent separated ion-pair III.⁴ For a system which does not show the special salt effect but does show evidence of a return process, the return is then inferred to be internal return from intimate ion-pair II.⁴ Since acetolysis of I would not give an observable special salt effect,⁸ one may then argue that only internal return is operative during acetolysis of I. However, since the contribution to the overall acetolysis reaction of I by the ionic process involving carbonium ion V or its equivalent amounts to only about 10 per cent,¹² under such circumstances, it is uncertain whether the absence of observable special salt effect would have the same significance as in systems with more stable carbonium ions. The quite sensitive isotope position rearrangement data given in Table I show an increase in the rearrangement ratios of from about 0.4 to about 0.5 for acetolysis of I in the absence and in the presence of added sodium *p*-toluenesulfonate. Such results again indicate a greater fraction of V undergoing return when the common *p*-toluenesulfonate anion is present. It is, therefore, very likely that during acetolysis as well as formolysis of I, returns to covalent bonding involve both external and internal returns.

EXPERIMENTAL

The preparation of 2-phenyl-1- ^{14}C -ethyl *p*-toluenesulfonate (I), the solvolyses of I, and the degradation of the solvolyses products have been described previously.¹ In the present work, acetolyses or formolyses of I, with or without added lithium perchlorate or sodium *p*-toluene- ^{35}S -sulfonate, were interrupted before completion and the reaction products as well as the "unreacted" 2-phenylethyl *p*-toluenesulfonate were recovered for degradation. A typical run, that of a formolysis in the presence of an equimolar quantity of sodium *p*-toluene- ^{35}S -sulfonate, is given below to illustrate the present experimental procedures.

Sodium p-toluene- ^{35}S -sulfonate. *p*-Toluene- ^{35}S -sulfonic acid was prepared by sulfonation of toluene with concentrated sulfuric acid containing ^{35}S . The method used was as described by Lucas and Pressman.¹³ The product obtained, after recrystallization from dioxane and petroleum ether, melted at 103–104°. A diethyl ether solution of this *p*-toluene- ^{35}S -sulfonic acid and 2-phenylethyl *p*-toluene-sulfonate showed no exchange of ^{35}S after standing at room temp for 1 week. The sodium *p*-toluene- ^{35}S -sulfonate was prepared from the acid by neutralization with sodium carbonate followed by complete removal of the excess water.

Formolysis in the presence of sodium p-toluene- ^{35}S -sulfonate. A mixture of 4.00 g (0.0145 mole) 2-phenyl-1- ^{14}C -ethyl *p*-toluenesulfonate, 2.82 g (0.0145 mole) sodium *p*-toluene- ^{35}S -sulfonate, and 1.22 g (0.0145 mole) potassium formate in 29 ml anhydrous formic acid (m.p. $8.3^\circ \pm 0.1^\circ$) was refluxed for 20 min. The resulting mixture was poured onto crushed ice and then extracted 3 times

¹² From the ^{14}C rearrangement of about 5% in the reaction product, 2-phenylethyl acetate.¹

¹³ H. J. Lucas and D. Pressman, *Principles and Practice in Organic Chemistry* p. 342. John Wiley, New York (1949).

with 40 ml portions ether. The combined extract was washed successively with water, dilute sodium carbonate solution and again with water. The washed extract, after drying over magnesium sulfate, was evaporated to about 5 ml. Low boiling petroleum ether was then added to induce crystallization of the "unreacted" 2-phenylethyl *p*-toluenesulfonate. After cooling in a refrigerator at -10° overnight, the crystals obtained weighed 2.1 g. Two additional recrystallizations from ether and petroleum ether gave a product with a m.p. of $39-40^{\circ}$. (lit.¹⁴ m.p. $35.5-36.5$; $39-40^{\circ}$).

The combined mother liquor and washings from the first crystallization of the recovered 2-phenylethyl *p*-toluenesulfonate was distilled to remove the solvents. Vacuum distillation of the residue yielded 0.81 g 2-phenylethyl formate, b.p. $60-62^{\circ}$ at 1.2 mm (lit.¹⁵ b.p. $73-75^{\circ}$ at 3 mm).

