TABLE I

PHYSICAL DATA OF 2-ACETYLBENZOIC ACID AND RELATED COMPOUNDS

Entry	Compound	Nmr data, δ^{CH_3} Ring	Nmr data, δ^{CH_3} Chain	Ultraviolet spectral data $\lambda_{max}^{2\text{-propanol}}$	Ultraviolet spectral data $\epsilon \times 10^{-3}$	Infrared data, cm^{-1}
	2-Acetylbenzoic acids					
1	Ia (R = NH_2)	1.68		218, 250, 335,	20.00, 7.70, 4.50,	3348, 3356, 1724, 1706, 1623
2	Ib (R = OH)	1.77		223, 302	6.15, 4.12	3280, 2700, 2500, 1742 (sh), 1704
3	Ic (R = H)	1.78	2.45	228, 272, 280	9.00, 0.98, 0.97	3257, 1727
4	Id (R = NO_2)		2.38	217	15.00	3300–3100, 2700–2500, 1720, 1695
				$\mu_{max}^{ethanol}$	$\epsilon \times 10^{-3}$	
	Acetophenones					
5	IIa (R = NH_2)		2.48	231,[a] 225 (infl), 368,	22.90, 10.00, 1.90	
6	IIb (R = OH)		2.53	218,[a] 252.5	25.12, 10.00	
7	IIc (R = H)		2.58	224,[a] 278	12.60, 1.00	
8	IId (R = NO_2)		2.68	226,[a]	22.40	
9	Methyl *o*-aminobenzoate[a]			247, 337	5.01, 5.01,	
10	Methyl *o*-hydroxybenzoate[a]			238, 306	9.33, 4.37	
	3-Ethyl-7-hydroxyphthalide[a]			234, 300	7.00, 4.60	
11	Methyl benzoate[a]			228, 273, 280	12.00, 0.87, 0.73	
	Phthalide[b]			227, 273, 280	9.90, 1.72, 1.66	
12	Ethyl *o*-nitrobenzoate			255 (infl), 325 (infl)	4.47, 0.52	

[a] "Organic Electronic Spectral Data," Vol. I–IV, Interscience Publishers, Inc., New York, N. Y. 1946–1966, various editors. [b] W. A. Schroeder, P. E. Wilcox, K. N. Trueblood, and A. O. Dekker, *Anal. Chem.*, **23**, 1740 (1951).

Summary.—Based upon nmr spectra of 6-substituted 2-acetylbenzoic acids in dimethyl sulfoxide-d_6 solutions, the presence of ring and chain tautomers could be deduced from the position of the methyl bands. A high-field signal indicated the presence of the ring form, while a low-field signal indicated the presence of the chain form.

Experimental Section

2-Acetylbenzoic acid was obtained from Aldrich Chemical Co., Inc., Milwaukee, Wis. 53210. The 6-nitro, 6-amino, and 6-hydroxy derivatives were prepared according to published procedures. Infrared spectra of samples in potassium bromide disks were determined on a Beckman IR-5 instrument. Ultraviolet spectra were measured on a Cary spectrophotometer (Model 14M). Nuclear magnetic resonance spectra (10–15% w/w dimethyl sulfoxide-d_6 solutions with tetramethylsilane as internal reference) were obtained on a Varian A-60 spectrometer. Melting points were checked on a Uni-melt Thomas–Hoover capillary melting point apparatus for comparison with literature values.[1]

Registry No.—Ia-B, 13619-67-5; Ib-B, 13619-68-6; Ic-A, 577-56-0; Ic-B, 1828-76-8; Id-A, 13619-70-0; IIa, 99-03-6; IIb, 121-71-1; IIc, 98-86-2; IId, 121-89-1; ethyl *o*-nitrobenzoate, 610-34-4.

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Absence of Rearrangement in the *p*-Nitrophenethyl Group

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p-Nitrophenethyltrimethylammonium iodide labeled with tritium was prepared[1] by Scheme I. Since one or more of these reactions could proceed by way of a nonclassical carbonium ion with possible rearrangement, it was necessary to establish the amount of rearrangement which occurred during the synthesis.

