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THERMAL DECOMPOSITION OF n-ALKYL[BIS(TRIPHENYLPHOSPHINE)]-(CARBONYL)IRIDIUM(I) COMPLEXES

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Summary

The decomposition of $L_2Ir(CO)R$, (R = n-alkyl) prepared in situ by the reaction of n-alkyllithium or -magnesium reagents with $L_2Ir(CO)Cl$ (**2**) produces a mixture of n-alkane and isomerized alkene, the ratio of which is strongly dependent on the concentration $[L]$ of triphenylphosphine as well as certain other additives. When $[L] = 0$, positional isomerism and isotope scrambling are extensive as is the isomerism of added olefin, suggesting that β-hydride elimination is rapid and reversible and that any olefins participating in an iridium hydride addition–elimination sequence are also capable of exchange with free olefin in solution. When $[Ph_3P]/[\mathbf{2}] \geq 1$, the principal product ($> 90\%$) is the 1-alkene. No positional isomerism or isotope scrambling is observed and only a minor amount of alkane is produced. A mechanistic scheme consistent with these observations is proposed.

Positional isomerism and isotope scrambling are generally recognized to accompany β-elimination in alkyl-transition metals [2–5]. The thermal decomposition of $(Ph_3P)_2Ir(CO)R$ (**1**, R = n-alkyl) is purported to be a unique exception to this behavior. β-Hydride elimination from **1** is reported to produce only the 1-olefin with no isotope scrambling [6,7]. In the course of our studies concerning the nature of the transition state associated with β-hydride elimination processes [8], we have examined this reaction in some detail and report here our findings.

Results

Products. Compound **1** (R = n-octyl), as originally reported, is the purported product of the reaction of a suspension of $(Ph_3P)_2Ir(CO)Cl$ (**2**) in ether with a

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TABLE 1

PRODUCT DISTRIBUTIONS RESULTING FROM THE REACTION OF n-$C_8H_{17}Li$ WITH **2**. n-$C_8H_{17}Li + [Ph_3P]_2Ir(CO)Cl \xrightarrow{H_3O^+}$

Entry	$L_2IrCOCl$ [a]	[n-$C_8H_{17}Li$] [b] (*M*)	Temperature (°C)	Additive (*M*)	Reaction [c] time (h)	Solvent	Products (%) [c]						
							n-Octane	1-Octene	*cis*-**2**	*trans*-**2**	*cis*- and *trans*-**3** + *cis*-**4**	*trans*-**4**	Σ Octene
1	0.5	0.5	0		0.5	ether	37	< 1	7	34	18	3	63
2	0.5	0.5	20		0.5	ether	39	2	12	32	12	3	61
3	0.1	0.1	0		0.08	ether	67	14	5	12	1	1	33
					0.25	ether	57	13	8	18	3	1	43
					0.50	ether	51	5	11	25	7	1	49
					1.0	ether	36	3	14	35	10	2	64
					2.0	ether	36	2	14	36	10	2	64
4	0.05	0.05	0		0.08	ether	70	13	4	11	1	< 1	30
5	0.05	0.05	0		0.5	ether	52	< 1	6	31	8	< 1	48
6	0.05	0.05	0		0.5	THF	47	< 1	10	33	10	< 1	53
7	0.025	0.025	0		0.5	THF	63	7	12	18	< 1	< 1	37
8	0.05	0.05	− 20		0.08	THF	41	7	17	28	7	< 1	59
9	0.05	0.05	− 20		0.5	THF	39	3	10	6	14	2	61
10	0.05	0.05	20	LiBr (0.25)	0.5	THF	29	8	19	25	18	< 1	71
11	0.05	0.05	20	LiBr (0.25)	15	THF	29	2	12	31	20	6	71
12	0.05	0.05	20	LiI (0.25)	0.5	THF	25	39	22	9	3	2	75
13	0.05	0.05	20	LiI (0.25)	15	THF	25	5	15	31	20	4	75

