estimated. Rearranging eq 11 affords:

$$\frac{\tau_2^{-1}[k_4k_{4\mathrm{p}}{}^{\mathrm{am}}[\mathrm{am}]^2/(k_{-4}+k_{4\mathrm{p}}{}^{\mathrm{am}}[\mathrm{am}])]}{[k_{-4}k_{-4\mathrm{p}}{}^{\mathrm{amH}}[\mathrm{amH}]/(k_{-4}+k_{4\mathrm{p}}{}^{\mathrm{am}}[\mathrm{am}])]-\tau_2^{-1}} = \frac{k_2k_{2\mathrm{p}}{}^{\mathrm{am}}[\mathrm{am}]^2}{k_{-2}+k_{2\mathrm{p}}{}^{\mathrm{am}}[\mathrm{am}]} \qquad (18)$$

The left-hand term of eq 18 that for the sake of simplicity we indicate as k_2^*, can be evaluated by introducing the approximate value of k_4 and $k_{4\mathrm{p}}{}^{\mathrm{am}}/k_{-4}$ just obtained.

Applying the same mathematical treatment of eq 16 to eq 18 affords:

$$\frac{[\mathrm{am}]}{k_2^*} = \frac{k_{-2}}{k_2k_{2\mathrm{p}}{}^{\mathrm{am}}[\mathrm{am}]} + \frac{1}{k_2} \qquad (19)$$

From the plot of $[\mathrm{am}]/k_2^*$ vs. $1/[\mathrm{am}]$, approximate values of k_2 and $k_{2\mathrm{p}}{}^{\mathrm{am}}/k_{-2}$ can be obtained.

With the introduction of these terms into eq 7, better values of $[k_4k_{4\mathrm{p}}{}^{\mathrm{am}}[\mathrm{am}]^2/(k_{-4}+k_{4\mathrm{p}}{}^{\mathrm{am}}[\mathrm{am}])]$ are obtained, and so on, until constant values of k_2, k_4, $k_{2\mathrm{p}}{}^{\mathrm{am}}/k_{-2}$, and $k_{4\mathrm{p}}{}^{\mathrm{am}}/k_{-4}$ are obtained.

Actually this iterative procedure was carried out with a personal computer by using a non-linear least-squares method.[24]

Registry No. 1·CO_4^-, 2930-37-2; **2**·$HClO_4$, 92314-76-6; **2H** (X = CH_2), 92314-68-6; **2H** (X = O), 87691-76-7; **2H**·$HClO_4$ (X = CH_2), 92314-69-7; **2H**·$HClO_4$ (X = O), 92314-70-0; **4H** (X = CH_2), 92314-71-1; **4H** (X = O), 92314-73-3; **4H**·$HClO_4$ (X = CH_2), 92314-72-2; **4H**·$HClO_4$ (X = O), 92314-74-4; $Me_4N^+OH^-$, 75-59-2; $CH_3C(O)O^-Me_4N^+$, 1058-12-1; piperidine, 110-89-4; piperidinium perchlorate, 57367-18-7; morpholine, 110-91-8; morpholinium perchlorate, 35175-75-8.

Supplementary Material Available: Tables S1–S5 summarizing all the kinetic measurements (6 pages). Ordering information is given on any current masthead page.

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Kinetics of the 1,2-Migration of Carbon-Centered Groups in 2-Substituted 2,2-Dimethylethyl Radicals[1]

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Abstract: The rearrangements $RCMe_2CH_2\cdot \rightarrow RCH_2\dot{C}Me_2$ (k_r) (R = Ph, $Me_3CC{\equiv}C$, $Me_3CC{=}O$, and $N{\equiv}C$) have been studied over a range of temperatures by product analyses with use of the common competing reaction $RCMe_2CH_2\cdot + CCl_4 \rightarrow RCMe_2CH_2Cl + CCl_3\cdot$ (k_{Cl}). For R = $H_2C{=}CH$ the rearrangement was so fast that only the rearranged chloride, RCH_2CMe_2Cl, was produced. All these rearrangements occur via a 3-membered cyclic intermediate radical (or transition state). Various considerations led to the following Arrhenius equation for chlorine abstraction: $\log (k_{Cl}/\mathrm{M^{-1}\ s^{-1}}) = (8.14 \pm 0.42) - (5.52 \pm 0.63)/\theta$, where $\theta = 2.3RT$ kcal/mol, and this equation is used to calculate Arrhenius parameters for migration of all but the $H_2C{=}CH$ group. Comparison of these parameters with those already available from kinetic EPR measurements leads to a choice of preferred Arrhenius parameters for all five rearrangements. The cyano group had an unexpectedly low mobility while the pivaloyl group underwent a surprisingly rapid 1,2-shift. Migratory aptitudes increase along the series R = $N{\equiv}C < Me_3CC{\equiv}C < Ph < Me_3CC{=}O < H_2C{=}CH$, with k_r at 25 °C = 0.9, 93, 762, 1.7×10^5, and $1.0 \times 10^7\ \mathrm{s^{-1}}$, respectively. The preferred pre-exponential factors all lie in the range $10^{10.9}$–$10^{12.0}\ \mathrm{s^{-1}}$, while the activation energies vary from 16.4 kcal/mol for R = $N{\equiv}C$ to 5.7 kcal/mol for R = $H_2C{=}CH$. These results are discussed in relation to the results of thermochemical kinetic calculations and to earlier work on the 1,2-migration of unsaturated groups in radicals.

In free radical chemistry the 1,2-migration of an unsaturated group has excited interest[3] ever since the discovery by Urry and Kharasch[4] in 1944 of the neophyl rearrangement, i.e., **1a** → **2a**.

$$\underset{\mathbf{1}}{\mathrm{RCMe_2CH_2\cdot}} \xrightarrow{k_r} \underset{\mathbf{2}}{\mathrm{Me_2\dot{C}CH_2R}} \qquad (1)$$

a, R = C_6H_5; **b**, R = $Me_3CC{\equiv}C$;
c, R = $CH_2{=}CH$; **d**, R = $Me_3CC{=}O$; **e**, R = $C{\equiv}N$

In the early 1970's kinetic EPR spectroscopic methods were developed for measuring the rates of unimolecular radical reactions.[5-9] This advance was important because once the Arrhenius parameters for a radical rearrangement have been determined the rearrangement can serve as a "clock" to measure rate constants for appropriate radical–molecule reactions.[10] We have used the EPR technique to measure Arrhenius parameters for the neophyl rearrangement[11] and for some related reactions;[11] for a homopropargylic rearrangement,[12] **1b** → **2b**; and for a homoallylic rearrangement,[13-16] **1c** → **2c**. To the best of our knowledge there

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(1) Issued as NRCC No. 23760.

(2) N.R.C.C. Research Associate 1982–1984.

(3) For recent reviews of radical rearrangements see: (a) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; pp 161–310. (b) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073–3100. (c) Surzur, J. M. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1982; pp 121–295.

