ample, with $PdCl_2(PhCN)_2$, the reaction of **1** and **2a** gave **8**[15] (11.9%) in addition to **3a** (40.0%) by refluxing in benzene for 3 hr. At room temperature, however, the reaction of **1** with **2a** catalyzed by $PdCl_2(PhCN)_2$ gave **3a** (27.5%) and **9**[16] (8.5%) after 3 days. Similarly with $PdCl_2(PhCN)_2$, the reaction of **1** with **2b** gave both **3b** (19.3%) and **10** (14.5%).[17]

We are actively exploring the related reactions and the details will be reported in a forthcoming paper.

Acknowledgment. We thank Toshiba Silicones Co., Ltd., for gifts of chlorosilanes.

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(5) The reaction of disilanes with dienes will be reported separately.
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(7) R. Noyori, T. Suzuki, and H. Takaya, *J. Am. Chem. Soc.*, **93**, 5896 (1971).
(8) All new compounds gave correct elemental analyses. Yields described in this paper are those after isolation with TLC on silica gel.
(9) Compound **3a:** mp 68.0–69.0; M^+ 300 (2) *m/e* 89 (100); NMR δ (CCl_4) 0.30 (12 H, s, Si–CH_3), 1.04 (4 H, t, J = 7 Hz, Si–CH_2–CH_2), 1.91 (2 H, q, J = 7 Hz, $SiCH_2$–CH_2), 3.70 (6 H, s, $COOCH_3$); ir (cm^{-1}) (KBr) 1725, 1715, 1250; λ_{max} (MeOH) 210.0 (10,000) 262.0 (1,500).
(10) Compound **3b:** an oil; n^{23}D 1.5365; M^+ 260 (64.3) *m/e* 135 (100); NMR δ (CCl_4) 0.12 (6 H, s, $SiCH_3$), 0.16 (6 H, s, $SiCH_3$), 0.92 (2 H, t, J = 6 Hz, *Si–CH_2–*), 0.94 (2 H, t, J = 6 Hz, Si–CH_2–), 1.88 (2 H, q, J = 6 Hz, $SiCH_2$–CH_2–), 6.44 (1 H, s, ═—H), 7.10 (5 H, m, Ph); ir (cm^{-1}) (neat) 1250; λ_{max} (*n*-hexane) 211.3 (18,100), 249.0 (10,000).
(11) Compound **3c:** an oil n^{23}D 1.4725; M^+ 184 (15) *m/e* 141 (100); NMR δ (CCl_4) 0.08 (12 H, s, Si–CH_3), 0.80 (4 H, t, J = 7 Hz, Si–CH_2–), 1.80 (2 H, q, J = 7 Hz, $SICH_2$–CH_2–), 6.72 (2 H, s, ═—H); ir (cm^{-1}) (neat) 1255, 690, λ_{max} (*n*-hexane) <210.0.
(12) Compound **5:** mp 640–65.0°; M^+ 288 (4) *m/e* 125 (100); NMR δ (CCl_4) 0.33 (18 H, s, Si–CH_3), 3.69 (6 H, s, $COOCH_3$); ir (cm^{-1}) (KBr) 1720, 1250, 850; λ_{max} (MeOH) 209.0 (10,000) 260.0 (1000).
(13) Y. Nakadaira and H. Sakurai, *J. Organomet. Chem.*, **47**, 61 (1973).
(14) Compound **7:** mp 243.0–244.0°; NMR δ ($CDCl_3$) −0.18 (6 H, s, Si–CH_3), 0.75 (6 H, s Si–CH_3), 3.64 (6 H, s, $COOCH_3$), 7.10 (20 H, M, Ph); ir (cm^{-1}) (KBr) 1720, 1250; λ_{max} (MeOH) 252.0 (23,700).
(15) Compound **8:** mp 146.0–147.0°; M^+ 600 (0.2) *m/e* 89 (100); NMR δ (CCl_4) 0.29 (24 H, s, Si–CH_3), 0.93 (8 H, t, J = 8 Hz, Si–CH_2–), 1.56 (4 H, m, Si–CH_2–CH_2–), 3.70 (12 H, s, $COOCH_3$); ir (cm^{-1}) (KBr) 1710, 1230; λ_{max} (MeOH) <210.0, 260.0 (3000).
(16) Compound **9:** an oil; n^{23}D 1.4850; M^+ 616 (1.5) *m/e* 375 (100); NMR δ (CCl_4) 0.14 (12 H, s, Si–CH_3), 0.27 (12 H, s, Si–CH_3), 0.76 (8 H, m, Si–CH_2–), 1.50 (4 H, m, $SiCH_2$–CH_2–), 3.74 (6 H, s, $COOCH_3$), 3.81 (6 H, s, $COOCH_3$); ir (cm^{-1}) (neat) 1720, 1250, 1050; λ_{max} (MeOH) <210.
(17) Compound **10:** mp 91.5–92.5°; M^+ 362 (19) *m/e* 78 (100); NMR δ (CCl_4) −0.18 (6 H, s, $SiCH_3$), 0.24 (6 H, s, Si–CH_3), 0.72 (2 H, t of d, J = 4 Hz, 15 Hz, Si–CH_2–), 1.20 (2 H, t of d, J = 7 Hz, 15 Hz, Si–CH_2–), 1.88 (2 H, t of t, J = 4, 7 Hz, Si–CH_2–CH_2–), 6.64 (2 H, s, ═—H), 7.28 (10 H, m, Ph); NOE 7% between peaks at δ 6.64 and 0.24; ir (cm^{-1}) (KBr) 1250; λ_{max} (*n*-hexane) 212.0 (26,100), 260.5 (27,700).