[a] Number of mmoles of reagent per ml of reaction medium at $t = 0$. [b] Earlier studies of the reaction of **2** with n-octyllithium [6] were carried out in the presence of 1 equiv. of dioxane, purportedly to provide halide-free conditions. We observed that the presence or absence of this additive has no effect on the product distribution reported here. [b] Reaction quenched by addition of CH_3OH/HCl. The failure to observe any deuterium-containing products when DCl/CH_3OD was used indicates that any alkane present is formed prior to work-up. [d] Absolute yields, corrected for residual hydrocarbon products in RLi.

solution of n-octyllithium. Table 1 summarizes the hydrocarbon product yields we observed under these conditions. In an effort to establish if the nature of the precursor organometallic reagent had any influence on the overall course of this reaction, we also examined the corresponding reaction between **2** and an equivalent organomagnesium reagent.

Collectively, these results (Tables 1, 2) reveal several points. First, they establish that the decomposition of the purported alkyliridium yields n-octane and an extensively isomerized mixture of 1-, 2-, 3- and 4-octenes. Moreover, it is apparent in the case of the reaction of n-octyllithium with **2**, that olefin isomerization is complete in $\leqslant 30$ min while the parallel reaction with n-octylmagnesium halide requires a significantly longer time to achieve a static product distribution.

Second, it appears that solvent effects are operating in certain instances: olefin production, for example, is greater in THF than in ether when n-octylmagnesium halide is employed. Third, these observations are not limited solely to the n-octyl system. Parallel behavior occurs with other homologues (Table 3).

Fourth, the observation that an appreciable quantity of olefin-d_3 is formed during the decomposition of **1** (R = n-alkyl-2,2-d_2) (vide infra) suggests that the olefin which is free in solution is subject to further addition–elimination reactions. This conclusion is strongly supported by the fact that when 1-octene is present during the reaction of **2** with either n-butyllithium or n-pentylmagnesium bromide, it is extensively isomerized (Table 4). Such behavior is characteristic of transition metal hydrides [5].

Labeling studies. The products from the reaction of n-pentyl-2,2-d_2-magnesium bromide with **2** in THF are summarized in Tables 5 and 6. They establish (i) that isotope scrambling is extensive, suggesting that β-hydride elimination is rapid and reversible and (ii) that the extent of deuterium incorporation in the product alkane remains essentially unchanged with extent of reaction (or elevated reaction temperature) while higher temperatures (or extended reaction times) favor increased deuterium incorporation into 2-pentene with a concomitant reduction in the deuterium content of 1-pentene.

Table 6 also shows the isotopic composition of the product distribution produced by the reaction of an equimolar mixture of n-pentyl-2,2-d_2-magnesium bromide and n-octylmagnesium bromide with **2**. These data reveal that a pathway exists whereby deuterium from the n-pentyl ligand is incorporated into the products derived from the n-octyl ligand. The addition–elimination sequence cited above provides a plausible vehicle for this exchange.

Influence of added ligand. The decomposition of **1** in the presence of added triphenylphosphine results in a significant reduction in the yield of alkane and a corresponding increase in the production alkene. Moreover, for values of $[L]/[\mathbf{2}] \geqslant 1$ the resulting olefin product shows essentially no positional isomerism. The studies summarizing these results are shown in Tables 7 and 8. No less surprising is the observation that isotope scrambling is also affected by the presence of added ligand. In fact, as Table 8 shows, there is essentially no isotope scrambling in the presence of additional triphenylphosphine. Taken together with the further observation that the olefin formed by the reaction of (n-octyl-2,2-d_2)-magnesium bromide with **2** is, within experimental limits [10a], exclusively 1-octene-2-d_1, this fact suggests that in the presence of added phosphine, β-elimination from **1** is irreversible [10b].