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are no other published absolute kinetic data available for the 1,2-migrations of unsaturated groups in $RCMe_2CH_2\cdot$ radicals which proceed by way of 3-membered cyclic intermediates or transition states.[17]

In order to gain a better understanding of the factors that control R migration rates (and, incidentally, to increase the horlogerie of primary alkyl radical clock reactions)[10] we have extended our kinetic studies of 1,2-group migrations. We decided to maintain the $RCMe_2CH_2\cdot$ structure for the rearranging radical because the geminal methyl groups on the β-carbon provide a strong driving force for this reaction.[3a] Thus, the corresponding $RCH_2CH_2\cdot$ radicals (appropriately labeled with deuterium) rearrange very much more slowly[16,18] and sometimes at rates which are too small to measure.[18,19] We also decided to use a competitive procedure so that *relative* migratory aptitudes of different R groups could be compared with greater precision than is generally possible when the individual absolute rate constants are measured by the EPR spectroscopic method. As our probe we chose carbon tetrachloride. Rates of rearrangement were measured relative to the rate of reaction of **1** with CCl_4 by GC and GC/MS analyses of the relative yields of **1**-Cl and **2**-Cl at known CCl_4 concentrations. Since the R group in **1** is remote from the radical center,

$$\underset{\mathbf{1}}{RCMe_2CH_2\cdot} + CCl_4 \xrightarrow{k_{Cl}} RCMe_2CH_2Cl + CCl_3\cdot \qquad (2)$$

$$\underset{\mathbf{2}}{RCH_2\dot{C}Me_2} + CCl_4 \rightarrow RCCH_2CMe_2Cl + CCl_3\cdot \qquad (3)$$

it seems reasonable to assume that k_{Cl} will be the same for all **1**, i.e., that it will be independent of the nature of R. By making measurements over a range of temperatures relative Arrhenius parameters have been determined for the rearrangements of radicals **1a**, **1b**, **1d**, and **1e**. Radical **1c** underwent rearrangement so rapidly that none of the unrearranged chloride, **1c**-Cl, could be detected among the products; this result was expected since we have previously shown that the **1c** → **2c** rearrangement is extraordinarily fast.[13] Estimated absolute Arrhenius parameters for all of these rearrangements are also reported and are discussed in relation to the estimated thermochemistries of these reactions. The rearrangement of **1d** is surprisingly rapid while that of **1e** is remarkably slow.

Experimental Section

In our previous investigations of reaction 1 we would generate radical **1** in the cavity of an EPR spectrometer by UV photolysis of solutions containing suitable precursors. The source of **1** was generally the parent hydrocarbon, **1**-H, i.e., $RCMe_3$, together with di-*tert*-butyl peroxide. The latter provided *tert*-butoxyl radicals which abstracted hydrogen from $RCMe_3$ to produce **1**.

$$Me_3CO\cdot + RCMe_3 \rightarrow Me_3COH + \mathbf{1} \qquad (4)$$

Unfortunately, this procedure could not be employed to produce **1d** because photolysis of di-*tert*-butyl ketone with UV yields *tert*-butyl and pivaloyl radicals. For this reason, it was decided to generate all **1** with *tert*-butoxyl radicals formed by the thermal decompostion either of di-*tert*-butyl peroxide (T = 80–130 °C) or di-*tert*-butyl hyponitrite (T = 40–60 °C).

$$Me_3COOCMe_3 \rightarrow 2Me_3CO\cdot \qquad (5)$$

$$Me_3CONNOCMe_3 \rightarrow 2Me_3CO\cdot + N_2 \qquad (6)$$

General Procedure. This is illustrated for *tert*-butylbenzene, the precursor of **1a**. Appropriate changes in the concentration of CCl_4 were employed for the other $RCMe_3$ substrates, i.e., higher $[CCl_4]$ were used for those substrates yielding **1** that underwent rearrangement more rapidly than **1a** and vice versa.

Reaction mixtures containing $PhCMe_3$ and CCl_4 in ratios varying from about 1:1 to 10:1 v/v together with ca. 1 to 5 vol % of di-*tert*-butyl peroxide or ca. 0.5–1.0 wt % of di-*tert*-butyl hyponitrite were sealed under vacuum in small Pyrex tubes. The dead volume was kept to a minimum so that the reactants would remain wholly in the liquid phase. Reaction tubes were heated in a thermostated oil bath (±0.1 °C) for a length of time such that the extent of reaction did not exceed 15% of the less abundant reactant. (Note: At elevated temperatures in particular there is a short chain reaction because some of the $CCl_3\cdot$ radicals abstract hydrogen from the $PhCMe_3$.) To prevent further reaction in the injection port of the gas chromatograph the hyponitrite was completely decomposed (10 half-lives at the temperature of the reaction). This was unnecessary for the peroxide. Product analyses were carried out on an HP 5995 GC/MS-FID instrument with a 12 m, 0.2 mm ID methyl silicone capillary column with temperature programming from 10 to 200 °C. Confirmation was provided when necessary by using GC/MS with chemical ionization by methane at 150 °C or isobutane at 125 °C on a HP 5985 GC/MS-C.I. instrument.

Product Identification. Products were identified by their mass spectrum and GC retention times. Whenever possible comparison was also made with authentic material. A commercial sample (Columbia Organic Chemicals) of **1a**-Cl was available and an authentic sample of **2e**-Cl (prepared by addition of HCl to $H_2C{=}CMeCH_2CN$) was kindly provided by Professor J. Warkentin. A sample of **1d**-Cl was prepared by photochlorination of di-*tert*-butyl ketone in deoxygenated CCl_4 at room temperature with use of molecular chlorine (30-min photolysis with 300-nm light in a Rayonet reactor, the solution being initially saturated with chlorine). The mass spectra of the unrearranged and rearranged chlorides were, in general,[20] sufficiently characteristic that there could be no doubt regarding the identification of these compounds. (The more important ions used to identify **1**-Cl and **2**-Cl have been tabulated and are available as Supplementary Material.) The mass spectral identification was further confirmed by experiments in which the concentration of CCl_4 was varied. Since the calculated values of the rate constant ratio k_r/k_{Cl} were always independent of the CCl_4 concentration the two products, **1**-Cl and **2**-Cl, must have been correctly identified in all cases.[20] Interestingly, the rearranged chloride products, **2a**-Cl, **2d**-Cl, and **2e**-Cl, had GC retention times that were 6–9% shorter than those of the corresponding unrearranged chlorides, whereas **2b**-Cl had a retention time that was 9% longer than that of **1b**-Cl.

