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.

Acknowledgment.—This work was sponsored by the U. S. Atomic Energy Commission under Contract AT(11-1)-1049 and the Research Foundation of Oklahoma State University.

(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

John B. Wilkes

Chevron Research Company, Richmond, California

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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

(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).

Similar results were obtained if the surface area of the potassium or potassium hydride was increased by spreading the potassium metal or potassium hydride on a support of dry, powdered potassium carbonate. Some relatively large particles of metal or metal hydride remained in this case and conversion of the potassium or potassium hydride to organopotassium compounds was incomplete, as shown by the hydrogen evolved upon alcoholysis and by visual observation in the case of the supported metal.

Dispersions of potassium made in the conventional manner with the addition of 0.5–1.0% of a stabilizing agent,[5] based on the weight of the potassium, are not satisfactory in this reaction, as coalescence to bulk metal occurs if these dispersions are reacted with propylene under conditions at which dimerization occurs. By using a much larger amount of dispersing agent, for example, 4 wt % of oleic acid, potassium dispersions can be prepared which do not coalesce under reaction conditions. These dispersions can be converted readily to their hydrides to form suspensions which do not agglomerate at reaction conditions.

The reaction conditions used for dimerizing propylene and converting potassium and potassium hydride to organopotassium compounds are shown in Table II.

TABLE II

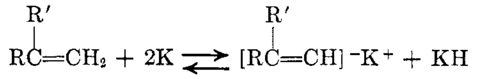
DIMERIZATION OF PROPYLENE WITH POTASSIUM AND POTASSIUM HYDRIDE CATALYSTS

	Catalyst			
	K	KH	K on K_2CO_3	KH on K_2CO_3
Particle size, μ	1–3	1–3	2–400	2–400
Catalyst, g	9.5	10	1.6	1.4
Solvent, ml	90	90	90	90
Propylene, g	135	124	85	90
Temp, °C	148 ± 2	156 ± 9	150 ± 2	152 ± 5
Time, hr	4	2.5	7.5	5.2
Induction period, hr	1.2	0.0	2.0	0.0
Pressure, atm				
Initial	79	81	62	66
Final	25	26	31	31

With potassium catalysts, an initial slow reaction (induction) period after reaction temperature was reached was observed, while reaction occurred immediately with use of potassium hydride catalysts. In the later stages of the reaction, the rate of pressure drop was the same for the catalyst made from either potassium or potassium hydride.

The organopotassium compounds may arise by several possible routes. A possible mechansim of the formation of potassium allyl from potassium and propylene has been outlined.[2] This mechansim involves the initial addition of a potassium atom to propylene to give a radical anion in what is probably the rate-determining step. Although it is generally plausible, the mechanism does not readily account for the different reactivities of simple olefins toward potassium. The literature[6] shows that reactions between ethylene and other simple olefins in the presence of potassium are extremely rapid compared to the dimerization of propylene. The initial reaction of ethylene with potassium to form organopotassium compounds also appears to be much more rapid than comparable reactions with other simple olefins. No induction period was observed in the oligimerization of ethylene with a stabilized potassium dispersion at 150° and 68–36 atm. The reaction of ethylene and propylene with stabilized potassium dispersion was rapid and showed no induction period at 110–125°, while propylene at 120° gave induction periods of 15–40 hr. By contrast, isobutene does not readily react with potassium at conditions that are suitable for oligimerization of ethylene and propylene. Hydrogen transfer to produce isobutane was the principal reaction observed when isobutene and stabilized potassium dispersion were heated together at 150–160° and 35–40 atm. This appears to be caused by failure of isobutene to react with potassium to form an organopotassium intermediate as, with potassium allyl catalyst prepared by the reaction of propylene and potassium dispersion, isobutene reacted smoothly under the same conditions to give mainly isomeric octenes and only traces of isobutane.

