

Thermal [1,5]-Sigmatropic Alkyl

Shifts of Isoindenes

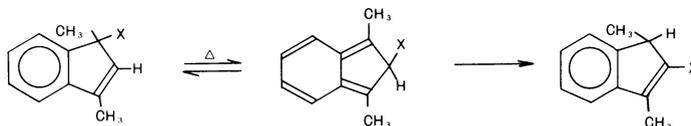
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ABSTRACT

2,2-Dialkylisoindenes are generated by the thermal extrusion of N_2O from bicycloazoxy compounds at 180° . Such isoindenes undergo facile 1,5-alkyl shifts which allow the determination of relative migratory aptitudes of a number of alkyl groups: Me:Et:isoPr:cyclopropylcarbinyl:benzyl = 1:6.2:5.3:7.8:55.6. Isolation of dimethylisoindene allowed the determination of activation parameters for its methyl-shift process: $\log A = 11.0$, $E_a = 26.1$ kcal/mole. 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.

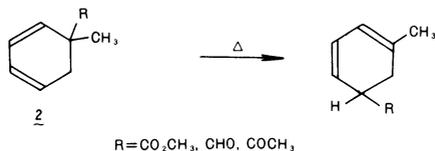
Differences in migratory aptitudes of various unsaturated groups in [1,5]-sigmatropic rearrangements have been examined by a number of groups in recent years.¹⁻⁶ Studying racemization rates of indenes (1), Field, Jones and Kneen concluded that substituent effects were in the order:

$CHO \gg COR > -C \equiv C - H \approx CN \approx H \gg -CH=CH_2 > CO_2R$.⁵



X = -CHO, -COR, -CO₂R, -CH=CH₂, -C≡C-R, CN, etc

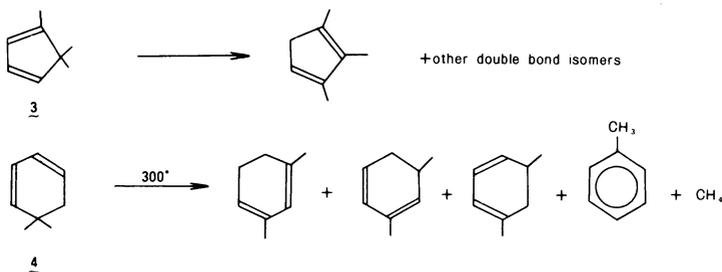
Similarly, Schiess and Funfschilling examined [1,5]-sigmatropic shifts in the 5-methyl-cyclohexa-1,3-diene system (**2**) and found $\text{CHO} \gg \text{H} \approx \text{COCH}_3 > \text{CO}_2\text{CH}_3$.



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.⁶

In other studies, Miller and Boyer determined that phenyl underwent 1,5-migration slower than H but faster than methyl in an indene system,⁷ while Paquette and Carmody discovered a very facile 1,5-shift of a 1,3-butadienyl group.⁸

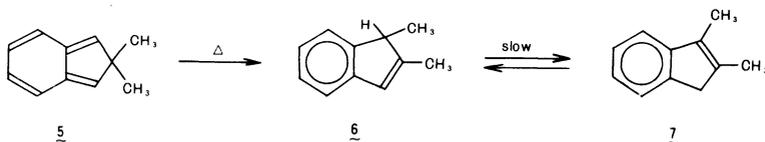
[1,5]-Sigmatropic shifts of alkyl groups, on the other hand, have been observed only under relatively harsh thermal conditions. 5,5-Dimethylcyclopentadienes, such as **3**, require activation energies of 41-46 kcal/mole,^{9,11} to induce a 1,5-methyl shift to occur, and 5,5-dimethylcyclohexa-1,3-diene (**4**) underwent a 1,5-methyl shift only at temperatures above 300°.¹² Both of these reactions give evidence of having non-concerted components in



their rearrangement mechanisms.¹³ The cyclopentadiene system was not useful for a determination of relative migratory abilities of alkyl groups, and