Results

Product Balances. The overall reaction of each $RCMe_3$ substrate with the *tert*-butoxyl radicals derived (for example) from di-*tert*-butyl peroxide would be expected to adhere to a scheme comprising reactions 1–5 together with reactions 7–10.

$$Me_3CO\cdot \rightarrow Me\cdot + Me_2CO \qquad (7)$$

$$Me\cdot + CCl_4 \rightarrow MeCl + CCl_3\cdot \qquad (8)$$

$$CCl_3\cdot + CCl_3\cdot \rightarrow C_2Cl_6 \qquad (9)$$

$$CCl_3\cdot + RCMe_3 \rightarrow CHCl_3 + \mathbf{1} \qquad (10)$$

Accordingly, the following product balances should be obtained:

$$[\mathbf{1}\text{-Cl}] + [\mathbf{2}\text{-Cl}] = [Me_3COH] + [CHCl_3] \qquad (11)$$

$$2\Delta[Me_3COOCMe_3] = [Me_3CO\cdot] = [Me_3COH] + [Me_2CO] \qquad (12)$$

$$2\Delta[Me_3COOCMe_3] = [Me_3CO\cdot] = 2[C_2Cl_6] \qquad (13)$$

where $\Delta[Me_3COOCMe_3]$ refers to the quantity of di-*tert*-butyl peroxide reacted. In the di-*tert*-butyl hyponitrite initiated reactions

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[13] Chatgilialoglu, C.; Ingold, K. U.; Tse-Sheepy, I.; Warkentin, J. *Can. J. Chem.* **1983**, *61*, 1077–1081.

[14] Spin trapping was also employed in this study, see ref 13.

[15] Arrhenius parameters for the rearrangement of a deuterium-labeled homoallyl radical, $H_2C{=}CHCH_2\dot{C}D_2$, have also been determined, see ref 16.

[16] Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734–1736.

[17] We exclude the case of R = R′C(O)O since such 1,2-rearrangements occur via a 5-membered cyclic transition state, see: Beckwith, A. L. J.; Tindal, P. K. *Aust. J. Chem.* **1971**, *24*, 2099–2116. Beckwith, A. L. J.; Thomas, C. B. *J. Chem. Soc., Perkin Trans. 2* **1973**, 861–872. Barclay, L. R. C.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 4399–4403. Barclay, L. R. C.; Lusztyk, J.; Ingold, K. U. *Ibid.* **1984**, *106*, 1793–1796. Saebo, S.; Beckwith, A. L. J.; Radom, L. *Ibid.*, in press.

[18] Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063–6068.

[19] The Ph group in $PhCO\dot{C}H_2$ does, however, migrate at a rate measurable by the EPR method, see: Brunton, G.; McBay, H. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4447–4450.

[20] A minor peak in the GC of the products from *tert*-butylbenzene and di-*tert*-butylacetylene appeared between the peaks due to **1**-Cl and **2**-Cl and exhibited an EI MS similar to that of **2**-Cl. However, its intensity relative to **1**-Cl did not change appropriately with changes in the concentration of CCl_4. Therefore, it could not have been **2**-Cl.

Table I. Typical Product Balances for the Reactions of *tert*-Butylbenzene and Di-*tert*-butyl Ketone with *tert*-Butoxyl Radicals in Carbon Tetrachloride

	$PhCMe_3$		$Me_3CCOCMe_3$	
	T = 130 °C	T = 60 °C	T = 130 °C	T = 60 °C
	Product Yields, M			
$[\mathbf{1}\text{-H}]_0$[a]	2.85	5.47	2.56	0.72
$[CCl_4]_0$[a]	4.57	1.09	4.57	8.77
[**1**-Cl]	0.063	0.108	0.023	0.019
[**2**-Cl]	0.014	0.022	0.153	0.048
$[Me_3COH]$	0.027	0.103	0.061	0.041
$[CHCl_3]$	0.057	0.008	0.068	0.002
$[Me_3CO\cdot]$[b]	0.118	(0.132)	0.186	(0.079)
$[Me_2CO]$	0.087	0.029	0.090	0.038
$[C_2Cl_6]$	0.042	0.048	0.091	0.044
	Product Balances			
[**1**-Cl] + [**2**-Cl]	0.077	0.130	0.176	0.067
$[Me_3COH]$ + $[CHCl_3]$	0.084	0.111	0.129	0.043
$[Me_3CO\cdot]$	0.118	(0.132)	0.186	(0.079)
$[Me_3COH]$ + $[Me_2CO]$	0.114	0.132	0.151	0.079
$2[C_2Cl_6]$	0.084	0.096	0.182	0.088

[a] Initial concentrations. [b] Yield of *tert*-butoxyl radicals based on the amount of $Me_3COOCMe_3$ decomposed (or, for $Me_3CONNOCMe_3$, on the yield of Me_3COH + Me_2CO which is approximately 90% of the initial concentration of hyponitrite).

the hyponitrite was decomposed completely, but the effective yield of *tert*-butoxyl radicals was determined only via eq 12 because some of the *tert*-butoxyls recombine in the solvent cage to form di-*tert*-butyl peroxide.

For those $RCMe_3$ substrates for which it was possible to quantify all the relevant products, the yields of these products were generally in reasonable agreement with the predictions of eq 11–13 under a variety of experimental conditions. This is illustrated in Table I with typical data for *tert*-butylbenzene and di-*tert*-butyl ketone at high (130 °C) and low (60 °C) temperatures. For pivalonitrile it was not possible to check these three equations because Me_3COH, Me_2CO, $CHCl_3$, and peroxide were incompletely resolved from the large quantity of substrate. However, a reasonable product balance was indicated by the fact that the yield of chloride (almost entirely unrearranged) plus acetone was approximately twice the yield of C_2Cl_6. A similar check with *trans*-1,2-di-*tert*-butylethylene (which gives only rearranged chloride) also showed that the yield of chloride was approximately twice that of C_2Cl_6. For di-*tert*-butylacetylene the yield of C_2Cl_6 in some runs was considerably less than in other, apparently identical, runs. No reason for this behavior was discovered, but for those runs with "normal" C_2Cl_6 yields the overall product balances were quite acceptable. Presumably $CCl_3\cdot$ radicals can be "lost" under some conditions, perhaps by addition to the triple bond. Fortunately, the relative yields of **1b**-Cl to **2b**-Cl were, for small extents of reaction, constant under each set of experimental conditions, so it is unlikely that either product is being consumed by side reactions.

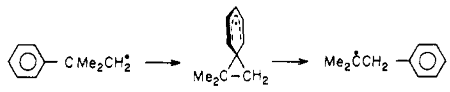
Since the overall product balances for the $RCMe_3$ substrates that we have examined are reasonably satisfactory we conclude that under our conditions potential side reactions, including radical attack on the R group of the substrate or products,[21,22] are relatively unimportant. We can therefore write:

$$\frac{k_r}{k_{Cl}} = \frac{[\mathbf{2}\text{-Cl}][CCl_4]}{[\mathbf{1}\text{-Cl}]} \qquad (14)$$

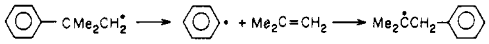
Measured relative concentrations of the **1**-Cl and **2**-Cl products derived from *tert*-butylbenzene (**1a**-H), di-*tert*-butylacetylene (**1b**-H), di-*tert*-butyl ketone (**1d**-H), and pivalonitrile (**1e**-H), at various temperatures and CCl_4 concentrations, together with the calculated values of k_r/k_{Cl} are available as Supplementary Material.

