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A THERMALLY-INDUCED RADICAL REARRANGEMENT OF 2-ARYLMETHOXYTROPONES TO 3- AND 5-ARYLMETHYLTROPOLONES

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2-Arylmethoxytropones, *i.e.*, 2-benzyloxytropone, 2-(*p*-tolylmethoxy)tropone, 2-(4-bromophenylmethoxy)tropone, 2-(4-chlorophenylmethoxy)tropone, 2-(4-methoxyphenylmethoxy)tropone, and 2-(1-naphthylmethoxy)tropone, rearranged upon heating to the 3- and 5-arylmethyltropolones *via* the radical intermediates. Similarly, 5-bromo-2-(*p*-tolylmethoxy)tropone gave 5-bromo-3-(*p*-tolylmethyl)tropolone.

The Claisen rearrangement, a typical 3,3-sigmatropic reaction, of the various troponoids has revealed some fascinating features in synthetic aspect.$^{1-4)}$ However, no other sigmatropy on troponoids seems to be investigated in detail. Herein, we wish to report a newly occurred thermal rearrangement on the 2-arylmethoxytropones which can be potential candidates for a 5,5-sigmatropy:$^{5)}$ The major process was a formation of 3-arylmethyltropolones *via* the radical intermediates.

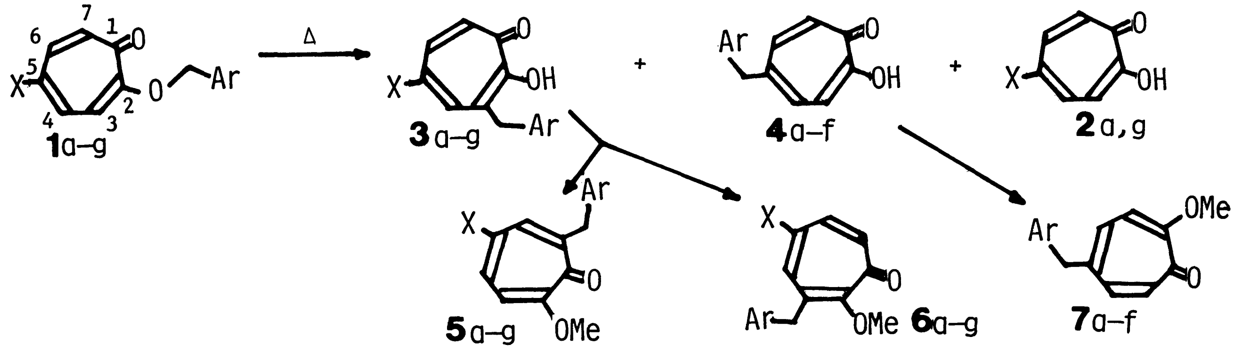


TABLE 1. THE THERMAL REARRANGEMENT OF 2-ARYLMETHOXYTROPONES.

Reactants	Conditions		Products (Yield/%, Mp/°C)		Yield/% of Regenerated **2**
	Temp/°C	Time/h	3-ArCH$_2$-	5-ArCH$_2$-	
1a: X=H, Ar=4-MeC$_6$H$_4$	190	11	**3**a(60, 94-96)	**4**a(6.6, 136-138)	10
b: X=H, Ar=C$_6$H$_5$	190	12	b(47, 51-52)	b(3.1, 119-120)	10
c: X=H, Ar=4-BrC$_6$H$_4$	190	17	c(46, 90-91)	c(3.2, 151-153)	11
d: X=H, Ar=4-ClC$_6$H$_4$	190	14	d(59, 87-88)	d(3.5, 154-156)	15
e: X=H, Ar=4-MeOC$_6$H$_4$	190	9	e(41, 79-80)	e(6.1, 109-110)	20
f: X=H, Ar=1-C$_{10}$H$_7$	190	7.5	f(52, 91-93)	f(20.0, 150-152)	5
g: X=Br, Ar=4-MeC$_6$H$_4$	190	10	g(22, 128-130)		20