The data in Tables 1, 2 also reveal that the addition of halide has a major

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TABLE 2

PRODUCT DISTRIBUTIONS RESULTING FROM THE REACTION OF n-$C_8H_{17}MgX + \mathbf{2} \xrightarrow{20-25°C} \xrightarrow{H_3O^+}$

Entry	$[L_2IrCOCl]$ [a] (*M*)	X	[RMgX] [b] (*M*)	Reaction [c] time (h)	Solvent	Additive (*M*)	Products (%) [c]						
							n-Octane	1-Octene	*cis*-**2**	*trans*-**2**	*cis*- and *trans*-**3** + *cis*-**4**	*trans*-**4**	Σ Octenes
I	0.05	Br	0.05	0.08	ether		86	12	1	1	<1	<1	14
				0.25	ether		79	16	2	3	<1	<1	21
				0.50	ether		68	23	4	5	<1	<1	32
				1.0	ether		61	27	5	7	<1	<1	39
				2.0	ether		54	36	4	6	<1	<1	46
				3.0	ether		53	29	7	10	1	<1	47
				4.0	ether		53	19	10	15	3	1	47
				6.0	ether		53	14	11	17	4	1	47
II	0.10	Cl	0.10	0.08	THF		65	17	5	9	2	<1	34
				0.25	THF		62	18	5	12	2	<1	38
				0.50	THF		56	14	10	15	3	<1	44
				1.0	THF		46	22	8	20	3	<1	54
				2.0	THF		39	10	13	28	8	2	61
				3.0	THF		38	6	12	32	9	2	61
				4.0	THF		38	3	12	34	10	2	61
				5.0	THF		37	2	11	35	11	3	62
				6.0	THF		37	2	10	36	11	3	62

III	0.10	Br	0.10	0.08	THF		60	17	8	13	1	< 1	40
				0.25	THF		57	23	5	13	1	< 1	43
				0.50	THF		42	21	10	23	3	< 1	58
				0.50	THF	$MgBr_2$(0.25)	41	46	7	4	< 1	< 1	59
				1.0	THF		39	18	10	26	5	< 1	60
				2.0	THF		39	14	11	28	7	1	61
				3.0	THF		39	8	14	31	7	1	61
				4.0	THF		38	4	11	36	9	2	62
				5.0	THF		37	2	9	38	11	3	63
				6.0	THF		37	1	9	39	11	3	63
				15	THF	$MgBr_2$(0.25)	40	16	22	11	10	1	60
IV	0.10	I	0.10	0.08	THF		37	22	13	26	1	< 1	63
				0.25	THF		37	20	13	27	2	1	63
				0.50	THF		36	15	14	28	5	1	64
				1.0	THF		36	13	14	30	6	1	64
				2.0	THF		36	8	14	34	7	1	64
				3.0	THF		36	7	16	34	6	1	64
				4.0	THF		36	6	15	35	6	2	64
				5.0	THF		36	4	16	36	6	2	64
				6.0	THF		36	2	17	37	6	2	64

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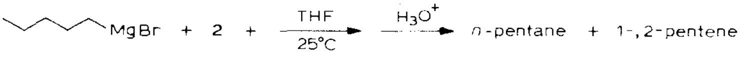
[a] Concentration at $t = 0$. [b] Earlier studies of the reaction of **2** with n-octyllithium [6] were carried out in the presence of 1 equiv. of dioxane, purportedly to provide halide-free conditions. We observed that the presence or absence of this additive has no effect on the product distribution reported here. [c] Reaction quenched by addition of CH_3OH/HCl. The failure to observe any deuterium-containing products when DCl/CH_3OD was used indicates that any alkane present is formed prior to work-up. [d] Absolute yields: corrected for residual hydrocarbon products in RLi.

TABLE 3

PRODUCT DISTRIBUTION PRODUCED BY THE REACTION OF n-PENTYLMAGNESIUM BROMIDE WITH **2** [a]

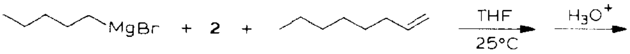


Time (h) [b]	n-Pentane (%)	1-Pentene (%)	2-Pentene (%)
1	38	39	23
3	40	29	31
4	40	23	37
5	40	17	43
6	42	10	48

[a] $[RMgBr]_0 = [\mathbf{2}] = 0.10$ *M*. [b] Reaction quenched by the addition of CH_3OH/HCl.