SCHEME I

$$\text{phenylacetic acid} \xrightarrow{\text{LiAlH}_4} \text{phenethyl alcohol} \xrightarrow[\text{and hydrolysis}]{\text{fuming HNO}_3\text{ on ester}}$$

$$p\text{-nitrophenethyl alcohol} \xrightarrow[\text{HBr}]{48\%}$$

$$p\text{-nitrophenethyl bromide} \xrightarrow[\text{N(CH}_3)_3]{\text{KI,}}$$

$$p\text{-nitrophenethyltrimethylammonium iodide}$$

Lee and Spinks[2] found that rearrangement occurred to the following extents when 2-phenylethanol-1-^{14}C was treated with thionyl chloride alone (49.4%), with thionyl chloride in pyridine (0.0%), with 48% hydrobromic acid (6.2%), with 55% hydriodic acid (2.7%), and with phosphorus and iodine (6.4%). Roberts and Regan[3] treated a number of 2-(*p*-substituted phenyl)-ethylamines with nitrous acid in water and in acetic acid and found that the most rearrangement (45%) occurred in acetic acid with 2-(*p*-methoxyphenyl)-ethylamine and that the least rearrangement (about 5%) occurred with 2-(*p*-nitrophenyl)ethylamine in water or acetic acid. The reaction of 2-phenylethylamine with nitrous acid in acetic acid, which has been reinvestigated with the aid of gas chromatography,[4] gives both 1-phenylethyl acetate (I) and 2-phenylethyl acetate (II). When 2-phenylethylamine-1-^{14}C is used, I shows 0.23% migration of carbon-14 and II shows 27% migration.

In this investigation, 2-(*p*-nitrophenyl)ethyl-1-^{14}C-trimethylammonium iodide was prepared by the same scheme shown earlier, each compound was oxidized with alkaline permanganate to benzoic acid or *p*-nitrobenzoic acid, and these acids were assayed for radioactivity. The results, given in Table I, indicate that

[1] E. M. Hodnett and J. J. Flynn, Jr., *J. Am. Chem. Soc.*, **79**, 2300 (1957); E. M. Hodnett and J. J. Sparapany, *Pure Appl. Chem.*, **8**, 385 (1964).

[2] C. C. Lee and J. W. T. Spinks, *Can. J. Chem.*, **32**, 1005 (1954).

[3] J. D. Roberts and C. M. Regan, *J. Am. Chem. Soc.*, **75**, 2069 (1953).

[4] J. L. Coke, *ibid.*, **89**, 135 (1967).

TABLE I

ASSAY OF OXIDATION PRODUCTS

Compd	Radioactivity, μcuries/mmole	Acid	Radioactivity, μcuries/mmole	Mp of acid, °C	Extent of rearrangement, %
$C_6H_5CH_2CO_2H$	125	$C_6H_5CO_2H$	0.0625	117[a]	0.05
$C_6H_5CH_2CH_2OH$	8.23	$C_6H_5CO_2H$	0.0156	121[a]	0.19
p-$O_2NC_6H_4CH_2CH_2OH$	3.15	p-$O_2NC_6H_4CO_2H$	0.0098	240[b]	0.31
p-$O_2NC_6H_4CH_2CH_2Br$	3.12	p-$O_2NC_6H_4CO_2H$	0.0164	242[b]	0.53
p-$O_2NC_6H_4CH_2CH_2N(CH_3)_3I$	3.10	p-$O_2NC_6H_4CO_2H$	0.0168	241[b]	0.54

[a] Melts 122.38°; F. W. Schwab and E. Wichers, *J. Res. Natl. Bur. Std.*, **34**, 333 (1945). [b] Melts 240°; E. P. Wightman and H. C. Jones, *Am. Chem. J.*, **46**, 89 (1911).

no significant rearrangement occurred in any of the steps.

Experimental Section

Preparation of 2-(*p*-Nitrophenyl)ethanol-1-^{14}C.—Phenylacetic acid-carboxyl-^{14}C was prepared by carbonation of benzylmagnesium chloride with radioactive carbon dioxide.[5] Reduction of this acid with lithium aluminum hydride[6] gave 2-phenylethanol-1-^{14}C. Nitration of the acetate of this compound and hydrolysis of the ester[7] gave 2-(*p*-nitrophenyl)ethanol-1-^{14}C.

Preparation of 2-(*p*-Nitrophenyl)ethyl-1-^{14}C Bromide.—2-(*p*-Nitrophenyl)ethanol-1-^{14}C (10.2 g, 61 mmoles) was refluxed for 24 hr with 7.5 ml of 48% hydrobromic acid and 0.5 ml of concentrated sulfuric acid. The product, extracted with benzene and recrystallized from ethanol, melted at 64° (lit.[8] mp 68°); yield 12.6 g (55 mmoles, 89% of theory), radioactivity yield 89%.