When a decalin solution of 2-(*p*-tolylmethoxy)tropone(**1**a) was heated in a sealed tube on a refluxing decalin bath for 11 h, the products identified, along with small amounts of regenerated tropolone(**2**a), were 3-(*p*-tolylmethyl)tropolone (**3**a)[δ[6]: 2.30(3H, s), 4.11(2H, s), 6.91(1H, ddd, J=10, 7.5, 3 Hz), 7.09(4H, s), 7.25(1H, dd, J=7.5, 1 Hz), 7.28(1H, dd, J=3, 1 Hz), 7.39(1H, dt, J=10, 1 Hz), and 7.35(1H, br., OH)], 60%, and 5-(*p*-tolylmethyl)tropolone(**4**a)[δ: 2.32(3H, s), 3.89 (2H, s), 7.05(4H, m), 7.22(4H, s), and 7.35(1H, br., OH)], 6.6%. Methylation of **3**a by diazomethane gave two methyl ethers, **5**a[δ: 2.27(3H, s), 3.85(3H, s), 4.00(2H, s), 6.6-6.9(3H, m), 7.0-7.2(4H, m), and 7.20(1H, m)], pale yellow needles, mp 90-92°C, and **6**a[δ: 2.28(3H, s), 3.85(3H, s), 3.99(2H, s), 6.6-7.2(4H, m), and 7.03 (4H, s)], a yellow oil, while **4**a gave a single product, **7**a[δ: 2.30(3H, s), 3.81 (2H, s), 3.88(3H, s), 6.65(1H, d, J=10 Hz), 6.92(1H, dm, J=10 Hz), 7.12(2H, m), 7.0-7.2(4H, m)], pale yellow crystals, mp 155-157°C. The structures of **3**a and **4**a thus identified were further supported by the ^{13}C-NMR spectra.

Similarly, 2-benzyloxytropone(**1**b), 2-(4-bromophenylmethoxy)tropone(**1**c), 2-(4-chlorophenylmethoxy)tropone(**1**d), 2-(4-methoxyphenylmethoxy)tropone(**1**e), and 2-(1-naphthylmethoxy)tropone(**1**f) gave the 3-(**3**b–f)[7] and 5-arylmethyltropolones (**4**b–f), while 5-bromo-2-(*p*-tolylmethoxy)tropone(**1**g) solely gave 5-bromo-3-(*p*-tolylmethyl)tropolone(**3**g). The reaction conditions and the yields are shown in Table 1. The products have been characterized by the elemental analyses, the mass spectra, and H- and ^{13}C-NMR spectra (Table 2).

According to variable temperature experiments, the reaction with **1**f revealed following features; a) the reaction rates were second order for the concentration of aryloxytropones; $k^{453.7}$=5.22 x 10^{-4} 1/sec·mol, $k^{44.2}$=2.1 x 10^{-4}, $k^{435.2}$=1.02 x 10^{-4}, and $k^{426.2}$=4.3 x 10^{-5} (Fig. 1), and b), the $\Delta S^{\neq}$ was a distinct positive value (+14.7 cal/deg, E_a=36600 cal/mol).[8]

In connection with these observations, we have then carried out the cross-over experiments in a hope of obtaining chemical evidence for the intermolecular mechanism; when **1**f was similarly heated in a presence of three-fold excess of **2**-d_3, the products isolated after methylation (**5**f, **6**f, and **7**f) were deuterium-free on the basis of the mass and NMR spectra.

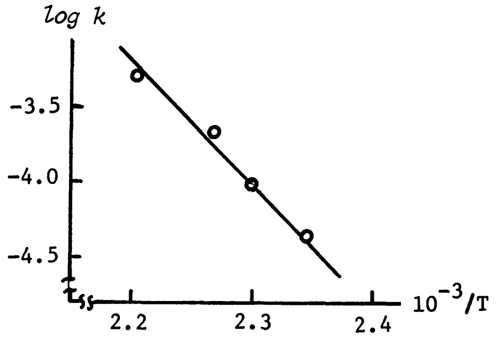


Fig. 1. The *k* of **1**f Determined Under Various Temperature.

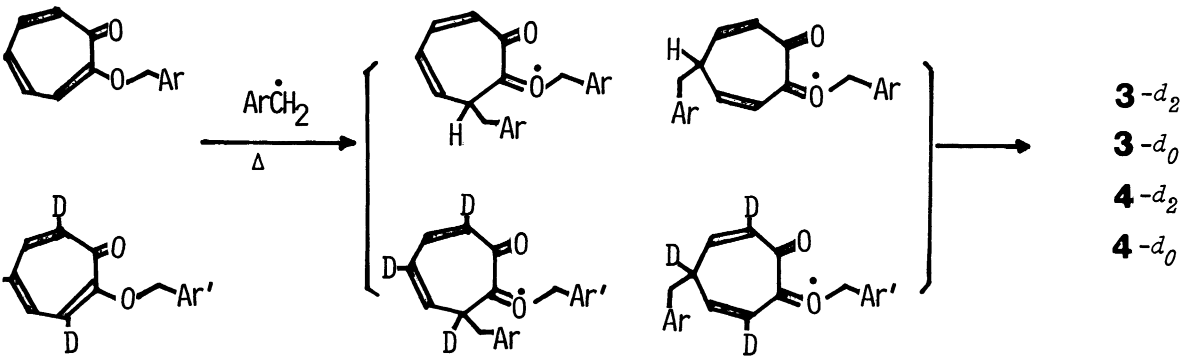
However, the reaction of a 1:1-mixture of **1**a-d_0 and **1**c-d_3 at 190°C for 9 h gave a scrambled product mixture: The isotope distributions of **5**a and **5**c, the main products isolated by means of a high-pressure liquid chromatograph, were determined by the mass spectrometry; **5**a showed the 1:1-peaks at *m/e*: 240 and 242(**5**a-d_0 and **5**a-d_2), while **5**c showed the 1:2:1-peaks at *m/e*: 304, 306, and 308(**5**c-d_0 and **5**c-d_2 with further splitting due to ^{79}Br and ^{81}Br). These complete shuffling of the isotope verified an intermolecular nature for the rearrangement. Same was the case for the minor products(**7**a-d_0 and **7**a-d_2, and **7**c-d_0 and **7**c-d_2). Moreover, a loss of the specificity in the deuterium-labelling even in the formation of 5-benzyl derivatives ruled out an involvement of