TABLE 4

PRODUCTS FROM THE REACTION OF n-PENTYLMAGNESIUM BROMIDE WITH **2** IN THE PRESENCE OF 1-OCTENE [a,b]

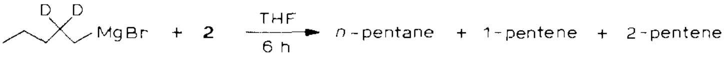


Time (h)	n-Pentane (%)	1-Pentane (%)	2-Pentane (%)	n-Octane (%)	1-Octene (%)	2-,3-,4-octenes (%)
1	29	41	28	7	46	45
3	28	34	38	7	33	60

[a] $[RMgBr]_0 = [\mathbf{2}] = 0.10$ *M*. [b] $[\text{1-Octene}]_0 = 0.15$ *M*.

TABLE 5

DEUTERIUM DISTRIBUTION IN THE HYDROCARBON PRODUCTS PRODUCED BY THE REACTION OF **2** WITH n-PENTYL-2,2-d_2-MAGNESIUM BROMIDE [a,b]



Reaction temperature (°C)	n-Pentane [c]				1-Pentene [c]				2-Pentenes [c]			
	d_0	d_1	d_2	d_3	d_0	d_1	d_2	d_3	d_0	d_1	d_2	d_3
0	3	10	11	14	11	13	6	2	6	13	8	2
25	3	7	11	11	2	2	1	<1	14	26	16	6

[a] $[RMgBr]_0 = [\mathbf{2}]_0 = 0.10$ *M*. [b] n-Pentyl-2,2-d_2-magnesium bromide was prepared from n-pentyl-2,2-d_2 bromide (96% d_2). [c] Isotopic composition, corrected for residual hydrocarbon content.

influence on the kinetics of olefin isomerism. Specifically, the presence of a 5-fold excess of lithium or magnesium bromide or iodide markedly reduces the rate of olefin isomerism, with iodide being more effective than bromide. Mechanistically, this influence is most likely related to the more pronounced effect which added triphenylphosphine has on olefin isomerism.

Discussion

The instability of **1** precludes any kinetic study of its thermal decomposition. Nonetheless, the observations presented above permit a description of several

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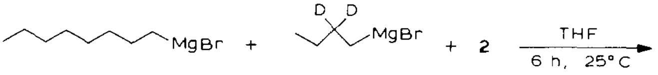
TABLE 6

DEUTERIUM DISTRIBUTION IN THE HYDROCARBON PRODUCTS RESULTING FROM THE REACTION OF **2** WITH n-PENTYL-2,2-d_2-MAGNESIUM BROMIDE AND n-OCTYLMAGNESIUM BROMIDE [a]

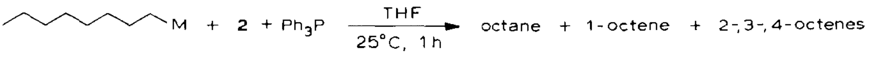


Isotopic composition (%)	Products				
	n-Pentane (28%) [b]	1-Pentene (2%) [b]	2-Pentenes (30%) [b]	n-Octane (16%) [b]	Σ-Octenes (24%) [b]
d_0	4	1	12	14	12
d_1	7	< 1	12	1	9
d_2	9	< 1	5	< 1	3
d_3	8	< 1	< 1	< 1	< 1

[a] $[n\text{-}C_8H_{17}MgBr]_0 = [CH_3(CH_2)_2CD_2CH_2MgBr]_0 = 0.05$ *M*; [**2**] = 0.1 *M*. [b] Relative yields.