Preparation of 2-(*p*-Nitrophenyl)ethyl-1-^{14}C-trimethylammonium Iodide.—*p*-Nitrophenethyl-1-^{14}C bromide (5 g, 22 mmoles) was placed in an erlenmeyer flask with 3 g (18 mmoles) of potassium iodide and 22.5 ml of a methanol solution containing 25% trimethylamine. The mixture was allowed to react at room temperature for 2 weeks. The yellow crystals which formed on the bottom and sides of the flasks were isolated by filtration and recrystallized from ethanol. The yield was 3.5 g (10 mmoles, 48% of theory), the melting point of the crystals was 207° (lit.[9] mp 199°), and the radioactivity yield in the reaction was 45%.

Registry No.—2-(*p*-Nitrophenyl)ethyl-1-^{14}C bromide, 13391-70-3; 2-(*p*-nitrophenyl)ethyl-1-^{14}C-trimethylammonium iodide, 13391-71-4.

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[5] W. Lamprecht and H. Rehberg, *Z. Physiol. Chem.*, **301**, 46 (1955).

[6] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 2548 (1947).

[7] H. M. Woodburn and C. F. Stuntz, *ibid.*, **72**, 1361 (1950).

[8] E. L. Foreman and S. M. McElvain, *J. Am. Chem. Soc.*, **62**, 1435 (1940).

[9] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 523 (1933).

Formation of Organopotassium Compounds from Propylene and Potassium or Potassium Hydride

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It is generally accepted[1,2] that the dimerization of propylene in the presence of potassium, rubidium, or cesium metals or their hydrides proceeds through the initial formation of an organoalkali compound which acts as a source of allyl carbanion. This adds to propylene, giving rise to a methylpentenyl carbanion which reacts with propylene to form 4-methyl-1-pentene,[3] the thermodynamically least stable of the methylpentenes, and to regenerate the allyl alkali metal compound. The formation of significant amounts of organoalkali compounds in the reaction has not been directly demonstrated, probably because of the complex nature of the catalyst residues which are formed under most reaction conditions. The coarse dispersions of alkali metal that are usually used leave large amounts of unreacted alkali metal in the residues. Furthermore, reaction temperatures above about 150° favor hydrogen-transfer reactions which lead to propane formation and concurrent production of cokelike solids in a manner similar to that found in the alkali metal catalyzed alkylation of toluene with propylene.[4]

We have found that providing a high surface to volume ratio of potassium by use of a stabilized potassium dispersion in the dimerization of propylene at 150° results in essentially complete conversion of the potassium metal to organopotassium compounds or other products. Alcoholysis of the catalyst residue and analysis of the recovered gaseous products showed that at least 60% of the potassium was converted to propylene derivatives, probably mostly potassium allyl (Table I). Small amounts of *n*-butane derivatives were also formed. Potassium derivatives of hexenes were present but were not determined quantitatively by the method of analysis used. Conversion of the potassium dispersion to potassium hydride and alcoholysis of this catalyst after its use in a propylene dimerization reaction showed that this catalyst was essentially identical with that obtained by the reaction of propylene with potassium metal.

TABLE I

GASES EVOLVED BY ALCOHOLYSIS OF USED CATALYSTS

	Catalyst			
	K	KH	K on K_2CO_3	KH on K_2CO_3
Gas, % of theory	63	59	66	78
Gas compn, mole %				
Hydrogen	0.6	1.4	25.8	12.0
Propylene	98.9	98.2	73.9	85.5
Propane	0.0	0.0	0.2	1.1
n-Butane	0.4	0.3	0.0	0.7
Butenes	0.0	0.1	0.0	0.7

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[1] H. Pines and V. Mark, *J. Am. Chem. Soc.*, **78**, 4316, 5946 (1956).

[2] A. W. Shaw, C. W. Bittner, W. V. Bush, and G. Holzman, *J. Org. Chem.*, **30**, 3286 (1965).

[3] R. M. Schramm, U. S. Patent 2,986,588 (May 30, 1961).

[4] R. M. Schramm and G. E. Langlois, *J. Am. Chem. Soc.*, **82**, 4912 (1960).