Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.61; H, 7.08; N, 12.25.

7-Isopropyl-7-methyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hepta-2,5-diene 5-*N*-Oxide (1d). The synthesis of azoxy **1d** from diester **7d** involved essentially the same procedure as that used in making **1a**. However, the oxidation was carried out with 90% H_2O_2. The purified product, a white powder, was isolated in 24% yield: mp 108–110 °C dec; NMR ($CDCl_3$) δ 0.75 (t, 6 H (on a Varian Model XL-100 spectrometer, this signal consists of two doublets)), 0.98–1.64 (m, 4 H, including a large singlet at 1.24), 5.08 (d, 1 H), 5.20–5.47 (m, 1 H), 7.05–7.67 (m, 4 H); IR (KBr) 3040 (w), 2975 (m), 2890 (w), 1515 (s), 1460 (s), 1365 (w), 775 (m), 730 (s), 710 (m) cm^{-1}; exact mass ($M^+ - N_2O$) calcd for $C_{13}H_{16}$ 172.1251, found 172.1252.

Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.21; H, 7.47; N, 13.00.

7-Benzyl-7-methyl-5,6-diaza-2,3-benzobicyclo[2.2.1]hepta-2,5-diene 5-*N*-Oxide (1e). This azoxy compound was prepared from diester **7e** using an almost identical procedure as that involved in the synthesis of **1a**. The oxidizing agent was 90% H_2O_2, and a 28% yield of white powder was obtained, mp 122–124 °C (with gas evolution): NMR ($CDCl_3$) δ 1.28 (s, 3 H), 2.36 (s, 2 H), 5.01 (d, 1 H), 5.10–5.38 (m, 1 H), 6.69–7.74 (m, 9 H); IR (NaCl) 3070 (w), 3040 (m), 2950 (w), 1605 (w), 1515 (s), 1465 (m), 1350 (w), 1215 (m), 765 (s), 740 (m), 708 (s) cm^{-1}; exact mass ($M^+ - N_2O$) calcd for $C_{17}H_{16}$ 220.1251, found 220.1256.

Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 77.13; H, 6.14; N, 10.54.

Keto Alcohol Side Product (9a): NMR ($CDCl_3$) δ 1.13 (s, 3 H), 1.25 (s, 3 H), 3.94–4.28 (m, 1 H), 4.89 (broad s, 1 H), 7.05–7.79 (m, 4 H); IR (NaCl) 3420 (broad, m), 3020 (w), 2925 (m), 1710 (s), 1615 (m), 1520 (w), 1455 (m), 1380 (m), 1325 (m), 1240 (m), 1065 (m), 762 (m), 725 (m) cm^{-1}; exact mass calcd for $C_{11}H_{12}O_2$ 176.084, found 176.086.

Acknowledgments. The authors wish to acknowledge, with thanks, the donors of the Petroleum Research Fund, administered by The American Chemical Society, for partial support of this research.

Registry No. 1a, 54963-23-4; **1b**, 70355-72-5; **1c**, 70355-73-6; **1d**, 70355-74-7; **1e**, 70355-75-8; **3**, 70355-76-9; **4a**, 17190-77-1; **4b**, 70292-52-3; **4c**, 70355-77-0; **4d**, 70355-78-1; **4e**, 70355-79-2; **5a**, 70355-80-5; **5b**, 70355-81-6; **5c**, 70355-82-7; **5d**, 70355-83-8; **5e**, 70355-84-9; **6a**, 70355-85-0; **6b**, 70355-86-1; **6c**, 70355-87-2; **6d**, 70355-88-3; **6e**, 70355-89-4; **7a**, 70355-90-7; **7b**, 70355-91-8; **7c**, 70355-92-9; **7d**, 70355-93-0; **7e**, 70355-94-1; **9a**, 59269-93-1; **10**, 876-83-5; dimethyl azodicarboxylate, 2446-84-6.