TABLE 7

INFLUENCE OF ADDED LIGAND ON THE PRODUCT DISTRIBUTION BY THE REACTION OF n-OCTYL-LITHIUM AND -MAGNESIUM BROMIDE WITH **2** [a]

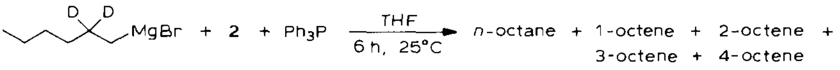


M	[*L*]/[**2**]	n-Octane	1-Octene	2-,3-,4-Octenes
Li	0	37	1	62
	1	–	–	–
	5	16	84	< 1
	10	11	89	
	20	5	95	< 1
MgBr	0	38	3	59
	1	10	89	< 1
	5	8	91	< 1
	10	7	92	< 1

[a] [**2**] = 0.05 *M*.

TABLE 8

ISOTOPIC COMPOSITION OF THE HYDROCARBON PRODUCTS RESULTING FROM THE REACTION OF n-OCTYL-2,2-d_2-MAGNESIUM BROMIDE WITH **2** IN THE PRESENCE OF TRIPHENYLPHOSPHINE [a]



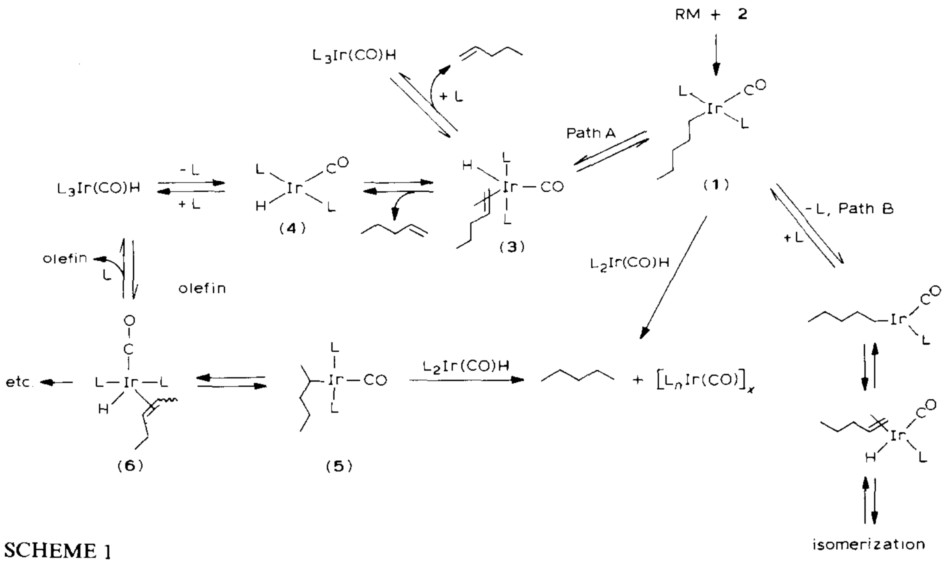
[*L*]/[**2**]	n-Octane (%)				1-Octene (%)				2-,3-,4-Octene (%)			
	d_0	d_1	d_2	d_3	d_0	d_1	d_2	d_3	d_0	d_1	d_2	d_3
0	< 1	< 1	33	6	4	3	1	0	13	22	13	3
1	< 1	< 1	< 1	10	< 1	89	< 1	< 1	< 1	< 1	< 1	< 1
5	< 1	< 1	< 1	10	< 1	90	< 1	< 1	< 1	< 1	< 1	< 1
10	< 1	< 1	< 1	8	< 1	91	< 1	< 1	< 1	< 1	< 1	< 1

[a] $[RMgBr]_0 = 0.10$ *M*.