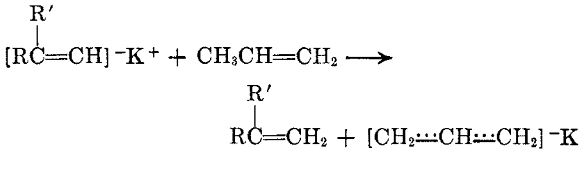
The reactivity sequence toward potassium metal of ethylene > propylene > isobutene indicates that a radical anion is probably not formed as an intermediate. A carbon–hydrogen cleavage appears to be a more probable route. The high reactivity of ethylene and poor reactivity of isobutene indicate that the initial reaction must occur at a vinylic rather than at an allylic position. It has been shown[7] that in the metalation of 1-dodecene with alkyl sodium compounds, removal of a proton at the terminal vinylic position is kinetically favored, even though removal of a proton at the allylic position is thermodynamically more favorable. A similar situation probably exists in the reaction of simple olefins with potassium metal. The olefin may be adsorbed or chemisorbed on the metal, permitting reaction to occur by a concerted mechanism as in eq 1,



$$\overset{R'}{\overset{|}{RC}}{=}CH_2 + 2K \rightleftarrows [\overset{R'}{\overset{|}{RC}}{=}CH]^-K^+ + KH \qquad (1)$$

where R and R′ are hydrogen or alkyl groups. A similar reversible reaction of this type would also result in deuterium exchange in partially deuterated alkylbenzenes.[8]

With propylene, the terminal vinyl carbanion then reacts to give the thermodynamically more stable potassium allyl and to regenerate the original olefin (eq 2).



$$[\overset{R'}{\overset{|}{RC}}{=}CH]^-K^+ + CH_3CH{=}CH_2 \longrightarrow \overset{R'}{\overset{|}{RC}}{=}CH_2 + [CH_2{\cdots}CH{\cdots}CH_2]^-K^+ \qquad (2)$$

The potassium hydride adds to propylene[9] to give propylpotassium, which reacts rapidly with propylene to give propane and potassium allyl. With potassium hydride as the catalyst precursor, the reaction proceeds directly as in eq 3 and 4. As shown by the lack of an

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(5) M. Sittig, "Sodium, its Manufacture, Properties and Uses," Reinhold Publishing Corp., New York, N. Y., 1956, p 140.

(6) W. V. Bush, G. Holzman, and A. W. Shaw, *J. Org. Chem.*, **30**, 3290 (1965), and references cited therein.

(7) C. D. Broaddus, T. J. Logan, and T. J. Flautt, *ibid.*, **28**, 1174 (1963).

(8) H. Hurt, *J. Am. Chem. Soc.*, **78**, 2619 (1956).

(9) S. M. Blitzer and T. H. Pearson, U. S. Patent 2,987,558 (June 6, 1961).

$$CH_3CH{=}CH_2 + KH \longrightarrow [CH_3CH_2CH_2]^-K^+ \quad (3)$$

$$[CH_3CH_2CH_2]^-K^+ + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH_3 + [CH_2 \cdots CH \cdots CH_2]^-K^+ \quad (4)$$

initial induction period in the reactions conducted with potassium hydride, reaction 3 proceeds more rapidly than reaction 1.

Experimental Section

Catalyst Preparation.—A mixture of 40 g of potassium metal, 352 g of heavy liquid petrolatum (Squibb's extra heavy mineral oil), and 1.0 ml of oleic acid in a 1-l. creased flask was stirred under nitrogen for 5 min at 99–100° at about 15,000 rpm, using a modified Morton stirrer. An additional 1.0 ml of oleic acid was then added and stirring was continued for 20 min before cooling to room temperature. Microscopic examination of the dispersion showed opaque, spherical particles with diameters of about 1–3 μ. Measurement of the volume of hydrogen evolved upon reacting a portion of the dispersion with 2-butoxyethanol showed that 99% of the potassium remained in the dispersion.

The potassium hydride dispersion was prepared by stirring a portion of the potassium dispersion at 190–210° in a hydrogen atmosphere for 2 hr. Microscopic examination showed that the solid was in the form of solid crystals with cross sections of 1–3 μ. Analysis as before showed that at least 89% of the potassium had been converted to the hydride.

Potassium on potassium carbonate was prepared in a nitrogen atmosphere by gradually adding pieces of the metal, washed in hexanes, to a stirred flask containing 80 g of Baker's K_2CO_3 (70% through a 200-mesh screen) at 90–120° until a total of 8 g of potassium was added. The cooled mixture was stored under heavy liquid petrolatum. Microscopic examination showed the mixture was mainly in the form of agglomerates of potassium and support, 200–400 μ in diameters, with a few smaller particles of potassium. Much of the added potassium had been lost, as analysis by alcoholysis showed that only 45% of the added potassium remained as the metal. A portion of the supported potassium in oil was converted to hydride by reacting with hydrogen as before. Microscopic examination showed that the opaque potassium had been converted to transparent crystals of approximately the original size.