Thermal [1,5] Sigmatropic Alkyl Shifts of Isoindenes

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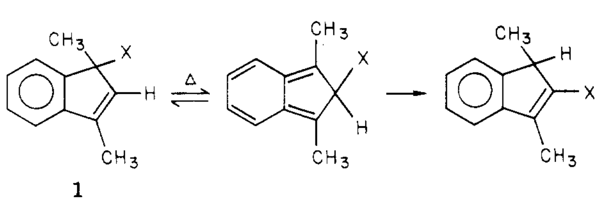
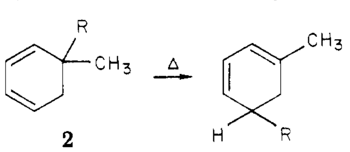
2,2-Dialkylisoindenes are generated by the thermal extrusion of N_2O from bicycloazoxy compounds at 180 °C. Such isoindenes undergo facile 1,5-alkyl shifts which allow the determination of relative migratory aptitudes of a number of alkyl groups: Me:Et:*i*-Pr:cyclopropylcarbinyl:benzyl = 1:6.2:5.3:7.9:55.6. Isolation of dimethylisoindene allowed the determination of activation parameters for its methyl-shift process: log A = 11.0, E_a = 26.1 kcal/mol. The results are discussed in terms of a pericyclic mechanism with the migrating group taking on a significant degree of radical character in the transition state.

Differences in migratory aptitudes of various unsaturated groups in [1,5] sigmatropic rearrangements have been examined by a number of groups in recent years.[1-7] Studying racemization rates of indenes (1), Field, Jones, and Kneen concluded that substituent effects were in the order: CHO > COR > H > $CH{=}CH_2$ > CONHMe > CO_2Ph > CO_2Me > CN ≈ C≡CH > alkyl.[5,6] Similarly, Schiess and Funfschilling examined [1,5] sigmatropic shifts in the 5-methylcyclohexa-1,3-diene system (2) and found CHO >> H ≈ $COCH_3$ > CO_2CH_3. The former workers rationalized their results in terms of a concerted migration involving an interaction of the HOMO of the diene system with the LUMO of the migrating group, a conclusion which was consistent with their most recent results in which it was shown that electron-poor vinyl groups migrate faster than electron-rich vinyl groups.[7]



1

X = -CHO, -COR, -CO$_2$R, -CH=CH$_2$, -C≡CH, -CN, etc.



2

R = CO_2CH_3, CHO, $COCH_3$

In other studies, Miller and Boyer determined that phenyl underwent 1,5 migration slower than H but faster than methyl in an indene system,[8] while Paquette and Carmody discovered a very facile 1,5 shift of a 1,3-butadienyl group.[9]

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[1] Taken in part from the Ph.D. Dissertation of K. E. Anapolle, University of Florida, 1979.

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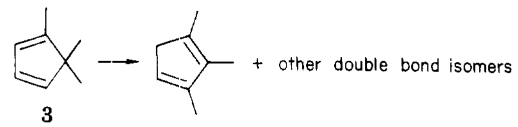
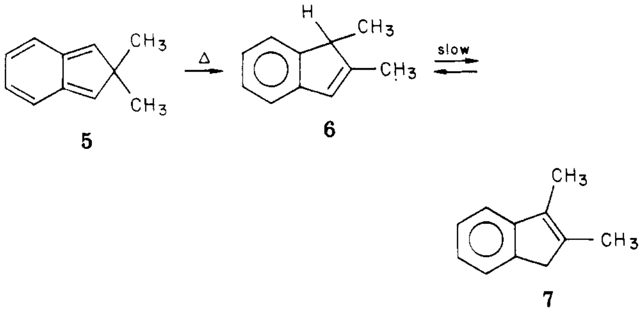
0022-3263/79/1944-2845$01.00/0

[1,5] sigmatropic shifts of alkyl groups, on the other hand, have been observed only under relatively harsh thermal conditions. 5,5-Dimethylcyclopentadienes, such as **3**, require activation energies of 41–46 kcal/mol[10–12] to induce a 1,5-methyl shift to occur. This reaction also gave evidence of having a free-radical chain component.[13] The cyclopentadiene system was not useful for a determination of relative migratory abilities of alkyl groups, and no comparison of such rates had been made prior to our initial report on isoindene isomerizations in 1975.[14] We would like to report, at this time, our further studies on the thermal isomerizations of 2,2-dialkyl-substituted isoindenes which have led to the determinations of migratory aptitudes of a series of alkyl groups in a [1,5] sigmatropic process.