TABLE 2. THE ^{13}C-NMR SPECTRA OF NEW COMPOUNDS.

Compds:	Chemical Shifts (δ) in $CDCl_3$ Solutions
3a:	21.0, 40.0, 120.9, 127.2, 129.0*, 129.2*, 135.9, 136.0*, 139.5, 140.6, 168.2, 172.5
b:	40.4, 120.9, 126.5, 127.2, 128.5*, 129.1*, 136.0, 139.1, 139.6, 140.4, 168.2, 172.6
c:	40.0, 120.3, 120.7, 127.3, 130.7*, 131.5*, 136.1, 138.1, 139.5, 140.0, 167.8, 172.7
d:	39.9, 120.6, 127.3, 128.6*, 130.4*, 132.3, 136.1, 137.6, 139.5, 140.1, 167.9, 172.8
e:	39.5, 55.1, 113.9*, 120.8, 127.2, 130.1*, 131.0, 135.8, 139.4, 140.8, 158.2, 168.0, 172.5
f:	36.8, 120.6, 124.1, 125.6, 125.8, 126.3, 127.4, 127.7, 128.0, 128.7, 132.2, 134.0, 134.8, 135.9, 138.9, 140.8, 167.3, 173.0
g:	21.1, 40.1, 119.5, 122.1, 128.9*, 129.4*, 135.1, 136.3, 138.3, 140.6, 142.5, 167.1, 172.4
4a:	21.0, 45.1, 123.9*, 128.7*, 129.5*, 136.4*, 138.4*, 142.0, 170.8*
b:	45.5, 123.9, 126.8, 128.8**, 138.4*, 139.4*, 141.6, 170.8*
c:	44.8, 120.8, 123.9*, 130.5*, 131.9*, 138.3, 138.4*, 141.6, 170.6*,
d:	44.7, 123.9*, 128.9*, 130.1*, 132.7, 137.9, 138.4*, 141.0, 170.8*
e:	44.6, 55.3, 114.2*, 124.0*, 129.8*, 137.7, 138.4*, 142.3, 158.4, 170.7*
f:	42.4, 123.6, 123.9*, 125.5, 125.9, 126.4, 127.6, 127.9, 128.9, 131.8, 134.0, 134.9, 138.2*, 141.4, 170.8*
5a:	21.0, 40.7, 56.2, 112.1, 126.9, 129.1*, 129.4* 130.9, 135.7, 136.2, 136.6, 149.2, 164.0, 179.2
b:	41.2, 56.2, 112.1, 126.2, 126.8, 128.4*, 129.4*, 131.4, 136.3, 139.7, 148.8, 164.0, 179.0
c:	40.9, 56.2, 112.1, 120.0, 126.8, 131.1*, 131.4*, 131.4, 136.4, 138.7, 148.1, 164.2, 178.9
d:	40.8, 56.2, 112.2, 126.8, 128.4*, 130.7*, 131.4, 132.0, 136.4, 138.2, 148.2, 164.2, 178.9
e:	40.3, 55.1, 56.1, 112.0, 113.8*, 126.8, 130.4*, 130.8, 131.6, 136.0, 149.3, 158.0, 164.0, 179.1
f:	37.4, 56.3, 112.3, 124.4, 125.6, 126.0, 126.8, 127.4, 128.3, 130.9, 132.2, 133.9, 135.6, 136.0, 148.2, 163.7, 179.2
g:	21.0, 40.7, 56.4, 111.0, 121.8, 129.2**, 132.7, 135.6, 136.1, 139.7, 148.6, 163.3, 178.5
6a:	21.0, 39.5, 58.7, 128.6*, 129.2*, 129.5, 135.2, 135.9, 136.3, 137.2, 138.4, 138.9, 163.7, 181.8
b:	40.1, 58.7, 126.1, 128.5*, 128.7*, 129.5, 135.2, 137.3, 138.5, 138.6, 139.4, 163.9, 181.9
c:	39.6, 58.8, 120.3, 129.6, 130.4*, 131.6*, 135.2, 136.9, 137.7, 138.4, 138.5, 163.8, 181.7
d:	39.5, 58.8, 128.6*, 129.7, 130.0*, 132.3, 135.3, 137.0, 137.9*, 138.6, 164.0, 182.0
e:	39.1, 55.2, 58.7, 113.9*, 129.5, 129.7*, 131.4, 135.2, 137.2, 138.5, 139.0, 158.2, 163.7, 181.9
f:	36.5, 58.9, 123.6, 125.8, 126.3, 126.9, 127.4, 128.7, 129.4, 132.1, 133.8, 135.1, 135.3, 136.3, 138.3, 138.7, 164.4, 181.5
g:	21.0, 39.6, 59.0, 110.5, 124.6, 128.6*, 129.4*, 135.6, 136.3, 137.4, 138.1, 138.9, 163.2, 180.9
7a:	21.0, 44.5, 56.1, 112.6, 128.7*, 129.4*, 131.3, 136.1, 136.3, 136.7, 139.2, 141.3, 163.9, 180.0
b:	45.0, 56.1, 112.6, 126.7, 128.7*, 128.8*, 131.5, 136.7, 139.2*, 141.0, 164.0, 180.1
c:	44.4, 56.2, 112.5, 120.8, 130.6*, 131.6, 131.8*, 136.8, 138.2, 138.9, 140.2, 164.2, 180.0
d:	44.3, 56.1, 112.4, 128.9*, 130.2*, 131.5, 132.0, 136.8, 137.7, 138.9, 140.3, 164.1, 180.0
e:	44.1, 55.2, 56.1, 112.7, 114.1*, 129.8*, 131.2*, 136.6, 139.2, 141.5, 158.4, 163.9, 180.0
f:	41.9, 56.0, 112.6, 123.6, 125.4, 125.7, 126.3, 127.6, 127.7, 128.7, 131.7, 133.9, 134.7, 136.5, 138.9, 140.5, 163.9, 179.9