Discussion

Intramolecular Migration or Dissociation and Readdition? All available experimental evidence[3a,11,18] indicates that the neophyl rearrangement occurs via a short-lived,[23–25] 3-membered cyclic ring intermediate or, possibly, transition state:


(15)

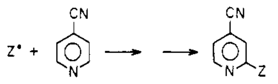
There is no evidence that would favor the dissociation–readdition process:


(16)

The same is true for the 1,2-migration of C═C double bonds,[3a,13,16] although for this rearrangement there is very strong evidence that cyclopropylcarbinyl radicals are intermediates in certain cases.[3a] There is also no evidence that would favor a dissociation–readdition process for the 1,2-migration of a C≡C triple bond.[12] However, there is a report by Minisci and co-workers[26] that suggests that the 1,2-migration of a C═O double bond can occur by an elimination–readdition pathway. These workers found that when β-acetylalkyl radicals were generated at 80 °C in aqueous acid by the silver-catalyzed decarboxylation of the appropriate acid precursor with peroxydisulfate, the acetyl radical could be trapped with (protonated) 4-cyanopyridine, **3**:

$$MeCOCHRCH_2CO_2H + Ag^{2+} \rightarrow MeCOCHRCH_2\cdot \qquad (17)$$

$$MeCOCHRCH_2\cdot \rightarrow Me\dot{C}O + CH_2{=}CHR \rightarrow MeCOCH_2\dot{C}HR \qquad (18)$$


(19)

3 **4**

R	Z	% yield of **4** (based on **3** consumed)
H	MeCO	6
H	$MeCOCH_2CH_2$	84
Me	MeCO	4
Me	$MeCOCHMeCH_2$	59
Me	$MeCOCH_2CHMe$	37

For R = H, ethylene was also detected. There can be little doubt that these two β-acetylalkyl radicals underwent at least some β-scission under the experimental conditions but, as the authors realized,[26] this does not necessarily imply that the rearrangement with R = Me occurred by this process. If, as we suspect, alkyl radical trapping was rather inefficient in this system then the formation of at least some free acetyl radicals is not too surprising. Certainly, it is diagnostically irrelevant with respect to the rearrangement process.

In other reports of 1,2-acyl group migrations[27–34] it appears to

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[21] Such as, for example, the known addition of carbon-centered radicals to the C═O double bond of ketones, see, e.g.: Knoll, H. *React. Kinet. Catal. Lett.* **1981**, *15*, 431–435. Drew, R. M.; Kerr, J. M. *Int. J. Chem. Kinet.* **1983**, *281*–291, 293–303; *J. Chem. Res., Synop.* **1983**, 254.

[22] Experiments with HC≡CCMe₃ were, however, frustrated by the very large number of products that were formed.

[23] The spiro intermediate has been shown in a CIDNP experiment to have a lifetime $<10^{-10}$ s at 105 °C (see ref 24) which places an upper limit of ca. 6 kcal/mol on the barrier for its ring opening. It has also been estimated that the spiro intermediate lies in a 2.2 ± 3.0 kcal/mol well (see ref 25).

[24] Shevlin, P. B.; Hansen, H. J. *J. Org. Chem.*, **1977**, *42*, 3011–3014.

[25] Franz, J. A.; Camaioni, D. M. *J. Org. Chem.* **1980**, *45*, 5247–5255.

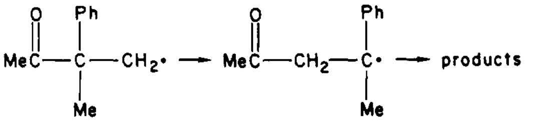
[26] Bertini, F.; Caronna, T.; Grossi, L.; Minisci, F. *Gazz. Chim. Ital.* **1974**, *104*, 471–478.

[27] Reimann, H.; Capomaggi, A. S.; Strauss, T.; Oliveto, E. P.; Barton, D. H. R. *J. Am. Chem. Soc.* **1961**, *83*, 4481–4482.

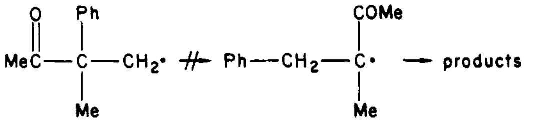
[28] Reusch, W.; Johnson, C. K.; Manner, J. A. *J. Am. Chem. Soc.* **1966**, *88*, 2803–2810.

[29] Karl, C. L.; Maas, E. J.; Reusch, W. *J. Org. Chem.* **1972**, *37*, 2834–2840.

have been generally assumed, either explicitly or implicitly, that the reaction proceeds via a 3-membered cyclic transition state or intermediate.[35,36] Very good evidence for an intramolecular process comes from a study of the directly comparable rearrangement of the $HCOCMe_2CH_2\cdot$ radical.[34] This occurs even in the presence of reactive olefins at concentrations that would certainly have trapped an intermediate $H\dot{C}O$ radical if one had been formed. A particularly interesting result is contained in Reusch and co-workers' early report[29] that at 130 °C the acetyl group in the $MeCOCMe(Ph)CH_2\cdot$ radical migrates in preference to the phenyl group, i.e.



$MeC(=O)-C(Ph)(Me)-CH_2\cdot \rightarrow MeC(=O)-CH_2-\dot{C}(Ph)(Me) \rightarrow$ products (20)



$MeC(=O)-C(Ph)(Me)-CH_2\cdot \not\rightarrow Ph-CH_2-\dot{C}(COMe)(Me) \rightarrow$ products (21)

The preference for reaction 20 over reaction 21 was, we estimate from their data, at least 33:1, a result that is quite consistent with our own finding, vide infra, that the activation energy for pivaloyl migration in **1d** is about 4 kcal/mol less than that for phenyl migration in **1a**, a difference in activation energies that translates to a 160-fold rate difference at 130 °C. That 1,2-acyl group migration occurs in preference to 1,2-phenyl migration (and also to 1,2-alkyl and 1,2-alkoxycarbonyl group migrations) has been further confirmed by the studies of Tada and co-workers.[32,33]

In our own case, C=O migration involves the pivaloyl group which is known to undergo rapid decarbonylation.[37,38]

$$Me_3C\dot{C}O \rightarrow Me_3C\cdot + CO \qquad (22)$$

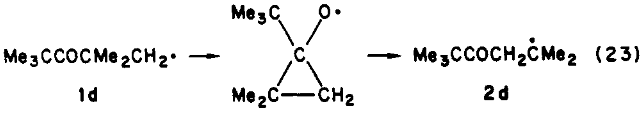
From kinetic data[37] the rate constant for reaction 22 can be calculated to be $2.5 \times 10^5\ s^{-1}$ at 40 °C and $7 \times 10^6\ s^{-1}$ at 130 °C, the bottom and top of our temperature range. The steady-state concentration of isobutylene would have to be appreciable if rearrangement were occurring by a dissociation–readdition pathway since the product balances (Table I) show that most of the pivaloyl radicals are trapped.[39] Nevertheless, to be "on the safe side" we carried out some experiments in which $Et_2C{=}CH_2$ was added to the usual reaction mixtures, since this compound should be just as good a trap for pivaloyl radicals as isobutylene. No evidence for the expected product, $Me_3CCOCH_2C(Cl)Et_2$, was found by GC/MS in reactions carried out with 100 μL of $Me_3CCOCMe_3$, 100 μL of CCl_4, and 5 μL of $Et_2C{=}CH_2$ at 60 °C (with 3.2 mg of $Me_3CONNOCMe_3$ for 17 h) or at 130 °C (with 5 μL of $Me_3COOCMe_3$ for 5 h). Furthermore, $Me_3CCOCH_2C(Cl)Et_2$ could not be identified even in the reaction of 100 μL of Me_3CCHO, 100 μL of CCl_4, 25 μL of $Et_2C{=}CH_2$, and 1 mg of $Me_3CONNOCMe_3$ at 60 °C for 15 h. In this last case, pivaloyl radicals must have been formed but decarbonylation occurred in preference to addition to the olefin.