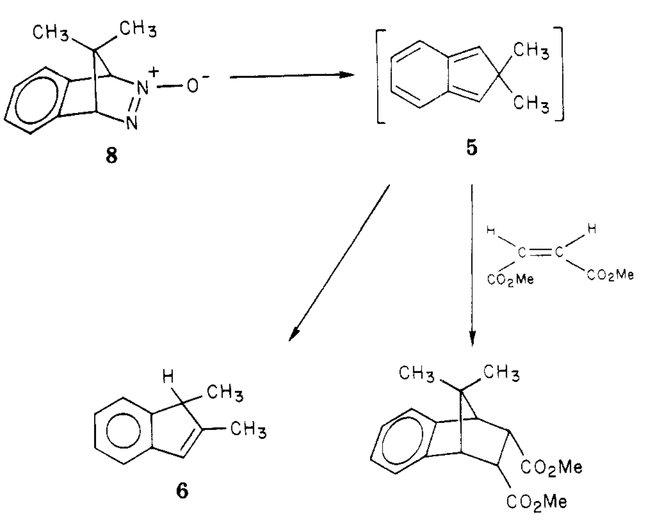
3 **4**

Isoindenes are ideal species for use in the study of 1,5-alkyl shifts because of the low temperature required for such rearrangements. The gain in aromaticity resulting from the alkyl shift is a tremendous activation-energy-lowering factor in this system, and the complicating hydrogen-shift process leading to isomeric indene **7** is slow relative to the process of interest, namely the conversion of **5** to **6**.

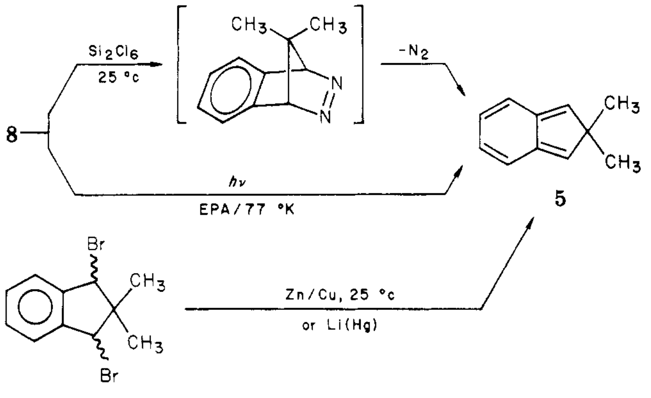


5 **6** **7**

We found that **5** could be generated conveniently and cleanly by the thermal extrusion of N_2O from azoxy compound **8** at 180 °C. Isoindene **5** then, in situ, underwent 1,5-methyl migration to give **6** in 80% yield. **5** could also be intercepted bimolecularly by various dienophiles, such as dimethyl maleate, to yield Diels–Alder adducts in a stereospecific manner. The intermediacy of **5** in this reaction was strongly implied by the above results and was further confirmed when **5** was actually isolated, characterized chemically and spectroscopically, and shown to convert thermally to **6** at 90 °C.[15] **5** could be generated by the debromination of dibromide **10**, using Zn–Cu couple or Li amalgam,[18] or by the photochemical extrusion of N_2O from **8** in an EPA matrix at 77 K.[15,18] The pale yellow **5** was characterized by UV, NMR, fluorescence, polarized excitation and emission, and magnetic circular dichroism (MCD) spectroscopy.[15,18] In addition, a determination of the activation energy for the 1,5-methyl shift conversion of **5** to **6** was made. The method used led to relatively large random error in the rate constants (~15%), but good first order character was observed for the determinations, and the Arrhenius parameters should be considered accurate within ±2 kcal/mol: $\log A = 11.0 \pm 0.07$; $E_a = 26.1 \pm 1$ kcal/mol.



8 **5** **6** **9**



5 **10**

According to our calculations using Benson's Group Equivalent Tables,[19] there is about a 20 kcal/mol difference in heats of formation between **5** and **6**. This is in excellent agreement with McCullough's approximation from kinetic data.[17] This being the case, and with reported activation parameters of $\log A = 13.7$ and $E_a = 45.1$ kcal/mol for the 1,5-methyl shift of 1,5,5-trimethylcyclopentadiene (**3**), one can see that a substantial part of the enthalpic gain incurred by **6** through aromatization is felt in the transition state of the rearrangement. Another useful comparison, that of experimental $\Delta G^{\ddagger}$'s, which are insensitive to the balance of log A and E_a, shows $\Delta G^{\ddagger} = 29.2$ kcal/mol for **5** and $\Delta G = 43.8$ for **3** at 92.4 °C, a difference of 14.6 kcal/mol.