2-Phenylethyl iodide and sodium p-toluenesulfonate from the recovered 2-phenylethyl p-toluenesulfonate. A mixture of 1.65 g (0.0060 mole) of the recovered 2-phenylethyl *p*-toluenesulfonate and 1.08 g (0.0072 mole) anhydrous sodium iodide in 55 ml reagent grade acetone was refluxed for 3.5 hr. The sodium *p*-toluenesulfonate, which appeared as an insoluble product during the reaction, was filtered off and thoroughly washed with acetone. It weighed 1.06 g (91%) and it was saved for ³⁵S assay.

The combined filtrate and washings after the removal of the sodium *p*-toluenesulfonate was evaporated to approximately 5 ml and then diluted with 50 ml petroleum ether. The resulting solution was washed with 10 ml 1% sodium bisulfite solution and then with two 20 ml portions water. After drying over magnesium sulfate, the solvent was removed and the residue distilled under reduced pressure to give 1.22 g (88%) 2-phenylethyl iodide, b.p. $67-68^{\circ}$ at 1.2 mm (lit.¹⁶ b.p. $114-116^{\circ}$ at 12 mm).

Hydrocinnamic acid. A solution of 1.58 g (0.0069 mole) 2-phenylethyl iodide in 8 ml anhydrous ether was added dropwise over a period of 10 min to a stirred mixture of 0.50 g (0.021 mole) reagent grade magnesium dust in 8 ml of anhydrous ether. The magnesium had been previously activated by the addition of a few small drops of ethyl bromide. Two to three minutes after the addition of the 2-phenylethyl iodide was completed, the Grignard solution was pipetted from the excess magnesium and put into a 250 ml Erlenmeyer flask cooled at about -20° . A slow stream of dry carbon dioxide was bubbled into the Grignard solution for 15 min. Cold, dil HCl was then added until the mixture was decidedly acidic. Any diethyl ether remaining was removed by a current of air, leaving behind the aqueous layer containing some oil which crystallized on cooling. The yellowish crystals were filtered off, dissolved in a few ml dil NaOH and then washed 3 times with 20 ml portions ether. Acidification of the aqueous solution resulted in a crystalline product which after air drying weighed 0.66 g (64%). Recrystallized twice from petroleum ether, it melted at 48° . (lit.^{17b} m.p. 47° , 48.5°).

The procedure described above gave the best yields of hydrocinnamic acid. Refluxing the Grignard reaction mixture during or after the addition of 2-phenylethyl iodide tended to cause the formation of 1,4-diphenylbutane, m.p. $51-52^{\circ}$ (lit.^{17a} m.p. 52°).

Benzoic acid from hydrocinnamic acid. A mixture of 200 mg hydrocinnamic acid, 1.5 g potassium permanganate and 1.0 g sodium hydroxide in 15 ml water was heated on a steam bath for 3 hr. The reaction mixture was then decolorized by addition of sodium bisulfite and dil HCl. Chilling the resulting solution and collecting the crystals formed gave benzoic acid in approximately 90% yield. The product was recrystallized several times from water and finally sublimed before being assayed for ¹⁴C activity.

Radioactivity assays. ¹⁴C activities were assayed by converting all compounds to barium carbonate and counting it as infinitely thick samples of constant geometry in a gas flow Geiger counter. Specific activity in c.p.m. on a molar basis was obtained by correcting for the presence of non-labeled carbon atoms in a given compound by multiplying the observed activity with the number of carbons per molecule in that compound.¹⁸

³⁵S activities were assayed by converting the S-containing compounds to sulfate in a Parr bomb calorimeter and counting the sulfate as infinitely thick samples of barium sulfate.

Acknowledgement—The financial support given by the National Research Council of Canada is gratefully acknowledged.

¹⁴ D. Klamann, *Montash.* **84**, 54 (1953).

¹⁵ R. E. Buckels and J. E. Maurer, *J. Org. Chem.* **18**, 1585 (1953).

¹⁶ A. I. Vogel, *Practical Organic Chemistry* (2nd Ed.) p. 287. Longmans, Green, London (1948).

¹⁷ I. Heilbron and H. M. Bunbury, *Dictionary of Organic Compounds* Vol. II, ^a p. 405; ^b p. 705. Eyre and Spottiswoode, London (1953).

¹⁸ J. D. Roberts, W. Bennett, E. W. Holroyd and C. H. Fugitt, *Analyt. Chem.* **20**, 904 (1948).