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Inversion of Configuration in a Bimolecular Homolytic Substitution at Saturated Carbon

Sir:

Despite the many studies of reactions of both organic and inorganic free radicals with organic compounds, it is only recently that apparent bimolecular homolytic substitution reactions at saturated carbon have been reported[1-3] (eq 1 and 2).

$$\text{MeCo(chelate-1)} + \text{Co(chelate-2)} \rightleftharpoons \text{MeCo(chelate-2)} + \text{Co(chelate-1)} \quad (1)^4$$

$$\text{Cr}^{2+}\text{(aq)} + \text{RCo(dmgH)}_2\text{(aq)} \longrightarrow \text{RCr}^{2+}\text{(aq)} + \text{Co(dmgH)}_2\text{(aq)} \quad (2)^5$$

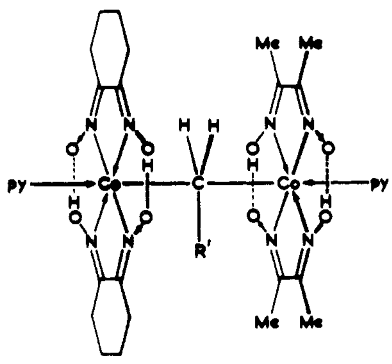


Figure 1. Transition state for bimolecular alkyl transfer reaction.

We now report kinetic and stereochemical studies of one such homolytic substitution (eq 3) which indicate that it involves effectively complete inversion of configuration at the saturated carbon center through a highly restricted transition state. Thus, under anaerobic conditions at 0°, a solution of bis(dimethylglyoximato)pyridinecobalt(II) (I, 10^{-2} *M*) in methanol reacts with an equal concentration of methylbis(cyclohexanedionedioximato)pyridinecobalt(III) (IIa) to give, within a few seconds, a mixture containing the corresponding methylbis(dimethylglyoximato)pyridinecobalt(III) (IIIa) and bis(cyclohexanedionedioximato)pyridinecobalt(II) (IV), such that at equilibrium the concentrations of I-IV are the same (eq 3);[6] i.e., $k_3 = k_{-3}$.

$$\underset{\text{I}}{\text{Co(dmgH)}_2\text{py}} + \underset{\text{II}}{\text{RCo(chgH)}_2\text{py}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{\text{III}}{\text{RCo(dmgH)}_2\text{py}} + \underset{\text{IV}}{\text{Co(chgH)}_2\text{py}} \quad (3)^5$$

IIa, R = Me	IIIa, R = Me
b, R = *n*-Pr	b, R = *n*-Pr
c, R = *n*-Oct	c, R = *n*-Oct
d, R = *threo*-PhCHDCHD	g, R = *t*-BuCHDCHD
e, R = *erythro*-PhCHDCHD	h, R = $CH_2{:}CH(CH_2)_4$
f, R = $PhCH_2CH_2$	i, R = c-$C_5H_9CH_2$
	j, R = c-C_6H_{11}