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(15) W. R. Dolbier, Jr., K. Matsui, J. Michl, and D. V. Horak, *J. Am. Chem. Soc.*, **99**, 3876 (1977). An isolation of 2,2-dimethylisoindene was also reported by Morrison and Palensky at about the same time[16] and aryl-substituted isoindenes have been observed spectroscopicaly and trapped by McCullough and co-workers.[17]

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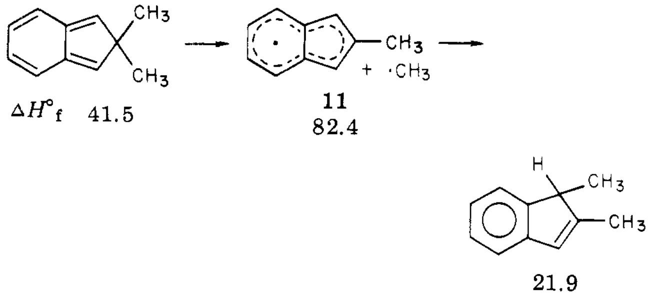
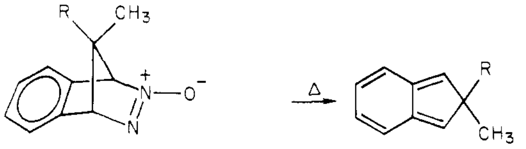
(19) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

Calculating the $\Delta H°_f$ for 5 and 6 and for the hypothetical



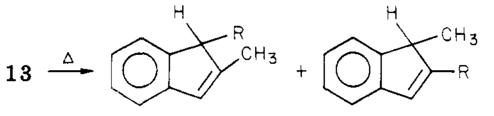
dissociated species 11,[19] assuming an indenyl radical stabilization energy of ~20 kcal/mol,[20] allows one to predict an E_a of 41 kcal/mol for the dissociation of 5 to 11. This discrepancy between the observed activation energy for rearrangement and that expected for a dissociative mechanism provides strong evidence that the rearrangement is concerted.

Azoxy compounds 12a–d were also synthesized and utilized to thermally generate the respective isoindenes, 13a–d. These in turn rearranged, in situ, to indenes 14



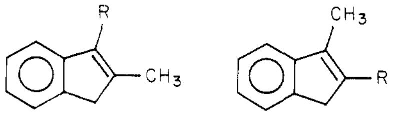
12a, R = Et
b, R = isopropyl
c, R = $C_6H_5CH_2$
d, R = cyclopropylcarbinyl

13a–d



14 15

and 15, the relative amounts of which are a direct reflection of the relative migratory abilities of R vs. methyl. Complications in the analyses of 14 and 15 resulted from small quantities of hydrogen-shift isomers 16 and 17 being



16 17

formed under the reaction conditions.

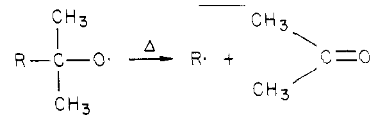
From careful analyses of the relative amounts of 14, 15, 16, and 17 in each system, it was possible to obtain values for the relative migratory aptitudes of methyl, ethyl, isopropyl, cyclopropylcarbinyl, and benzyl, the values being 1, 6.2, 5.3, 7.9, and 55.6, respectively.