Table II. Ratio of Arrhenius Parameters and Rate Constants for Some $RCMe_2CH_2\cdot \rightarrow RCH_2\dot{C}Me_2$ Rearrangements vs. $RCMe_2CH_2\cdot + CCl_4 \rightarrow RCMe_2CH_2Cl + CCl_3\cdot$ Reactions

1	R	temp range, °C	log (A_r/A_{Cl}),[a] M	$E_r - E_{Cl}$,[a] kcal/mol	k_r/k_{Cl} at 25 °C, M
a	Ph	60–130	3.41 ± 0.14	6.30 ± 0.23	6×10^{-2}
b	$Me_3CC{\equiv}C$	40–130	3.20 ± 0.28	7.26 ± 0.45	8×10^{-3}
d	$Me_3CC{=}O$	40–130	2.80 ± 0.07	2.25 ± 0.12	14
e	$N{\equiv}C$	80–130	1.48 ± 0.27	6.96 ± 0.47	1.5×10^{-3}

[a] Errors correspond to one standard deviation.

We conclude that under our experimental conditions the pivaloyl migration is an intramolecular reaction:



$Me_3CCOCMe_2CH_2\cdot \rightarrow [\text{cyclopropyloxy radical}] \rightarrow Me_3CCOCH_2\dot{C}Me_2$ (23)

This conclusion receives further support from a comparison of the Arrhenius pre-exponential factors for this reaction and for the migrations of the other unsaturated groups studied in this work (vide infra).

There are no authentic and unequivocal reports of 1,2-cyano group migrations.[41] However, 1,3-CN group migrations in radicals[45] and biradicals,[46] 1,4-CN group migrations in radicals[47–49] and biradicals,[50] "incomplete" 1,4-CN group migrations in radicals, i.e., radical cyclization onto a C≡N group to form a cyclopentiminyl radical,[51–54] and 1,5- and 1,6-CN group migrations in radicals[54] are well established. Theoretical studies suggest that the intramolecular 1,2-migration of a cyano group should be a facile process which occurs almost as readily as the 1,2-migration of a formyl group.[36] To our surprise the cyano group migration was found to be slower than that of any of the other groups examined.

Relative Rates for 1,2-Group Migrations. Relative kinetic data for the **1** → **2** rearrangements studied in this work are summarized in Table II. The data for pivalonitrile, i.e., the **1e** → **2e** rearrangement, are much less reliable than those for the other three arrangements. This is because the CN group migration was so slow that the ratio, [**1e**-Cl]/[**2e**-Cl], of chlorinated products was too large for accurate measurement by GC (see Supplementary Material); moreover, the temperature range that could be covered

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(36) Russell, J. J.; Rzepa, H. S.; Widdowson, D. A. *J. Chem. Soc., Chem. Commun.* **1983**, 625–627.

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(38) See also: Applequist, D. E.; Kaplan, L. *J. Am. Chem. Soc.* **1965**, *87*, 2194–2200.

(39) Even if trapping occurred without activation energy, the rate of addition would be expected not to exceed $5 \times 10^8\ M^{-1}\ s^{-1}$, see ref 40.

(40) Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley-Interscience: New York, 1976.

(41) There are only two previous reports of the 1,2-migration of a cyano group.[42,43] In the gas phase at temperatures of 1090–1250 K, the (endothermic) rearrangement $Me\dot{C}HCH_2CN \rightarrow MeCH(CN)CH_2\cdot$ has been proposed as an "attractive alternative" to a 1,2-H atom shift.[42] A report[43] that the rearrangement $N{\equiv}CCHMeCH_2\cdot \rightarrow N{\equiv}CCH_2\dot{C}HMe$ is rapid in CCl_4 solution at room temperature has subsequently been shown to be in error.[44] There is no detectable migration of the cyano group in this radical under a wide variety of experimental conditions.[44]

(42) King, K. D.; Goddard, R. D. *Int. J. Chem. Kinet.* **1975**, *7*, 837–855.

(43) Nazran, A. S.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 236–237.

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Table III. Preferred Arrhenius Parameters and Rate Constants for Some $RCMe_2CH_2\cdot \rightarrow RCH_2\dot{C}Me_2$ Rearrangements[a]

1	R	log A_r, s^{-1}	E_r, kcal/mol	k_r at 25 °C, M^{-1} s^{-1}	ref
a	Ph	**11.55 ± 0.28**[b]	**11.82 ± 0.40**[b]	**762**	59 (eq 32)
		(11.7_5 ± 1.0)[c]	(13.6 ± 1.0)[c]	(59)[c]	11 (eq 24)
b	$Me_3CC{\equiv}C$	**11.34 ± 0.70**	**12.78 ± 1.08**	**93**	this work
		(12.4 ± 1.5)[c]	(14.6 ± 2.4)[c]	(49)[c]	12 (eq 25)
c	$H_2C{=}CH$	**11.25**[d]	**5.7**	**1.0 × 10^7**	see text
		(12.5 ± 0.6)[c]	(6.6 × 0.4)[c]	(4.5 × 10^7)	13
d	$Me_3CC{=}O$	**10.94 ± 0.49**	**7.77 ± 0.75**	**1.7 × 10^5**	this work
e	$N{\equiv}C$	**12.0**[d]	**16.4**	**0.9**	this work
		(9.62 ± 0.69)	(12.48 ± 1.10)	(2.9)	this work

[a] Preferred values are given in boldface. [b] Standard parameters used to calculate Arrhenius parameters for Cl-atom abstraction from CCl_4 (eq 33) and hence Arrhenius parameters for the other rearrangements. [c] Kinetic EPR method. [d] Assigned value.

was more limited. The very low yield of **2e**-Cl was shown not to be due to its thermal decomposition since authentic **2e**-Cl survived without appreciable decomposition when heated under vacuum in pivalonitrile both at 80 °C and at 130 °C for the length of time it took to do experiments at these temperatures. Attempts to measure the [**1e**-Cl]/[**2e**-Cl] ratios at 80 °C and 100 °C with di-*tert*-butyl hyponitrite were not successful. Three new products were formed in significant amounts, presumably because of the higher radical flux which would favor radical–radical reactions. The product balance was very poor, and the [**1e**-Cl]/[**2e**-Cl] ratios were more than twice those found under comparable conditions with di-*tert*-butyl peroxide as the initiator.