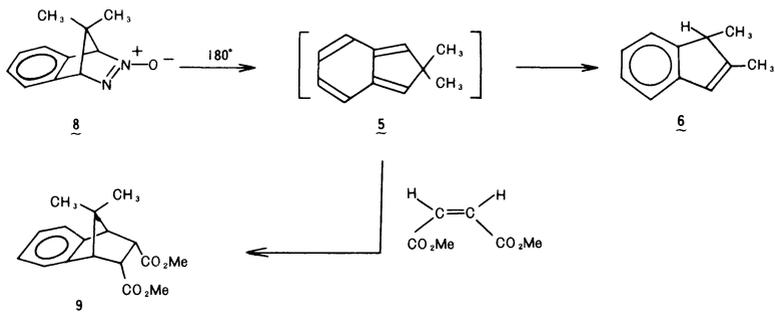
no comparison of such rates had been made prior to our initial report on isoindene isomerizations in 1975.¹⁴ We would like to report at this time, our further studies on the thermal isomerizations of 2,2-dialkyl-substituted isoindenes which have led to the determinations of migratory aptitudes of a series of alkyl groups in a [1,5]-sigmatropic process.

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



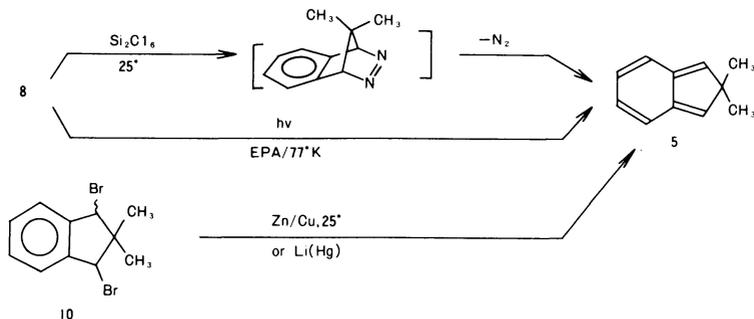
process leading to isomeric indene **7** is slow relative to the process of interest, namely the conversion of **5** to **6**.

We found that **5** could be generated conveniently and cleanly by the thermal extrusion of N_2O from azoxy compound **8** to 180° . Isoindene **5**



then, *in situ*, underwent 1,5-methyl migration to give **6** in 80% yield. **5** could also be intercepted biomolecularly 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, characteriz-

ed chemically and spectroscopically, and shown to convert thermally to **6** at 90° .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 m.c.d.



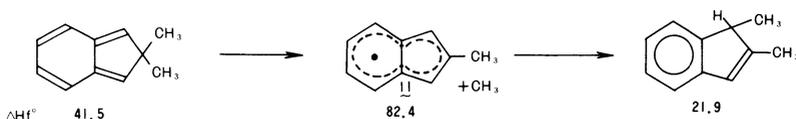
spectroscopy.^{15, 18} In addition, a determination of the activation energy for the 1,5-methyl shift conversion of **5** to **6** was made. The method used led to relatively large random error in the rate constants ($\sim 15\%$) but good first order character was observed for the determinations, and the Arrhenius parameters should be considered accurate within ± 2 kcal/mole.

$$\log A = 11.0 \pm .7 \quad E_a = 26.1 \pm 1 \text{ kcal/mole}$$

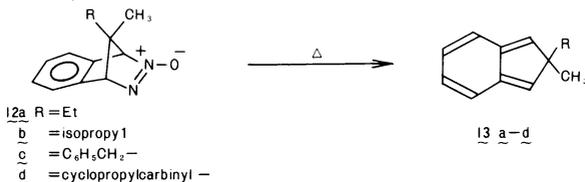
According to our calculations using Benson's Group Equivalent Tables,¹⁹ there is about a 20 kcal/mole difference in heats of formation between **5** and **6**. This is in excellent agreement with McCullough's approximation from kinetic data.¹⁷ This being the case, and with reported activation parameters of $\log A = 13.7$ and $E_a = 45.1$ kcal/mole for the 1,5-methyl shift of 1,5,5-trimethyl-cyclopentadiene (**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. Since our $\log A$ has a relatively large error associated with its measurement, it is useful to set $\log A$ for our reaction at 13.7 and calculate E_a for comparison purposes. This would give **5** an E_a of 29.0 kcal/mole compared with the 45.1 kcal/mole of **3**, a difference of 16

kcal/mole. In any event, a comparison of experimental ΔG^\ddagger 's, which are insensitive to the balance of $\log A$ and E_a 's shows $\Delta G^\ddagger = 29.2$ kcal/mole for **5** and $\Delta G^\ddagger = 43.8$ for **3** at 92.4°C , a difference of 14.6 kcal/mole.