A careful examination of the product mixture from 12a (R = Et) revealed less than 0.2% of the potential cross-over product 6, which would have resulted from the intervention of a free-radical chain process in the rearrangement. Further indication of the pericyclic nature of the reaction can be derived from the mere 55.6-fold rate enhancement produced when benzyl is the migrating group. While such a rate ratio is certainly indicative of stabilization of the transition state during benzyl migration, the magnitude

Table I. Typical GLC Analytical Data for the Pyrolysis of 12a

peak	retention time, min	rel ratio of peak areas	% of total peak area
A	34.0	24.3	72.6
B	40.8	3.6	10.7
C	49.1	4.6	13.7
D	59.7	1.0	3.0

of this enhancement is not consistent with a fragmentation process being involved, since benzyl-carbon bond-dissociation energies (BDE's) are generally about 16 kcal/mol less than methyl-carbon BDE's.[19] Indeed in a process where fragmentation is known to occur, such as in the thermal cleavage of 2-substituted 2-propylalkoxy radicals (18), benzyl radical was shown to form at a rate 900 times

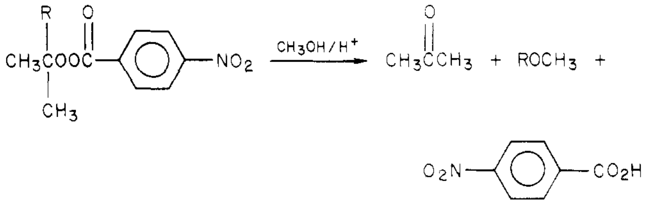


18

that of methyl radical.[22] Moreover, this alkoxy radical cleavage process should have been *much less endothermic* than the hypothetical isoindene cleavage, and thus the transition state for the former process should be less radical-like than that for the latter process.

Another indication that the migrating group never attains full radical character is that the cyclopropylcarbinyl group remains totally intact after migration. No conversion to allylcarbinyl can be detected.[23]

The migratory aptitudes observed in this study are consistent with the transition state having radical char-



Me:Et:isopropyl:*t*-Bu:benzyl = 1:45:2940:228 000:1630

acter, and it may be that the relative migratory aptitudes reflect the relative stabilities of the migrating alkyl groups. In similar processes involving pericyclic carbonium ion rearrangements, the migratory aptitudes of Me, Et, isopropyl, *tert*-butyl and benzyl were found to reflect their relative carbonium ion stabilities.[22,24]

At this point, however, one must be careful in placing too much significance on small differences in the observed relative rates. A comparison of isopropyl migration rate with that of ethyl requires the assumption that the methyl migration rate in each case is identical. This is by no means certain, since steric effects of the group "left behind" could give rise to varying methyl migration rates. At the present time, we are developing techniques for accurate and reproducible measurement of the absolute rates of these rearrangements which should lead to more meaningful absolute, rather than relative, rate data. Soon we should be able to address with less ambiguity the question of the relationship of the migratory aptitude of

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[20] The indenyl radical stabilization energy should be similar to that of cyclopentadienyl radical which has been estimated to be no more than 20 kcal/mol.[21]

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Table II. NMR Data for Compounds 6, 7, 14, 15, 16, and 17