For the three substrates for which fairly accurate kinetic measurements could be made, the ratio of pre-exponential factors for rearrangement vs. chlorine atom abstraction, i.e., log (A_r/A_{Cl}/M), have similar values. This provides further evidence to support the view that Ph, C≡C, and C=O group 1,2-migrations proceed via similar reaction pathways involving, in each case, a 3-membered cyclic radical as an intermediate or, less probably, as a transition state. Differences in the rates of migration of these three groups are due primarily to differences in the activation energies for the three reactions.

Absolute Rate Constants for 1,2-Group Migrations. Choice of a Standard. Conversion of the relative rate data given in Table II to absolute rate data requires accurate knowledge of the absolute Arrhenius parameters for chlorine atom abstraction from CCl_4 by a primary alkyl radical (preferably, a neopentylic radical). Unfortunately, reported values for the absolute rate constants for Cl-atom abstraction from CCl_4 cover such a large range,[55–64] for closely related and even for identical alkyl radicals, that they are all but useless for present purposes.

As an alternative, we can choose one of the **1** → **2** rearrangements as our primary standard. Kinetic EPR spectroscopy has been used to determine the Arrhenius equations for the neophyl rearrangement,[11] **1a** → **2a**, and for the homopropargylic rearrangement,[12] **1b** → **2b**:

$$\log (k_r^{\mathbf{1a}}/\mathrm{s}^{-1}) = (11.7_5 \pm 1.0) - (13.6 \pm 1.0)/\theta \quad (24)$$

$$\log (k_r^{\mathbf{1b}}/\mathrm{s}^{-1}) = (12.4 \pm 1.5) - (14.6 \pm 2.4)/\theta \quad (25)$$

where $\theta = 2.3RT$ kcal/mol and the errors were either estimated[11] or represent one standard deviation.[12] Combination of the appropriate data from Table II with eq 24 yields:

$$\log (k_{Cl}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = (8.34 \pm 1.14) - (7.30 \pm 1.23)/\theta \quad (26)$$

with $k_{Cl} = 9.6 \times 10^2$ M^{-1} s^{-1} at 25 °C, while eq 25 yields:

$$\log (k_{Cl}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = (9.2 \pm 1.78) - (7.34 \pm 2.85)/\theta \quad (27)$$

with $k_{Cl} = 6.3 \times 10^3$ M^{-1} s^{-1} at 25 °C.

Although the agreement between eq 26 and 27 is gratifying, the validity of eq 24 (and hence of eq 26) has recently been challenged by Franz and co-workers.[65] They have examined the products of reaction of neophyl chloride with tri-*n*-butyltin hydride over a temperature range from 120 to 219 °C. The overall process can be represented by:

$$PhCMe_2CH_2Cl + n\text{-}Bu_3Sn\cdot \rightarrow \mathbf{1a} + n\text{-}Bu_3SnCl \quad (28)$$

$$\mathbf{1a} \rightarrow \mathbf{2a} \quad (1a)$$

$$\mathbf{1a} + n\text{-}Bu_3SnH \rightarrow \mathbf{1a}\text{-}H + n\text{-}Bu_3Sn\cdot \quad (29)$$

$$\mathbf{2a} + n\text{-}Bu_3SnH \rightarrow \mathbf{2a}\text{-}H + n\text{-}Bu_3Sn\cdot \quad (30)$$

The products **1a**-H and **2a**-H yielded the Arrhenius relationship:

$$\log (k_r^{\mathbf{1a}}/k_{29}/\mathrm{M}) = (2.48 \pm 0.04) - (8.13 \pm 0.08)/\theta \quad (31)$$

Combination of this last equation with the Arrhenius equation determined in this laboratory for H-atom abstraction from *n*-Bu_3SnH by primary alkyl radicals[66] yields:

$$\log (k_r^{\mathbf{1a}}/\mathrm{s}^{-1}) = (11.55 \pm 0.28) - (11.82 \pm 0.40)/\theta \quad (32)$$

The pre-exponential factor is in satisfactory agreement with our EPR value[11] (see eq 24), but the activation energy is lower by 2 kcal/mol, being in better agreement with an approximate activation energy for the **1a** → **2a** rearrangement of 10.3 ± 2.2 kcal/mol reported by Hamilton and Fischer[67] (who also used an EPR method).

The kinetic EPR method for studying radical rearrangements must be employed at temperatures where the rearrangement competes with radical–radical reactions and under conditions where the unrearranged and rearranged radical can be observed simultaneously. This means that measurements are actually made in that temperature range where k_r lies between 10^2 s^{-1} and 10^4 s^{-1}. Since the neophyl rearrangement was studied[11] over the temperature range 10–34 °C the value of 59 s^{-1} calculated for $k_r^{\mathbf{1a}}$ at 25 °C from eq 24 appears to be much too small. In contrast, eq 32 yields $k_r^{\mathbf{1a}} = 762$ s^{-1} at 25 °C, which appears to be rather more reasonable.

In order to avoid the inherent uncertainties in the EPR method, we have arbitrarily chosen to use eq 32 for the neophyl rearrangement as the Arrhenius equation which will serve as our primary standard. For chlorine atom abstraction we then obtain:

$$\log (k_{Cl}/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = (8.14 \pm 0.42) - (5.52 \pm 0.63)/\theta \quad (33)$$

which gives $k_{Cl} = 1.2 \times 10^4$ M^{-1} s^{-1} at 25 °C. Combination of

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(55) The following rate data (given as alkyl radical and rate constant in M^{-1} s^{-1} units at 25 °C, when possible, or at the temperature specified) have been reported: c-$C_6H_{11}\cdot$, 1.0 (ref 56), 1.2 × 10^5 (ref 57); c-$C_5H_9\cdot$, 28 (ref 58), 2 × 10^3 (ref 59); $Me_3C\cdot$, 4.9 × 10^4 at 37 °C (ref 60); $HOCH_2\cdot$, 2.5 × 10^5 at −40 °C (ref 61); $CH_3\cdot$, 24 (ref 62), 69 (ref 63); $C_2H_5\cdot$, 1.4 × 10^2 (ref 63); $Me_2CH\cdot$, 33 (ref 63); $Cl_3C(CH_2CH_2)_n\cdot$, $n = 1$, 3.9 × 10^3; $n = 2$, 9.0 × 10^4; $n = 3$, 1.4 × 10^5 all at 40 °C (ref 64).

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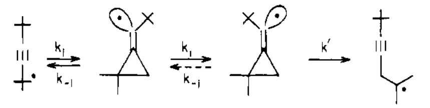
eq 33 with the data from Table II yields the preferred Arrhenius parameters for the rearrangement of **1b** and **1d** that are summarized in Table III. Preferred Arrhenius parameters for the rearrangement of **1c** and **1e** were estimated as described in the following section. Table III also lists the older kinetic EPR Arrhenius parameters.