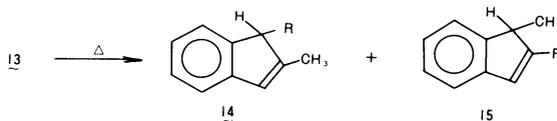
Calculating the ΔH_f° for **5**, **6** and for the hypothetical dissociated species **11**,¹⁹ assuming an indenyl radical stabilization energy of ~ 20 kcal/mole,²⁰ allows one to predict an E_a for dissociation of 41 kcal/mole.



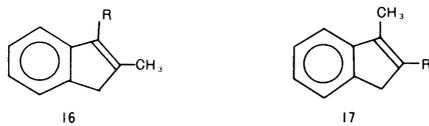
Azoxy compounds **12 a-d** were also synthesized and utilized to thermally generate the respective isoindenes, **13 a-d**. These in turn rearranged, in situ, to indenes **14** and **15**, the relative amounts of which are



a direct reflection of the relative migratory abilities of R versus methyl. Complications in the analyses of **10** and **11** resulted from small quantities



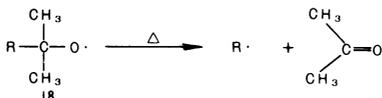
of hydrogen-shift isomers **16** and **17** being formed under the reaction conditions.



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, cyclopropylcarbonyl and benzyl, the

values being 1, 6.2, 5.3, 7.8 and 55.6, respectively.

A careful examination of the product mixture from **12a** (R=Et) revealed less than 0.2% of the potential crossover 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 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/mole 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 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 character. As such the rates of migration should depend on three factors:

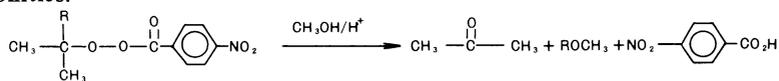
- (1) The absolute BDE of each R bound to the isoindenyl system,
- (2) The resonance stabilizing ability of R,
- (3) Ground state effects of R (i.e. back strain which would effectively reduce the apparent BDE.)

It has been proposed that a significant part of the difference in BDE's of

Me-C, Et-C, isopropyl-C and t-butyl-C bonds may be attributed to the latter factor, and that the inate BDE's of these alkyl-C bonds are very similar.²⁴ In all cases where radicals are formed by dissociative or abstraction processes, such ground state effects can be invoked to effectively explain the $3^\circ > 2^\circ > 1^\circ > \text{CH}_3$ order of reactivity. Similarly, in free radical addition processes, the observed regioselectivity may also be rationalized on the basis of steric effects.²⁴ Thus ambiguity exists regarding the actual relative stabilities of various simple alkyl radicals.

Our observation that isopropyl and ethyl groups have near identical migratory aptitudes may eventually provide the insight necessary to probe this question. First of all, the steric environments of R in product and starting material are relatively unchanged. (i.e. R is bound to an sp^3 carbon in both cases). This is in contrast to dissociative and abstraction sources of $\text{R}\cdot$ where the product enters into a much less sterically demanding sp^2 state.

It may be that these relatively migratory aptitudes are giving a pretty true reflection of the inate stabilities of various alkyl radicals, tempered of course by the fact that the pericyclic mechanism never really attains true free radical character. In similar processes involving pericyclic carbonium ion rearrangements, the migratory aptitudes of Me, Et, isopropyl, t-butyl and benzyl certainly reflect their relative carbonium ion stabilizing abilities.^{22, 25}



Me : Et : Isopropyl : t-Bu : Benzyl = 1 : 45 : 2920 : 228,000 : 1600

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

EXPERIMENTAL

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 TMS 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, Georgia).

The glpc qualitative analyses were carried out on a Varian Aerograph model 90-P gas chromatograph, equipped with the columns listed in the text. The glpc 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 silicone oil bath, and a Hallikainen model 1053-A Thermotrol temperature controller was used to maintain a constant temperature.

Preparation of azoxy compounds **8** and **12 a-d** and of 1,3-dibromo-2,2-dimethylindane, **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, 2 ml of benzene were added in order

to wash down the inner walls of the tube to make a 0.05M soln. of each reagent. The tube was sealed under N_2 and heated to 180° for 3 hr. The solvent was then removed in vacuo and 1 ml of CCl_4 was added to the residue. Glpc analysis using a $1/4'' \times 18'$, 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-demethylindene was obtained. Nmr of 9 (CCl_4); δ 0.68 (s, 3H), 1.18 (s, 3H), 2.92–3.05 (m, 2H), 3.35 (s, 6H), 3.48–3.60 (m, 2H), 6.95–7.14 (m, 4H).