compd	solvent	aromatic protons, δ	vinylic protons, δ	alkyl protons, δ
6	CCl_4 (60 MHz)	6.86-7.42 (m, 4 H)	6.34 (br, s, 1 H)	1.26 (d, 3 H), 2.04 (s, 3 H), 3.14 (q, 1 H)
7	CCl_4 (60 MHz)	6.79-7.34 (m, 4 H)		2.01 (s, 6 H), 3.15 (s, 2 H)
14a	$CDCl_3$ (60 MHz)	6.95-7.49 (m, 4 H)	6.44 (s, 1 H)	0.60 (t, 3 H), 1.60-2.27 (m, 5 H), 3.27 (t, 1 H)
15a	CCl_4 (60 MHz)	6.87-7.40 (m, 4 H)	6.25-6.47 (m, 1 H, J = 1.5 Hz)	0.97-1.42 (m, 6 H), 2.37 (q, 2 H), 3.19 (q, 1 H)
16a	$CDCl_3$ (60 MHz)	6.92-7.59 (m, 4 H)		1.16 (t, 3 H), 2.06 (s, 3 H), 2.55 (q, 2 H), 3.27 (s, 2 H)
17a	CCl_4 (60 MHz)	6.83-7.67 (m, 4 H)		1.16 (t, 3 H), 2.03 (s, 3 H), 2.49 (q, 2 H), 3.24 (s, 2 H)
14b	CCl_4 (60 MHz)	6.78-7.47 (m, 4 H)	6.40 (s, 1 H)	0.59 (d, 3 H), 1.15 (d, 3 H), 1.87-2.63 (m, 4 H), 3.14 (br, s, 1 H)
15b	CCl_4 (60 MHz)	6.87-7.37 (m, 4 H)	6.33-6.47 (m, 1 H)	1.23 (t, 9 H), 2.68 (hept., 1 H), 3.36 (q, 1 H)
16b	CCl_4 (60 MHz)	6.77-7.49 (m, 4 H)		1.34 (d, 6 H), 2.08 (s, 3 H), 2.84-3.41 (m, 3 H)
17b	CCl_4 (60 MHz)	6.77-7.47 (m, 4 H)		1.16 (d, 6 H, J = 7 Hz), 2.04 (t, 3 H), J = 2 Hz), 2.72-3.49 (m, 3 H)
14c	$CDCl_3$ (60 MHz)	6.72-7.62 (m, 9 H)	6.30-6.57 (m, 1 H)	2.08 (s, 3 H), 2.37-2.97 (m, 1 H), 3.06-3.97 (m, 2 H)
16c	$CDCl_3$ (60 MHz)	6.84-7.67 (m, 9 H)		2.17 (s, 3 H), 3.42 (s, 2 H), 3.96 (s, 2 H)
14d	$CDCl_3$ (100 MHz)	6.96-7.51 (m, 4 H)	6.45 (s, 1 H)	0.10-0.80 (m, 5 H), 1.40-1.85 (m, 2 H), 2.08 (s, 3 H), 3.32 (t, 1 H, J = 6 Hz)
15d	$CDCl_3$ (100 MHz)	7.00-7.51 (m, 4 H)	6.58 (s, 1 H)	0.12-0.66 (m, 4 H), 0.76-1.14 (m, 1 H), 1.25 (d, 3 H, J = 8.0 Hz), 2.30 (d, 2 H, J = 7.0 Hz), 3.35 (q, 1 H, J = 8.0 Hz)
16d	$CDCl_3$ (100 MHz)	6.98-7.42 (m, 4 H)		0.08-0.55 (m, 4 H), 0.78-1.16 (m, 1 H), 2.04 (s, 3 H), 2.51 (d, 2 H, J = 7.0 Hz), 3.26 (s, 2 H)
17d	$CDCl_3$ (100 MHz)	7.04-7.46 (m, 4 H)		0.14-0.62 (m, 4 H), 0.70-1.00 (m, 1 H), 2.04 (s, 3 H), 2.34 (d, 2 H, J = 7.0 Hz), 3.40 (s, 2 H)

an alkyl group in a sigmatropic process to its radical stabilizing ability.

Experimental Section

Boiling points and melting points were uncorrected, the latter taken on a Thomas-Hoover capillary melting point apparatus. Infrared spectral data were obtained from either a Perkin-Elmer Model 137 or a Beckman Model IR-10 spectrophotometer, and all absorption bands are listed in cm^{-1}. Nuclear magnetic resonance spectra were obtained from a Varian Model A-60A spectrometer, unless specified as the XL-100 model, utilizing Me_4Si as an internal standard. Mass spectral data were determined using an AEI-MS 30 high-resolution mass spectrometer, which was connected to a DS-30 data system. Elemental analyses were performed by Atlantic Microlab, Inc. (Atlanta, Ga.).

The GLC qualitative analyses were carried out on a Varian Aerograph Model 90-P gas chromatograph, equipped with the columns listed in the text. The GLC product ratio analyses were performed on a Hewlett-Packard Model 5710A gas chromatograph, with a flame ionization detector. A Vidar Autolab 6300 digital integrator was used to determine relative peak areas.

Pyrolyses were done in a silicon oil bath, and a Hallikainen Model 1053-A Thermotrol temperature controller was used to maintain a constant temperature.

Preparation of azoxy compounds **8** and **12a–d** and of 1,3-dibromo-2,2-dimethylindan (**10**) are described in the preceding paper.