The rates of exchange of alkyl groups in the corresponding reactions of a series of alkylbis(dioximato)pyridinecobalt(III) complexes were determined[9,10] from the rate of increase of III in the total organocobalt(III) complex (II + III) isolated at intervals prior to the establishment of equilibrium, in the manner well documented for isotopic exchange reactions.[12,13] The observed rate of exchange (*R*) in the case of IIb was shown to be first order in the initial concentrations both of the organocobalt(III) complex (II) and in the inorganic cobalt(II) complex (I),[14] and a second-order rate coefficient k_3 (Table I) for the forward path of reaction 3 was derived from *R*.

The variation of k_3 for several different alkyl substituents, shown in Table I, strongly supports a mechanism involving bimolecular displacement at the saturated α-carbon, though it does not distinguish between retention and inversion of configuration at the carbon center.[15,16] The appreciable steric compression in the transition state is evident from the large characteristic influence of both α- and β-substituents on the rate of the reaction.

That an inversion of configuration is involved (Figure 1) was demonstrated by the formation of a mixture of IId ($J_{1,2}$ = 5.3 Hz)[17] and IIe ($J_{1,2}$ = 12.6 Hz)[17,18] in the reaction of the latter with the cobalt(II) species IV (eq 6). The presence of the single diastereoisomer in the reagent and of the

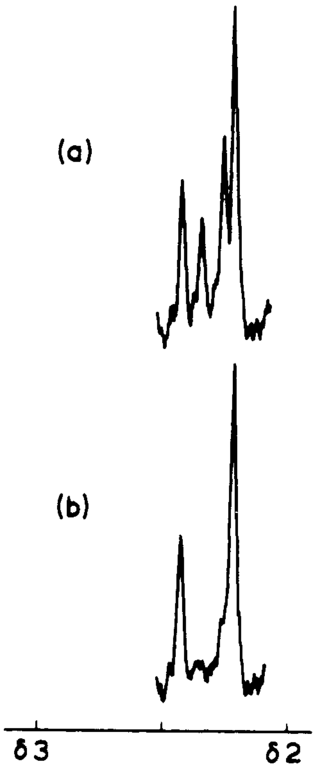
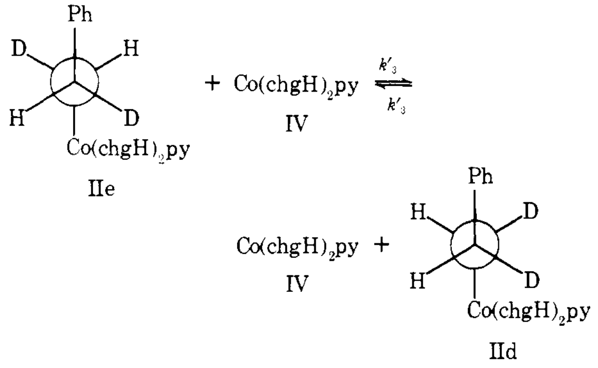


Figure 2. ^{2}H decoupled ^{1}H nmr spectra of (a) IId + IIe, and (b) IIe.

mixture of diastereoisomers in the product mixture is clearly seen in the ^{2}H decoupled ^{1}H nmr spectra (Figure 2).[20]



(6)

As the rate constant (k'_3, Table I) for the formation of the threo from the erythro diastereoisomer in the presence of IV (eq 6) is the same, within experimental error, as that (k_3) for the alkyl transfer between the ^{1}H analog IIf and I (eq 3), it is apparent that each act of exchange involves an inversion of configuration at the carbon center.

Alternative mechanisms involving prior disproportionation of the cobalt(II) into cobalt(III) and cobalt(I) species followed by reaction of the latter with the organocobalt(III) complex II can be ruled out not only because the cobalt(I) species is *less* reactive for alkyl transfer but also because the alkyl transfer between IIc and I takes place only 12 times faster in methanol than in methylene chloride. The latter solvent is known to react readily with such cobalt(I) species. The high rate of reaction in methylene chloride also indicates that prior electron transfer does not take place to a significant extent and that charge separation in the transition state is minimal.

