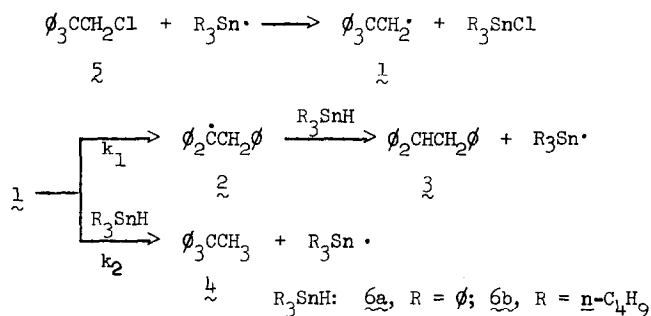


COMPETITIVE ATOM TRANSFER AND REARRANGEMENT REACTIONS
OF 2,2,2-TRIPHENYLETHYL RADICAL

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Most early attempts to generate 2,2,2-triphenylethyl radical (1) led either to products largely derived from its rearrangement to 1,1,2-triphenylethyl radical (2)¹ or to failure to form it.² However, Kaplan³ observed both rearranged (2) and unrearranged (4) triphenylethanes during reduction of 2,2,2-triphenylethyl chloride (5) with triphenyltin hydride (6a). Rearrangement was promoted by decreasing [6a]⁴ and increasing temperature. Hydrocarbons 3 and 4 were formed in comparable amounts at 100° with [6a] ~ 1 M, from which observation Carlsson



and Ingold⁵ estimated $k_1 \sim 5 \times 10^7 \text{ sec}^{-1}$ based on their measurements of absolute rate constants of reactions of representative radicals with 6a. We report herein a more detailed study of this and certain other systems in which atom transfer and rearrangement of radical 1 compete.

Solutions of chloride 5,⁶ tri-n-butyltin hydride (6b),⁷ an appropriate radical initiator, and diphenylmethane in benzene were degassed, sealed into tubes, and heated at constant temperature. Quantitative nmr analysis gave values of [2]_o, [2]_f, [6b]_o, [6b]_f, [3]_f, and [4]_f⁸ compared to the diphenylmethane standard.⁹ Because of the small absolute value of

$[4]_f$, it was felt more accurate to determine the ratio $[3]_f/[4]_f$ by glpc analysis. For the reaction scheme above: $d(4)/d(3) = k_2[6b]/k_1$ if the highly exothermic phenyl migration process is effectively irreversible. Since the material balances were satisfactory, we could write: $[6b] = [6b]_0 - [3] - [4]$, and integrate to give:

$\exp(k_2/k_1)[3]_f = \left\{ (k_2/k_1)[6b]_0 + 1 \right\} / \left\{ (k_2/k_1)[6b]_f + 1 \right\}$. Since this formulation in terms of $[3]_f$ rather than $[3]_f/[4]_f$ as a function of $[6b]_0$ and $[6b]_f$ overemphasizes any discrepancies in material balance, the value of $[3]_f$ used to solve for k_2^{6b}/k_1 was chosen as:

$[3]_f = \left\{ [6b]_0 - [6b]_f \right\} \left\{ [3]_f/[4]_f \right\} \left\{ [3]_f/[4]_f + 1 \right\}^{-1}$. Data at varying temperatures and $[5]_0/[6b]_0$ ratios are listed in the Table. An Arrhenius plot covering 90° gives $(E_2^{6b} - E_1) = -5.1 \pm 0.3$ kcal/mole and $\log A_2^{6b}/A_1 = -3.3$ ($\Delta S_2^{6b} - \Delta S_1^{\ddagger} = -15$ e. μ .) where the superscript indicates atom transfer step 2 for $6b$. A single run at 75° with 2,2,2-triphenylethyl bromide¹⁰ fell on the same correlation line.

Similar runs with stannane $6a$ are also shown in the Table. Since $[6a]_f$ could not be determined by the above method, k_2^{6a}/k_1 was calculated with the assumption:

$[6a]_f = [6a]_0 - [3]_f - [4]_f$. The Arrhenius values are $(E_2^{6a} - E_1) = -5.8 \pm 0.2$ kcal/mole and $\log A_2^{6a}/A_1 = -3.3$. Hence the recognized¹¹ greater hydrogen transfer ability of stannane $6a$ compared to $6b$ is quantified for radical 1 as $(E_2^{6b} - E_2^{6a}) \approx 0.7$ kcal/mole with $\log A_2^{6b}/A_2^{6a} = 0$.

Reaction of chloride 5 with triphenylgermane (7)¹² was sluggish at 75° but could be carried out with initiation by *t*-butyl peroxide at 135° to give a mixture of 3 and 4 in quantitative yield based on 5 ; however, approx. 2 moles of 7 disappeared for each mole of 5 . The value of k_2^7/k_1 using observed values of $(7)_0$ and $(7)_f$ was 0.06 ± 0.01 for two runs. Thus at 135°, germane 7 is a poorer hydrogen donor towards radical 1 than the analogous stannane $6a$ by a factor of 10-fold.¹³ All attempts to reduce chloride 5 with triphenylsilane¹⁴ failed.