Thermolyses of Azoxy Compounds 12 a–d

Azoxy compounds 12 a–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 12-a 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 under vacuum. After heating the tube in an oil bath at 190° for 4.0 hr., 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 mg to 215 mg and the concentration from 0.05M to 0.2M while the conditions varied from 187° (for 3.2 hr) to 200° (for 3.2 hr).

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 ($\sim 25\%$ sample V/V). The following columns were used in various phases of glpc work:

Column A: $1/8'' \times 8'$, 3% FFAP on 60/80 Chromosorb P reg.

Column B: $1/8'' \times 15'$, 5% FFAP on 60/80 Chromosorb P reg.

Column C: $1/4'' \times 10'$, 5% FFAP on 60/80 Chromosorb P reg.

Column D: $1/4'' \times 10'$, 20% Apiezon L on 60/80 acid washed Chromo-

sorb P.

Column E: 1/4" x 5', 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° and had a flow rate of 20ml/min on a Varian Aerograph Model 90-P gc.

The chromatogram showed 4 peaks with typical data as in Table I.

Table 1. Typical Glpc Analytical Data for the Pyrolysis of 12-a

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

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° for 25 hr. The usual work-up 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**.

Table 2. NMR Data for Compounds 6, 7, 14, 15, 16, & 17.

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

Table 3. Exact Mass Data on Thermolysis Products

Compound	Exact Mass (mean of 7 scans)	Std. Dev.	Theoretical Mass	Deviation
14-a	158.10877	0.00124	158.10950	-0.00073
15-a	158.10933	0.00140	158.10950	-0.00017
16-a	158.10983	0.00200	158.10950	+0.00033
17-a	158.10926	0.00056	158.10950	-0.00024
14-b	172.12558	0.00096	172.12510	+0.00048
15-b	172.12511	0.00073	172.12510	+0.00001
16-b	172.12564	0.00080	172.12510	+0.00054
17-b	172.12509	0.00131	172.12510	-0.00001
14-c	220.12491	0.00051	220.12510	-0.00019

Determination of Relative Migratory Aptitudes for Alkyl Shift in Isoindenes 13 a-d

Quantitative glpc analyses of product mixtures were run on the HP 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 & C were combined as were those of B & D to determine the migratory aptitudes. Table IV details the results.

Table 4. Relative Migratory Aptitudes of R vs Methyl

Run No.	Azoxy Used	Thermolysis Temp. (°C)	Thermolysis Time (hr)	Glpc Column	Glpc Temp. (°C)	Relative Ratio R/Me	Std. Deviation
1	12 a	190°	4.0	A	120°	6.41	0.04
2	12 a	190°	4.0	B	120°	5.92	0.03
3	12 a	200°	3.2	B	120°	6.24	0.06
4	12 b	185°	4.0	A	120°	5.34	0.04
5	12 b	194°	4.5	A	120°	5.26	0.02
6	12 b	190°	3.25	B	120°	5.20	0.08
7	12 c	175°	3.2	A	170°	51.36	0.86
8	12 c	190°	2.8	A	170°	59.61	3.83
9	12 d	180°	3.0	A	160°	7.85	0.08

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 elsewhere¹⁸ 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 PMO 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 was 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 2,3-dimethylindene.

Table 5. Rates of Rearrangement of 2,2-Dimethylisoidene(5) to 2,3-dimethylindene in pentane

Run No.	Temp. (°C)	k x 10 ⁵	Correlation Coefficient
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

$$\text{Log } A = 11.00 \pm 0.65$$

$$EA = 26100 \pm 1100 \text{ cal/mol}$$

$$\text{Correlation Coefficient} = 0.997$$

$$\Delta H^\ddagger = 25,300 \text{ cal/mol at } 365,6^\circ\text{K}$$

$$\Delta S^\ddagger = -10.6$$

$$\Delta G^\ddagger = 29,200 \text{ cal/mol}$$

References and Footnotes

- *. Co-workers are W. R. Dolbier, Jr., K. E. Anapolle, L. McCullagh, J. M. Riemann and D. Rolison. Department of Chemistry, University of Florida.
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