TABLE 9

A COMPARISON OF THE PRINCIPAL MECHANISTIC ASPECTS OF THE THERMAL DECOMPOSITION OF DI-n-BUTYL[BIS(TRIPHENYLPHOSPHINE)]PLATINUM(II) AND n-OCTYL[BIS(TRIPHENYLPHOSPHINE)](CARBONYL)IRIDIUM(I)

Metal alkyl	Added L	Products	Comments
$(n\text{-}C_4H_9)_2PtL_2$	No	n-butane/1-butene (1/1)	Extensive intramolecular deuterium isotope scrambling; little or no isomerism of or exchange with free olefin. Rate-determining step: initial dissociation of one L to form a 3-coordinate intermediate [3].
$n\text{-}C_8H_{17}Ir(CO)L_2$	No	n-octane/1-,2-,3-,4--octene (~ 30/70)	Extensive intramolecular deuterium isotope scrambling together with extensive isomerism of and isotopic exchange with free olefin. Rate-determining step: unknown
$(n\text{-}C_4H_9)_2PtL_2$	Yes	n-butane/1-butene	Extensive intramolecular deuterium isotope scrambling; little or no isomerism of or exchange with free olefin. Rate-determining step: reductive elimination of alkane [3].
$n\text{-}C_8H_{17}Ir(CO)L_2$	Yes	n-octane/1-octene	No olefin isomerism or deuterium isotope scrambling. Rate-determining step: unknown; possibly β-hydride elimination from $L_2Ir(CO)R$.



SCHEME 1

aspects of the overall mechanism that are understandable within the context of Scheme 1 in which olefin formation, olefin isomerism and isotope scrambling are all explicable in terms of an unexceptional β-hydride elimination–olefin insertion mechanism.

Less usual is the strong influence which added ligand has on product distribution. As proposed (Scheme 1), this effect originates from one of two pathways. The first (Path A), **1** $\rightarrow$ **3** $\rightarrow$ **4**,**5** $\rightarrow$ $L_3Ir(CO)H$, involves β-hydride elimination from the coordinatively unsaturated alkyl **1**, yielding the coordinatively saturated intermediate **3** which, in the absence of added phosphine, proceeds to **4** and/or **5**. In the presence of additional phosphine, **3** is subject to ligand (olefin) replacement which, if appreciably faster than olefin isomerization, would account for the apparent influence of added phosphine on olefin isomerism and isotope scrambling. By comparison, Path B affords the more generally accepted 14-electron, dissociative pathway traditionally associated with β-hydride elimination processes involving Groups VIII alkyls [3,4,5a]. This pathway is effectively blocked by the presence of added phosphine.

There remains the question of the origin of the alkane. Schwartz and Cannon [6] have suggested that this minor product arises via a bimolecular reaction between **1** and the coordinatively unsaturated intermediate **4**. Our data does not permit a further evaluation of this proposal, which seems to be a reasonable one [11].

Finally, it is informative to compare the mechanistic features concerned with the thermal decomposition of n-alkyl[bis(triphenylphosphine)](carbonyl)iridium(I) with those of another transition alkylmetal, viz., di-n-alkyl[bis(triphenylphosphine)]-platinum(II) [3]. These are summarized in Table 9.

Experimental

General. All reactions and transfers involving organometallic compounds were carried out under a nitrogen or helium atmosphere. Solids were transferred in a

Vacuum Atmospheres glove box under an atmosphere of nitrogen. Diethyl ether and tetrahydrofuran (THF) were distilled from lithium aluminium hydride under nitrogen. Dioxane was distilled under nitrogen from sodium benzophenone dianion. Yields of organolithium reagents were determined by the double titration procedure of Gilman. The titer of Grignard reagents was determined by titration against 2-propanol in xylenes using 2,2-diquinoline as an indicator. Grignard reagents were prepared in diethyl ether or THF. Organolithium reagents were prepared in pentane by reaction of the corresponding dialkylmercurial with excess lithium. These solutions were filtered through a bed of diatomaceous earth and stored under nitrogen. Mass spectral determinations, including isotopic compositions, were determined on a Hewlett-Packard 5985 GC/MS spectrometer. Analysis conditions were optimized to conform to those cited by Bieman [12]. Hydrocarbon analyses were obtained on a Hewlett-Packard 5840 gas chromatograph equipped with electronic integration and employing either a 50 m, 0.25 mm capillary column of silicone gum rubber (Column A) or a 12 ft, 0.25 in stainless steel column packed with n-octyl Porasil (Column B). Absolute yields were determined by unexceptional internal standard procedures.