Trapping of 2,2-Dimethylisoindene with Dimethyl Maleate. In a Pyrex tube suitable for sealing were placed 41 mg (2.2 × 10^{-4} mol) of azoxy compound **8** dissolved in 2.0 mL of benzene. After adding 31 mg (2.2 × 10^{-4} mol) of dimethyl maleate to the solution, 2 mL of benzene were added in order to wash down the inner walls of the tube, making a 0.05 M solution of each reagent. The tube was sealed under N_2 and heated at 180 °C for 3 h. The solvent was then removed in vacuo and 1 mL of CCl_4 was added to the residue. GLC analysis using a 0.25 in. × 18 ft., 20% SE-30 column showed the presence of 1,2-dimethylindene and indicated the only Diels–Alder product to be adduct **9** as demonstrated by authentic synthesis; 7.3 mg (12%) of adduct **9** and 2.2 mg of 1,2-dimethylindene were obtained. NMR of **9** (CCl_4): δ 0.68 (s, 3 H), 1.18 (s, 3 H), 2.92–3.05 (m, 2 H), 3.35 (s, 6 H), 3.48–3.60 (m, 2 H), 6.85–7.27 (m, 4 H).

Table III. Exact Mass Data on Thermolysis Products

compd	exact mass (mean of 7 scans)	theoretical mass
14a	158.1088	158.1095
15a	158.1093	158.1095
16a	158.1098	158.1095
17a	158.1093	158.1095
14b	172.1256	172.1251
15b	172.1251	172.1251
16b	172.1256	172.1251
17b	172.1251	172.1251
14c	220.1249	220.1251
16c	220.1253	220.1251
16d	184.1254	184.1251
6	144.0939	144.0936
7	144.0939	144.0930

Thermolyses of Azoxy Compounds 12a–d. Azoxy compounds **12a–d** were thermolyzed in benzene solution in sealed Pyrex tubes. Such tubes had been previously dried in an oven and flushed with N_2 prior to introduction of the samples. In a typical thermolysis, 100 mg (4.95 × 10^{-4} mol) of **12a** in 2 mL of benzene was placed in a Pyrex tube. Benzene (3 mL) was used to wash down the inner walls of the tube. The tube was then sealed, either at atmospheric pressure under N_2 or after degassing

Table IV. Relative Migratory Aptitudes of R vs. Methyl

run no.	azoxy used	thermolysis temp, °C	thermolysis time, h	GLC column	GLC temp, °C	rel ratio R/Me	stand dev
1	**12a**	190	4.0	A	120	6.41	0.04
2	**12a**	190	4.0	B	120	5.92	0.03
3	**12a**	200	3.2	B	120	6.24	0.06
4	**12b**	185	4.0	A	120	5.34	0.04
5	**12b**	194	4.5	A	120	5.26	0.02
6	**12b**	190	3.25	B	120	5.20	0.08
7	**12c**	175	3.2	A	170	51.36	0.86
8	**12c**	190	2.8	A	170	59.61	3.83
9	**12d**	180	3.0	A	160	7.85	0.08

Table V. Rates of Rearrangement of 2,2-Dimethylisoindene (5) to 1,2-Dimethylindene in Pentane[a]

run no.	temp, °C	$k \times 10^5$	correl coeff
1	105.0	8.33	0.9999
2	105.0	7.55	0.9990
3	99.1	4.63	0.9975
4	99.1	4.95	0.9998
5	92.0	3.51	0.994
6	92.0	3.62	0.9991
7	92.0	3.42	0.9930
8	86.0	1.84	0.9991
9	86.0	1.26	0.9997
10	74.0	0.623	0.998

[a] Log $A = 11.00 \pm 0.65$; $E_A = 26100 \pm 1100$ cal/mol; correlation coefficient = 0.997; $\Delta H^{\ddagger} = 25\,300$ cal/mol at 365.6 K; $\Delta S^{\ddagger} = -10.6$ cal/day; and $\Delta G^{\ddagger} = 29\,200$ cal/mol.

under vacuum. After heating the tube in an oil bath at 190 °C for 4.0 h, approximately 90% of the azoxy compound will have undergone decomposition. Such thermolyzed mixtures usually have a clear, pale yellow appearance. In general, quantities of azoxy compounds used in thermolyses varied from 44 to 215 mg and the concentration from 0.05 to 0.2 M while the conditions varied from 187 (for 3.2 h) to 200 °C (for 3.2 h).