Reaction through free radical intermediates, though unlikely to be stereospecific, can be ruled out because (a) secondary alkyl cobalt(II) complexes react slower than primary complexes and (b) no cyclopentylmethyl- or cyclohexylcobalt(III) complexes (IIIi and IIIj, respectively) can be detected in the hexenylcobalt(III) complex (IIIh) recovered after 10 days at room temperature in the presence of I, during which time a number of complete alkyl exchanges have occurred. Had hexenyl radicals or cations been formed, they would have partially rearranged[22] to cyclopentylmethyl radicals or cyclohexyl cations, respectively, and would have been recaptured to give IIIi and IIIj, respectively.

Table I. Kinetics of Exchange of Alkyl Groups in the Reaction of I and II (eq 3)

R	T, °C	$[\mathrm{I}]_0 = [\mathrm{II}]_0$ (M)	R (mol l.$^{-1}$ sec^{-1})	k_3 (l. mol^{-1} sec^{-1})^a
Me	0	1.97×10^{-3}	1.9×10^{-4}	50
Et	0	4.4×10^{-3}	2.1×10^{-6}	1.1×10^{-1}
n-Oct	0	5.0×10^{-3}	1.69×10^{-7}	6.8×10^{-3}
n-Oct	28	5.0×10^{-3}	3.2×10^{-6}	1.3×10^{-1}
n-Pr	28	6.1×10^{-3}	4.7×10^{-6}	1.2×10^{-1}
i-Pr	28	5.0×10^{-3}	1.5×10^{-7}	5.9×10^{-3}
n-Bu	28	4.1×10^{-3}	1.6×10^{-6}	9.6×10^{-2}
i-Bu	28	4.5×10^{-3}	2.0×10^{-8}	9.8×10^{-4}
$PhCH_2CH_2$	28	4.0×10^{-3}	5.6×10^{-7}	3.5×10^{-2} ^{b}
PhCHDCHD	28	2.2×10^{-3} ^{c}	3.3×10^{-7}	3.7×10^{-2} ^{d}

^{a} Values ±10% except where stated $k_3 = R/[\mathrm{I}]_0[\mathrm{II}]_0$. ^{b} From rate of incorporation of dioximato ligands in II. ^{c} Concentration of alkylcobalt(III) reagent; that of the cobalt(II) reagent was 4×10^{-3} M. ^{d} From rate of conversion of erythro to threo diastereoisomer; i.e., k_3' ± 25% eq 6.

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(3) G. Mestroni, C. Cocevar, and G. Costa, *Gazz. Chim. Ital.*, **103**, 273 (1973).

(4) Chelate-1 and chelate-2 may be a variety[1,3] of dissimilar tetradentate ligands known to be capable of stabilizing carbon–cobalt bonds. Reactions 1 and 2 have also been considered to be inner sphere electron transfer processes *via* a saturated carbon bridge.[2]

(5) dmgH and chgH are the conjugate bases of dimethylglyoxime and cyclohexanedionedioxime, respectively.

(6) In solutions of II and III,[7] and especially in solutions of I and IV,[8] the axial pyridine ligand is partially lost and hence both methanol and pyridine complexes are present. However, these species almost certainly react in a similar manner, possible *via* five-coordinate complexes, and only the absolute values of the rate coefficients in the table are likely to be significantly affected.

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(8) A. Rockenbauer, E. Budo-Zahonyi, and L. I. Simandi, *J. Coord. Chem.*, **2**, 53 (1972).

(9) The proportion of III in the mixture of II and III was determined from comparison of the area of the broad lower field cyclohexanedionedioximato resonance with that of the dimethylglyoximato resonance in the ^{1}H nmr spectrum of the isolated total organocobalt(III) complex after removal of all traces of cobalt(II) species.

(10) Under the conditions used for the measurement of exchange rates for the alkylcobalt(III) complexes, rapid "randomization" of the equatorial ligands takes place between the cobalt(II) complexes I and IV with the formation of the mixed ligand cobalt(II) complex Co(dmgH)(chgH)py, such that some mixed ligand alkylcobalt(III) complex (RCo(dmgH)(chgH)py, V) is present in the isolated mixture containing II and III. However, such randomization, which involves the formation *at equilibrium* of the complexes II, III, and V, in the ratio 1:1:2, respectively, does *not* take place directly between dioximato ligands and the alkylcobalt(III) complexes II and III.[11]

(11) D. Dodd and M. D. Johnson, paper in preparation.