Arrhenius Pre-exponential Factors. The *A* factors for the rearrangements of **1a** (Ph group) and **1d** (pivaloyl group) are $10^{11.55}$ and $10^{10.94}$ s^{-1}, respectively. These values are in the range expected[40,68] since two C–C bond rotations ($RCMe_2–CH_2·$ and $R–CMe_2CH_2·$) must be "frozen" in the transition state leading to the formation of the 3-membered ring. An *A* factor closer to 10^{13} s^{-1} would have been expected if the rate-controlling process for rearrangement had involved loss of R· from **1**, i.e., if reaction had occurred by an elimination–readdition process.

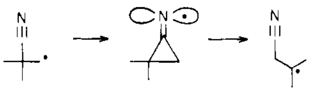
In contrast to **1a** and **1d**, the *A* factors for the rearrangements of **1b** ($Me_3C{\equiv}C$ group) and **1e** (CN group) do not have values close to 10^{12} s^{-1} (which would be expected because only one C–C rotation ($RCMe_2–CH_2·$) need be frozen in an intramolecular addition to a triple bond). For experimental reasons (vide supra) the error in the *A* factor for the **1e** rearrangement is large, and no significance should therefore be attached to its precise value. A possible explanation for the "low" *A* factor of the **1b** rearrangement resides in a complication that has been pointed out previously,[12] namely the known preference under free radical conditions for trans addition to acetylenes[69] via nonlinear vinyl radical intermediates.[70] Thus, the intramolecular addition step in the overall rearrangement of **1b** is expected to lead to radical **5** in preference to **6**:



1b **5** **6** **2b** (34)

The principle of microscopic reversibility implies that the stereoelectronically preferred ring opening pathway for **5** is that leading back to **1b** rather than directly forward to **2b**. In order to reach **2b** by the pathway of lowest activation energy, it would seem necessary to invert **5** to **6**. A possible consequence of the expected stereoelectronic preference is significant return of **5** to **1b** since the **5** → **6** inversion may be relatively slow.[73] It may even be endothermic since **6** would appear to be sterically more crowded than **5**. Even if **6** always undergoes ring opening to form **2b** (i.e., even if $k' \gg k_{-i}$), the experimental rate constant for the **1b** → **2b** rearrangement will be represented by $k_1\, k_i/(k_{-1} + k_i)$ rather than by k_1 alone. The unexpectedly small *A* factor for the **1b** → **2b** rearrangement can therefore be quite satisfactorily accounted for by assuming that reversal of the initial ring closure competes with the **5** → **6** inversion process, i.e., by assuming that $k_{-1} \geq k_i$.

It is unfortunate that the experimental *A* factor for the cyano group migration is unreliable. We favor a value of 10^{12} s^{-1} because there is no requirement for inversion of the intermediate iminyl radical prior to ring opening.[75] Such a value, when combined with the experimental k_r^{1e}/k_{Cl} values, yields a "preferred" activation energy of 16.4 kcal/mol for this rearrangement.



1e **2e** (35)

Cyclization of carbon-centered radicals onto C═C double bonds generally appears to have "early" transition states in which there is little or no "loosening" of the double bond.[3] The homoallyl rearrangement, **1c** → **2c**, would therefore be expected to proceed via a transition state in which two bond rotations have been frozen but the C═C bond has not been unfrozen. We have therefore taken as the preferred *A* factor for this rearrangement a value of $10^{11.25}$ s^{-1}, the mean of the values found for the **1a** → **2a** and **1d** → **2d** rearrangements. This value for the *A* factor has been combined with the kinetic data reported for the **1c** → **2c** rearrangement[13] to obtain the preferred activation energy of 5.7 kcal/mol listed in Table III.

Activation Energies. The assumption that the rate-determining step for 1,2 R-group migrations lies in the formation of a 3-membered ring can (in theory) be checked by comparing the measured activation energies (see Table III) with the calculated endothermicities for ring closure with use of thermochemical data and group additivity principles.[40,76] Unfortunately, much of the required thermochemical data are either unknown or are of questionable accuracy. The most reliable data relate to the cyclization of **1c** which can be calculated to be endothermic by ca. 6–7 kcal/mol, a value which is in satisfactory agreement with experiment. We have previously reported a *minimum* calculated endothermicity for the cyclization of **1a** of 16 kcal/mol.[12,77] Unfortunately, the uncertainties involved in this calculation were very large as can be illustrated by the conclusion of Franz and Camaioni[25] that the endothermicity for cyclization of **1a** is only 11.4 kcal/mol. We have repeated our calculations on this reaction and have obtained endothermicities as low as 10.9 and as high as 16.9 kcal/mol depending on the value taken for the C–H bond strength in cyclohexadiene.[78] Jackson,[81] using the lowest value reported for $D[c\text{-}C_6H_7–H]$, estimated that the addition of a particular radical to ethylene is ca. 11 kcal/mol more exothermic than the corresponding addition to benzene to give a cyclo-

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(70) The unpaired electron in vinyl radicals having H or alkyl substituents at the radical center lies in an orbital having appreciable s character and such radicals are therefore bent σ-radicals (see ref 71). This is true even in the face of fairly severe steric constraints (see ref 72).

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(73) In the absence of steric constraints the available experimental evidence indicates that 1-alkyl-substituted vinyl radicals invert fairly rapidly.[71a] Nevertheless, the rates of inversion are not so fast that the initial vinyl radical cannot be trapped before it isomerizes (see ref 74).

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(75) Iminyl radicals have the unpaired electron in a nitrogen $2p_y$ orbital which lies in the plane of the radical; see, e.g.: Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1962**, *36*, 1938–1942. Brivati, J. A.; Root, K. D. J.; Symons, M. R. C.; Tinling, D. J. A. *J. Chem. Soc. A* **1969**, 1942–1945. Wood, D. E.; Lloyd, R. V.; Pratt, D. W. *J. Am Chem. Soc.* **1970**, *92*, 4115–4117. Neta, P.; Fessenden, R. W. *J. Phys. Chem.* **1970**, *74*, 3362–3365. Symons, M. C. R. *Tetrahedron* **1973**, *29*, 615–619. Griller, D.; Mendenhall, G. D.; Van Hoof, W.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6068–6070.

(76) O'Neil, H. E.; Benson, S. W. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 17.

(77) Walsh, R., private communication.