a) Asterisked figures mean overlapped two carbon signals(*) and four carbon signals(**).

the two-fold 3,3-sigmatropy, and the absence of **5**f-d_2, **6**f-d_2, and **7**f-d_2 in the reaction of **1**f with **2**-d_3 shows that the free tropolones must be less reactive than the alkoxytropones toward an attack of the benzyl radical.



Furthermore, the rearrangement of **1**a was accelarated by a certain amount of benzoylperoxide, a radical initiator, as shown in Fig. 2. The rearrangement occurring under such mild conditions is therefore a radical chain reaction.

Previously, Nozoe *et al.*,[9] have observed a radical substitution at C-3 of **2**a to verify the theoretical prediction given by Kurita and Kubo.[10,11] It is interesting that the major site of the present reaction is also C-3 of the 2-alkoxytropones.

Currently, some related aspects of this reaction is under intensive investigations, and the results will be reported elsewhere.

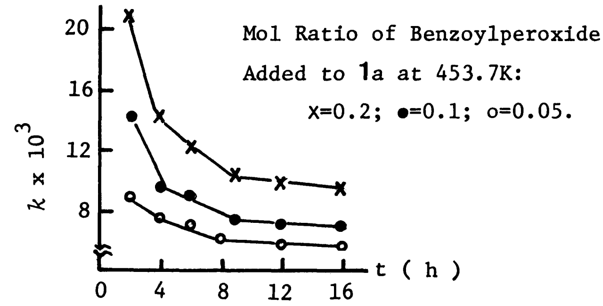


Fig. 2. Enhancement of the *k* of **1**a by Addition of Variable Amounts of Benzoylperoxide.

References and Notes

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6) The NMR spectra were measured in $CDCl_3$ solutions and the chemical shifts were expressed in the δ unit from the internal standard, Me_4Si.

7) For synthesis of **3**b and its derivatives, see T. Nozoe, T. Mukai, and I. Murata, *Proc. Japan Acad.*, 29, 167 (1953).

8) The measurements of kinetical data were carried out in the NMR tubings with *ca.* 50 mg of the samples, and the integrations of the NMR signals were average values of several runs.

9) T. Nozoe, T. Ikemi, N. Miyai, and Y. Kikuchi, *Proc. Japan Acad.*, 32, 476 (1956).

10) Y. Kurita and M. Kubo, *Bull. Chem. Soc. Jpn.*, 24, 13 (1951).

11) Once, Dewar (*Nature*, 166, 790 (1950)) predicted an occurrence of the radical substitution at C-5 of tropolones.

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