Competitive reduction of chloride 5 and neopentyl chloride with a limited supply of stannane $6b$ at 75° showed 5 to be 7.8 times more reactive towards the tri-*n*-butylstannyl radical. Hence a significant enhancement in reactivity of 5 compared to typical primary chlorides¹⁵ does exist, although suggestions of anchimeric assistance to chlorine abstraction seem inappropriate in view of the conformity of the results in the Table to the stepwise rearrangement scheme used herein.

Table
Reduction of Chloride $\underline{2}$ with Stannanes $\underline{6a}$ and $\underline{6b}$

Temp	Time	$[\underline{2}]_o^a$	$[\underline{6}]_o^b$	[Init.] $_o^c$	$[\underline{2}]_o - [\underline{2}]_f^a$	$[\underline{6}]_o - [\underline{6}]_f^d$	$[\underline{3}]_f + [\underline{4}]_f^a$	$\frac{[\underline{3}]_f}{[\underline{4}]_f}$	k_2/k_1
45°	21 hr	0.51	1.01	A, 0.028	0.395	0.38	0.395	0.72 ^f	1.70
	68	0.485	0.69	A, 0.023	0.485	0.485	0.435	1.49 ^e	1.57
	68	1.015	0.46	A, 0.026	0.465	0.46	0.44	3.76 ^e	1.31
75°	5	0.51	2.20	A, 0.009	0.51	0.54	0.435	0.64 ^e	0.82
	5	0.52	1.08	A, 0.010	0.52	0.56	0.555	1.70 ^e	0.76
	5.3	0.53	1.05	A, 0.028	0.53	0.51	0.52	1.73 ^e	0.76
	5.7	0.74	0.73	A, 0.015	0.66	0.73	0.635	4.06 ^e	0.73
	5.3	0.90	0.44	A, 0.023	0.43	0.44	0.425	6.76 ^e	0.75
	5.3	0.96	0.46	A, 0.009	0.45	0.46	0.425	5.73 ^e	0.82
135°	4	0.505	1.33	B, 0.006	0.505	0.64	0.48	3.57 ^e	0.28
	5.2	0.485	1.08	C	0.40	0.48	0.42	3.75 ^f	0.31
	4	0.975	0.51	B, 0.010	0.49	0.51	0.52	19. ^e	0.20
45°	17	0.47	1.44	A, 0.021	0.36	0.39	0.39	0.175 ^f	4.63
	21	0.48	1.05	A, 0.023	0.38	0.38	0.38	0.23 ^f	5.13
75°	1.5	0.46	1.58	A, 0.008	0.36	0.34	0.34	0.36 ^f	1.98
	5	0.50	1.06	A, 0.011	0.50	0.55	0.55	0.72 ^f	1.82
	2	1.05	0.52	A, 0.007	0.42	0.47	0.47	2.03 ^f	1.86
135°	0.25	0.48	1.47	C	0.23	0.22	0.22	1.09 ^f	0.67
	0.33	0.51	1.47	B, 0.009	0.51	0.40	0.40	1.27 ^f	0.62
	1	0.48	1.02	C	0.39	0.35	0.35	2.07 ^f	0.58
	0.25	0.475	1.01	C	0.195	0.20	0.20	1.68 ^f	0.65
	0.25	0.47	0.87	C	0.18	0.17	0.17	2.13 ^f	0.60

^aMolar concentration in benzene determined by nmr compared to a weighed internal standard of diphenylmethane (0.25-0.4M). ^bFirst twelve entries: $\underline{6} = \underline{6b}$, concentration by nmr; last ten entries, $\underline{6} = \underline{6a}$, concentration by initial weight. ^cA = azobisisobutyronitrile, B = t-butyl peroxide, C = none; molar concentration. ^dFor $\underline{6b}$, by nmr; for $\underline{6a}$, equated to $[\underline{3}]_f + [\underline{4}]_f$. ^eBy glpc analysis. ^fBy nmr analysis.

Previous studies^{1a, b} of the decarbonylation of 3,3,3-triphenylpropionaldehyde (8) reported rearranged 3 and triphenylethylene to be the major hydrocarbon products but a small amount of unrearranged 4 could not be ruled out. From a decarbonylation of neat 8 with 18 mole % t-butyl peroxide which proceeded to approx. 35% completion in 6 hr at 135-140°, we could set an upper limit of < 2% 4 in the hydrocarbon fraction. Thus $k_2^8/k_1 < 0.005$ at 135-140°.

In contrast, based on the known greater atom transfer ability of several halogenating

agents such as t-butyl hypochlorite (9)¹⁶ compared to stannanes, we anticipated that chlorination of hydrocarbon 4 should produce largely unrearranged chloride 5 rather than 1,1,2-triphenylethyl chloride (10). Indeed this expectation is qualitatively correct to the extent that photo-initiated reaction of 4 with 9 (or with molecular chlorine) at 25-40° sluggishly gave 5 in low yield with no 10 detectable. However, because of the inefficiency of the reactions and the thermal instability of 10, no quantitative evaluation of k_2^2/k_1 could be made. The major course of the reaction with chlorine was chlorine addition to a phenyl ring of 4.

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