(12) H. A. C. McKay, "Principles of Radiochemistry," Butterworths, London, 1971, p 295.

(13) The McKay equation[12]

$$-R = \ln (1 - \alpha/0.5)[\mathrm{I}]_0[\mathrm{II}]_0/([\mathrm{I}]_0 + [\mathrm{II}]_0)t$$

where α is the fraction of the dimethylglyoximato ligand in the isolated mixture of organocobalt(III) complexes, the subscript zero refers to initial concentrations, t is the time, and R (in mol l.$^{-1}$ sec^{-1}) is the con-

stant rate of exchange of the alkyl group, is equally applicable to reactions of the form shown in eq 3, 4, and 5, provided the dioximato ligands have equal influence on the rate of exchange.[11] The latter proviso is supported by the observed random ratio of organocobalt(III) complexes, II, III, and V in the equilibrium mixture.

$$\mathrm{RCo(dmgH)_2py + Co(dmgH)(chgH)py \rightleftharpoons RCo(dmgH)(chgH)py + Co(dmgH)_2py} \quad (4)$$

$$\mathrm{RCo(chgH)_2py + Co(dmgH)(chgH)py \rightleftharpoons RCo(chgH)(dmgH)py + Co(chgH)_2py} \quad (5)$$

(14) The reverse of reaction 3 and the forward and reverse reactions 4 and 5 must similarly be second order.

(15) G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, **91**, 3341 (1969).

(16) C. K. Ingold, *Quart. Rev., Chem. Soc.*, **11**, 1 (1957).

(17) The resonance of H-2 (δ 2.29) is clearly visible (Figure 2) in CH_2Cl_2, whereas that for H-1 (δ 1.84) is partly obscured by the broad upfield resonance of the cyclohexanedionedioximato ligand.

(18) The corresponding coupling constant observed[19] for IIIg was 13.1–13.2 Hz.

(19) P. L. Bock and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 2826 (1974); H. L. Fritz, J. H. Espenson, D. A. Williams, and G. A. Molander, *ibid.*, **96**, 2378 (1974).

(20) The initial erythro organocobalt complex (IIe eq 6), prepared from *threo*-[1-^{2}H-2-^{2}H]-2-phenylethyl 4-toluenesulfonate, contained less than 10% of the corresponding threo diastereoisomer (IId, eq 6). The observation, in the ^{1}H nmr spectrum of the subsequently formed mixture (Figure 2, spectrum a), of coupling constants ascribed to both threo and erythro diastereoisomers is novel and provides a further example, and additional proof, of the inversion of configuration which occurs when an organocobalt(III) complex is formed from an organic ester and a nucleophilic dioximatocobalt(I) reagent (in this case $Co(chgH)_2py^-$).

(21) D. Dodd, B. L. Lockman, and M. D. Johnson, unpublished observations.

(22) A. J. Beckwith and G. Moad, *J. Chem. Soc., Chem. Commun.*, 472 (1974), and references cited therein.

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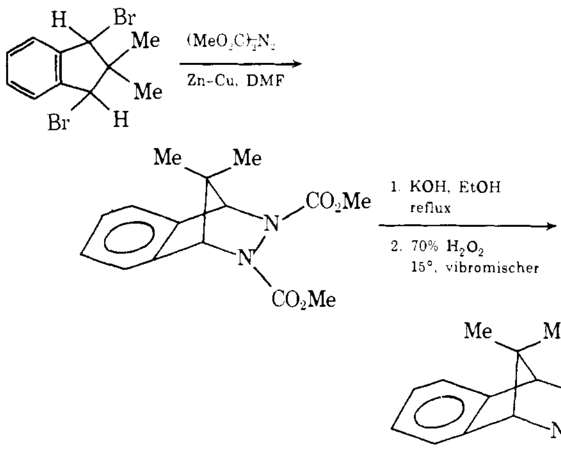
An Intramolecular [1,5]Sigmatropic Alkyl Shift in the Isoindene System

Sir:

Recently, it was demonstrated by Willcott and Rathburn that the thermal [1,5] methyl shift of 1,5,5-trimethylcyclopentadiene was, to a significant extent, an *inter*molecular process.[1] While isomerizations of spirodienes, such as that of the spiro[4,4]nona-1,3-diene system,[2] must undoubtedly proceed intramolecularly, Willcott's results raised the question as to whether any *potentially intermolecular* [1,5] alkyl shift processes are indeed intramolecular. We wish to report at this time the first unambiguous example of such an intramolecular process.