(78) For *tert*-butylbenzene $\Delta H_f°$ is calculated to be −5.61 kcal/mol on the basis of the group values listed in Table A.1. of ref 40; taking D-[$PhCMe_2CH_2–H$] = 99 kcal/mol, we obtain $\Delta H_f°(PhCMe_2CH_2·) = 41.3$ kcal/mol. For 1,1-dimethylspiro[2.5]hexa-4,7-diene, $\Delta H_f°$ is calculated to be 34.5 kcal/mol with use of data from the same source plus cyclopropyl ring strain = 27.6 kcal/mol, 1,4-cyclohexadiene ring strain = 0.5 kcal/mol, and $[C–(C_d)_2(C)_2] = [C–(C)_4] + [C(C_d)_2(H)_2] - [C–(C)_2(H)_2] = 1.14$ kcal/mol (a value of 0.6 kcal/mol was used for this quantity in ref 25). From ref 40, $D[c\text{-}C_6H_7–H]$ can be calculated to be 75.8 kcal/mol which yields for the intermediate spiro radical, $\Delta H_f° = 58.2$ kcal/mol. That is, the endothermicity for the formation of the spiro intermediate from **1a** = 58.2 − 41.3 = 16.9 kcal/mol. Reference 79 gives $D[c\text{-}C_6H_7–H] = 69.8$ kcal/mol which yields an endothermicity of 10.9 kcal/mol, while ref 80 gives $D[c\text{-}C_6H_7–H] = 73$ kcal/mol and hence an endothermicity of 14.1 kcal/mol. Walsh[77] has estimated that the endothermicity for this reaction is probably ca. 21 kcal/mol.

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(80) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493–532.

(81) Jackson, R. A. *J. Chem. Soc., Chem. Commun.* **1974**, *573*–*574*.

hexadienyl radical; the endothermicity for the cyclization of **1a** might therefore be expected to be at least 11 kcal/mol greater than the 6–7-kcal/mol endothermicity calculated for the cyclization of **1c**. Our earlier thermochemical calculations[12] suggested that the minimum endothermicity for cyclization of **1b** was 18 kcal/mol, a value that remains unchanged. For the cyclization of **1d** we obtain an endothermicity of ca. 22 kcal/mol. The endothermicity for cyclization of **1e** could not be calculated.[82]

We have previously remarked on the fact that the minimum estimated endothermicities for the **1a** → **2a** and **1b** → **2b** rearrangement are greater than the experimental activation energies.[12] Our revised calculations indicate that while this *may* not be true for **1a** → **2a** it remains true for the **1b** → **2b** and **1d** → **2d** rearrangements. We have attributed[12] this phenomenon to the relief of steric compression which accompanies formation of a *gem*-dialkyl-substituted 3-membered ring (the Thorpe–Ingold effect[83]). The problem lies in the fact that calculated enthalpies based on group equivalents and additivity do not reflect such steric factors adequately.[12] For this reason, current thermochemical kinetics cannot be used even for "order of magnitude" estimates of absolute rates in systems where the Thorpe–Ingold effect operates. We consider that Thorpe-Ingold effects provide the most likely explanation for the unexpectedly low activation energies for this class of rearrangements. However, we do not rule out the possibility that these reactions proceed in a concerted manner with the three-membered ring being a transition state rather than a discrete, though short-lived, intermediate.

"Preferred" activation energies for migration increase along the series $R = H_2C{=}CH < Me_3CC{=}O < Ph < Me_3CC{\equiv}C < N{\equiv}C$, and of course, rates of migration decrease along this series. The preeminent migratory ability of the vinyl group is in agreement with the results of thermochemical kinetic calculations, but such calculations are too imprecise to rank the migratory abilities of the other four groups.

Comparison with Other Data. The preferred rate constants and Arrhenius parameters for the rearrangements of **1a**, **1b**, and **1c** can be compared with the values found by kinetic EPR spectroscopy which are also listed in Table III. The agreement is fairly satisfactory except for **1a**. However, the neophyl rearrangement was one of the first to be studied by the EPR method[11] and probably not all of the potential complications involved in this method[84] were appreciated at that time.

It is also interesting to compare our results for the pivaloyl group migration with the rate constants for an analogous benzoyl group migration that can be calculated from some data reported by Tada and co-workers.[33] Reaction of 2-benzoyl-2-phenylpropyl bromide with 0.1 and 1.0 M tri-*n*-butyltin hydride gave 2-benzoyl-2-phenylpropane (**7**) and 1,3-diphenyl-1-butanone (**8**), in ratios of 15:85 and 56:44, respectively.[33]

$$\mathrm{PhCOC(Ph)MeCH_2Br} + n\text{-}\mathrm{Bu_3Sn}\cdot \rightarrow \mathrm{PhCOC(Ph)MeCH_2}\cdot + n\text{-}\mathrm{Bu_3SnBr} \quad (36)$$

$$\mathrm{PhCOC(Ph)MeCH_2}\cdot \rightarrow \mathrm{PhCOCH_2\dot{C}(Ph)Me} \quad (37)$$

$$\mathrm{PhCOC(Ph)MeCH_2}\cdot + n\text{-}\mathrm{Bu_3SnH} \rightarrow \underset{\mathbf{7}}{\mathrm{PhCOC(Ph)Me_2}} + n\text{-}\mathrm{Bu_3Sn}\cdot \quad (38)$$

$$\mathrm{PhCOCH_2\dot{C}(Ph)Me} + n\text{-}\mathrm{Bu_3SnH} \rightarrow \underset{\mathbf{8}}{\mathrm{PhCOCH_2CH(Ph)Me}} + n\text{-}\mathrm{Bu_3Sn}\cdot \quad (39)$$

The temperature range was not specified, but earlier work[32] suggests that the reaction was probably carried out in benzene at reflux, i.e., at 80 °C. At this temperature k_{38} can be calculated to be ca. 6.1×10^6 M^{-1} s^{-1},[66] and hence $k_{37} = 3.5 \times 10^6$ s^{-1} (0.1 M n-Bu_3SnH) or 4.8×10^6 s^{-1} (1.0 M n-Bu_3SnH). For comparison, $k_r^{1d} = 1.3 \times 10^6$ s^{-1} at 80 °C. Note that it was the benzoyl group not the phenyl group that underwent the 1,2-migration. Although the neophyl rearrangement was the first radical rearrangement to be discovered,[4] phenyl groups are relatively reluctant to undergo 1,2-shifts. Nevertheless, phenyl migration is slightly faster than the migration of a triple bond and is a lot faster than the migration of a CN group, of an ROC=O group,[32,85] or of an RSC=O group.[85]

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Registry No. 1a, 25087-41-6; **1b**, 74056-27-2; **1c**, 87110-24-5; **1d**, 91759-16-9; **1e**, 57433-43-9; CCl_4, 56-23-5.

Supplementary Material Available: Tables IV–VIII giving mass spectral data for reaction products and Tables IX–XII giving product yields and k_r/k_{Cl} values for each experiment (9 pages). Ordering information is given on any current masthead page.

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(82) The thermochemistry of iminyl radicals appears to rest on a single estimate of the heat of formation of the $CH_3CH{=}N\cdot$ radical.[76] Moreover, although the strain energies for cyclopropane (27.6 kcal/mol) and methylenecyclopropane (41.7 kcal/mol) are known, the strain energy in $c\text{-}C_3H_4{=}NH$ is unknown. It is probably greater than 41.7 kcal/mol since such a value yields a calculated endothermicity for formation of $c\text{-}C_3H_4{=}N\cdot$ of ca. 14 kcal/mol, implying that the **1e** → **2e** rearrangement should be faster than all but the **1c** → **2c** rearrangement.

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