Anhydrous lithium iodide and bromide were prepared as described by Wittig and Harborth [13]. Anhydrous magnesium bromide was prepared by a previously described procedure [14].

$[(C_6H_5)_3P]_2Ir(CO)Cl$ (**2**) and $[(C_6D_5)_3P]_2Ir(CO)Cl$ were synthesized by a reported literature procedure [15]. The preparation of triphenylphosphine-d_{15} was also accomplished according to a recognized procedure [16].

Deuterium isotope content. The deuterium composition of all hydrocarbon products was determined by mass spectral analysis of the eluting component (Column B) at 70 eV by integrating the intensity of $M-1$, M, $M+1$, $M+2$ and $M+3$ peaks of the respective molecular ion cluster. In all instances, the $M-1$ ion was $<1\%$ and was reasonably neglected. Final values were obtained with the aid of a computer program and are believed accurate to within ±2% [17].

*Reaction of **2** with n-octyllithium.* Bis(triphenylphosphine)(carbonyl)(chloro)-iridium(I) (**2**, 40 mg, 0.050 mmol) was placed in a flame-dried, 2 ml ampule equipped with a Teflon-coated magnetic stirrer bar. The ampule was stoppered with a rubber septum and flushed with nitrogen before adding 0.50 ml of ethyl ether. The vessel was then equilibrated in a constant ($\pm0.1°$) temperature bath. A solution of n-octyllithium in pentane (50 μl, 0.45 M) was added with efficient stirring. After a predesignated period of time, the reaction mixture was treated with 20 μl of methanolic hydrochloric acid and the products determined by GLC.

*Reaction of **2** with n-octylmagnesium bromide.* Compound **2** (40 mg, 0.05 mmol) was placed in a flame-dried, 2 ml ampule equipped with a Teflon-coated magnetic stirrer bar. The ampule was stoppered with a rubber septum, removed from the glove box and placed in a constant temperature bath. Tetrahydrofuran (1.0 ml) was added by syringe followed by a solution of n-octylmagnesium bromide (50 μl, 0.05 mmol) in THF. The resulting mixture was stirred thoroughly and, after an appropriate period of time, quenched with methanolic hydrochloric acid. Product analysis was accomplished by direct analysis of this reaction mixture by GLC.

Butanol-1,1-d_2, n-bromobutane-1,1-d_2 were prepared by appropriate literature procedures [18,19].

Preparation of n-bromopentane-2,2-d_2. Valeric acid-2,2-d_2 was prepared by treating n-bromobutane-1,1-d_2 (8.2 g, 0.060 mmol) in methanol (100 ml) with KCN (10 g, 0.15 mmol) at reflux for 16 h [20]. The resulting reaction mixture was distilled to near dryness and the distillant treated with water (30 ml). The combined solution was extracted with benzene, the organic layer separated, dried ($MgSO_4$) and fractionated through a micro-spinning band column to remove most of the light volatiles. To the residual oil was added a 5% solution of aqueous H_2SO_4 and the resulting mixture refluxed for 15 h, then cooled and extracted with ether. The ether layer was dried ($MgSO_4$) and the ether removed to yield 3.0 g of valeric acid-2,2-d_2 (48% yield) which, when treated with lithium aluminum hydride followed by Ph_3P/Br_2 as described above for the corresponding synthesis of n-bromobutane, yielded n-bromopentane-2,2-d_2 in 89% yield from n-pentyl alcohol-2,2-d_2. Isotopic composition: 95.5% d_2, 2.5% d_0.

References and notes

1 Supported by NSF Grant CHE 83-12730.

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