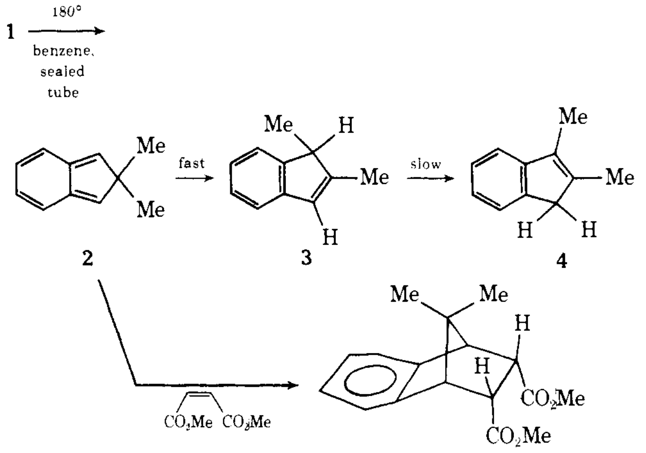
2,2-Dialkyl-substituted 2*H*-indenes seemed to be particularly attractive molecules for use in a systematic study of intramolecular, sigmatropic [1,5] alkyl shifts because: (a) the gain of aromaticity in such rearrangements should induce them to occur with relatively low activation energies, (b) subsequent H-shift processes possibly might be noncompetitive due to the resultant loss of aromaticity, and (c) the nature of the system facilitates identification of the migrating group when two *different* groups are available. The most significant problem in utilizing this system was the devising of a method whereby the isoindene species could be generated under conditions whereby its unimolecular processes might be competitive with its recognized, facile bimolecular processes. This problem was solved by utilizing a smooth, retro[2 + 4] process to generate the isoindene species.

Azoxy species **1** was synthesized from 1,3-dibromo-2,2-dimethylindane[3] by a modification of Snyder's method.[4]



1

A 0.05 *M* solution of **1** in benzene extruded N_2O at 180°, exhibiting therein a half-life of about 40 min.[5] The transient 2,2-dimethyl-2*H*-indene (**2**) thus generated was found to undergo a smooth [1,5] methyl shift to form 1,2-dimethylindene (**3**). **3** was relatively stable, on this time scale, at 180° to subsequent [1,5] hydrogen shifts,[7,8] but, with adequate time or higher temperatures, the thermodynamically more stable 2,3-dimethylindene (**4**) was formed from **3**. After 3 hr at 180°, the ratio of **3**:**4** was 20:1, while after 1.33 hr at 204° this ratio was 2:1. The glpc determined yield (~80%) of the products was found to be insensitive to (a) temperature of reaction (180-204°), (b) concentration (0.02-0.05 *M*), and (c) time of reaction (0.5-3 hr). The latter observation indicated that N_2O extrusion is rate determining, the rate of the sigmatropic process thus not able to be measured directly. Also there is *no* decrease in yield when cumene was utilized as solvent for the reaction, this speaking strongly against a free-radical-chain mechanism being involved in the rearrangement process.



2 3 4

5

Concerted transformation of **1** to **3** was ruled out by the observation that intermediate **2** could be trapped efficiently by various dienophiles under the reaction conditions. For example the presence of an equal molar amount of dimethyl maleate diverted 75% of the reaction to adduct **5**.[9] The observed stereospecificity of this Diels–Alder reaction indicates that **3** is behaving similar to a simple diene in this respect, rather than as a triplet species.

The possibility of a chain process being involved was conclusively ruled out by a crossover experiment. Azoxy species **6**, consisting of a mixture of the 7-position epimers,[10] fragmented to the 2-ethyl-2-methyl-2*H*-indene (**7**) which underwent [1,5]sigmatropic alkyl shift to yield exclusively a