Propylene Dimerization.—The catalyst and necessary additional mineral oil were charged to a 630-ml stainless steel rocking autoclave. After purging with nitrogen, the appropriate amount of Matheson CP propylene (over 99% propylene) was pressured into the autoclave. The autoclave was then heated while rocking. Reaction temperature was reached in about 45 min. The initial time was taken when a temperature of 148° was reached. When the desired pressure drop had occurred, the autoclave was cooled to room temperature without shaking. The light hydrocarbons were vented, the autoclave was opened, and dry nitrogen was bubbled through the autoclave contents at room temperature for several hours until all volatile components were removed. The catalyst slurry in mineral oil was then analyzed.

Microscopic analysis showed that both the potassium and potassium hydride dispersions had been converted to transparent spheres, 1–10 μ in diameter and light yellow to brown in color. The catalyst from potassium on potassium carbonate showed a number of transparent particles up to 250 μ in diameter and some free metal particles up to 2 mm in diameter.

Catalyst Analysis.—Portions of the used catalysts were reacted with 2-butoxyethanol in a nitogen atmosphere and the gases were collected in a gas buret. Yields were calculated from the volume change. The gaseous products were analyzed by mass spectrometry. The analysis was verified by gas–liquid partition chromatography for the samples made from the dispersions with the same results except that hydrogen was not detected.

Registry No.—Propylene, 115-07-1; potassium hydride, 7693-26-7.

Acknowledgment.—The author is indebted to Dr. S. J. Lapporte of this laboratory for suggestions concerning the mechanism of reaction.

The Reduction of Alkoxysulfonium Salts with Sodium Borohydride[1,2]

Carl R. Johnson[3] and W. Gary Phillips[4]

Department of Chemistry, Wayne State University,
Detroit, Michigan 48202

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In connection with our work concerning nucleophilic displacement at trigonal sulfur, we have investigated the borohydride reduction of alkoxysulfonium fluoroborates. These salts are smoothly and efficiently converted to the parent sulfides when treated with sodium borohydride in alcohols or tetrahydrofuran (THF) (Table I).

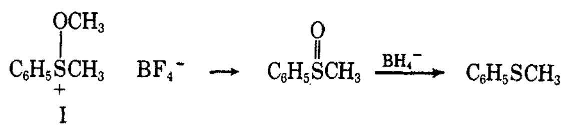
Table I
Borohydride Reduction of Alkoxysulfonium Salts

Fluoroborate	Solvent	Yield of sulfide,[a] %
Methylphenylmethoxysulfonium	Methanol	78
Phenylvinylmethoxysulfonium	Ethanol	27[b]
Diphenylmethoxysulfonium[c]	Methanol	78
Methylphenyltrideuteriomethoxysulfonium	THF	86
Dibenzylethoxysulfonium	Ethanol	90

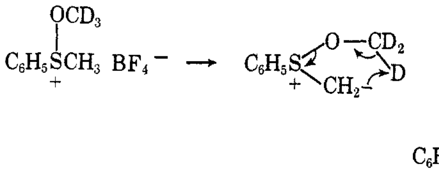
[a] Yields are for isolated and purified sulfides. [b] Phenyl vinyl sulfide. [c] The facile reduction of the diphenyl salt also provides evidence that ylides are not involved in these reactions.

Previous experiences with alkoxysulfonium salts led us to consider five possible mechanistic pathways for this reaction, employing methylphenylmethoxysulfonium fluoroborate, as illustrated in Schemes I–V. The intermediate sulfoxide depicted in Scheme I could arise through nucleophilic attack at the O-methyl by alcohol or hydride to produce an ether or methane, respectively. Scheme I was immediately ruled out by the

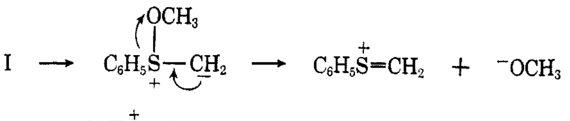
Scheme I



Scheme II



Scheme III



$$C_6H_5\overset{+}{S}{=}CH_2 + BD_4^- \longrightarrow C_6H_5SCH_2D$$

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(1) (a) Part VIII in the series Chemistry of Sulfoxides; (b) Part VII: C. R. Johnson and W. G. Phillips, *J. Org. Chem.*, **32**, 1926 (1967).

(2) We gratefully acknowledge support by the National Science Foundation, Grant No. GP-5944.

(3) Alfred P. Sloan Research Fellow, 1965–1968.

(4) National Aeronautics and Space Administration Trainee, 1965–1967.