Gas Chromatographic Analyses of the Azoxy Thermolyses Product Mixtures. Analyses could be done directly on the benzene solutions, but more commonly the solvent was evaporated and analyses done on neat mixtures or mixtures with small quantities of benzene added (~25% sample v/v). The following columns were used in various phases of GLC work: column A, $^1/_8$ in. × 8 ft, 3% FFAP on 60/80 Chromosorb P reg; column B, $^1/_8$ in. × 15 ft, 5% FFAP on 60/80 Chromosorb P reg; column C, 0.25 in. × 10 ft, 5% FFAP on 60/80 Chromosorb P reg; column D, 0.25 in. × 10 ft, 20% Apiezon L on 60/80 acid washed Chromosorb W; and column E, 0.25 in. × 5 ft, 18% DC-200 on 60/80 Chromosorb P reg.

In a typical analysis, a pyrolysis product mixture from **12a** was evaporated and then diluted with benzene to a 25% solution. Column C was heated to 128 °C and had a flow rate of 20 mL/min on a Varian Aerograph Model 90-P GC.

The chromatogram showed four peaks with typical data as in Table I.

The four components were collected and purified using the same column and conditions. Structure determination (using NMR, IR, and MS (exact mass)) led to identification of component A as 1-ethyl-2-methylindene (**14a**), component B as 1-methyl-2-ethylindene (**15a**), component C as 2-methyl-3-ethylindene (**16a**), and component D as 2-ethyl-3-methylindene (**17a**).

Thermal Rearrangement of 1-Ethyl-2-Methylindene (14a) to 2-Methyl-3-Ethylindene (16a). It was demonstrated that, in general, compounds **14** and **15** were converted thermally, under the regular thermolysis conditions, to compounds **16** and **17**, respectively. Typically, a Pyrex tube containing **14a** in benzene was heated at 200 °C for 25 h. The usual workup and analysis indicated components A and C to be the only compounds in the product mixture. They had a ratio of 1.0:9.0, respectively. Collection and identification indicated component C to be compound **16a**.

Determination of Relative Migratory Aptitudes for Alkyl Shifts in Isoindenes 13a–d. Quantitative GLC analyses of product mixtures were run on the Hewlett-Packard Model 5710A GC in coordination with a Vidar Autolab 6300 digital integrator. Repetitive injections were utilized to obtain an accurate measure of the peak ratios. Areas of components A and C were combined as were those of B and D to determine the migratory aptitudes. Table IV details the results.

Kinetics of the Rearrangement of 2,2-Dimethylisoindene (5). A dilute solution of 2,2-dimethylisoindene (**5**) in pentane was prepared on a vacuum line as described elsewhere[18] and was transferred in vacuo to a U-frame cuvette UV cell which was sealed in vacuo. Such sample tubes were heated for periods of time in a thermostated oil bath, removed, cooled, absorbance determined, returned to the oil bath and the cycle repeated again and again. One such tube was used per run. Absorbances were determined using a Zeiss PMQ II spectrophotometer. Temperature was measured using a Chromel-Alumel thermocouple coupled with a Tinsley Model 3387E potentiometer. Thermocouple readings were calibrated against standard calibrated thermometers (Brooklyn Thermometer Co.). Table V gives the accumulated rate data which were utilized in determination of the Arrhenius activation parameters. Rates and activation parameters were determined from the data using a least-squares method. The *only* product of the rearrangement was demonstrated to be 1,2-dimethylindene.

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Registry No. **5**, 54963-24-5; **6**, 70063-93-3; **7**, 4773-82-4; **8**, 54963-23-4; **9**, 70416-65-8; **12a**, 70355-72-5; **12b**, 70355-74-7; **12c**, 70355-75-8; **12d**, 70355-73-6; **13a**, 70416-66-9; **13b**, 70428-85-2; **13c**, 70416-67-0; **13d**, 70416-68-1; **14a**, 70416-69-2; **14b**, 70416-70-5; **14c**, 70416-71-6; **14d**, 70416-72-7; **15a**, 63265-70-3; **15b**, 70416-73-8; **15d**, 70416-74-9; **16a**, 51293-55-1; **16b**, 14237-69-5; **16c**, 70416-75-0; **16d**, 70416-76-1; **17a**, 66703-20-6; **17b**, 70416-77-2; **17d**, 70416-78-3; dimethyl maleate, 624-48-6.