Table III. Reaction of Allyl Organocopper Reagents Derived from $CuCN{\cdot}2LiBr$ with Benzoyl Chloride

entry	allyl chloride[a]	PhCOR[b]	% yield[c]
1	$ClCH_2CH{=}CH_2$	$PhCOCH_2CH{=}CH_2$	65
2	$AcOCH_2CH{=}CH_2$	$PhCOCH_2CH{=}CH_2$	63
3	$ClCH_2C(CH_3){=}CH_2$	$PhCOCH_2C(CH_3){=}CH_2$	75
4	$CH_3CH(Cl)CH{=}CH_2$	$PhCOCH(CH_3)CH{=}CH_2$	72
5	$ClCH_2CH{=}C(CH_3)_2$	$PhCOC(CH_3)_2CH{=}CH_2$	74

[a] To a solution of active copper at −100 °C was added the allyl chloride (0.25 equiv) which was previously cooled to −78 °C in a vial admixed with THF (1 mL). The PhCOCl (3 equiv based on organocopper) was added neat via syringe at −100 °C and allowed to react for 15 min. [b] All products had consistent ^1H, ^{13}C, and ^{13}C DEPT NMR spectra. [c] Isolated yields.

addition was not seen by GC analysis.

The chemistry of allyl organocopper reagents has received renewed interest with Lipshutz's development of higher order (HO) allylic cyanocuprates,[7] which have been shown to be among the most reactive cuprates yet developed. A common route to allylic organocopper reagents is the transmetalation of allylic stannanes with an appropriate organocopper reagent, itself derived from a transmetalation of an organolithium or Grignard reagent. Significantly, the active copper reported in this paper reacts with allylic chlorides and acetates at −100 °C to produce the corresponding allylic organocopper species with less than 10% of the homocoupled diene byproduct.[8] The resulting organocopper reagents were trapped with benzoyl chloride to produce the ketones shown (Table III). Unsymmetrical allyl chlorides presumably yield the primary organocopper reagent upon reaction with active copper. Since the 1,4-conjugate addition of prenylcopper with cyclohexenone proceeded via α attack (Table II, entry 12), reaction of prenylcopper with benzoyl chloride must involve γ attack (Table III, entry 5). This is the first reported formation of an allyl organocopper reagent formed directly from an allyl chloride and acetate.

In summary, a new type of highly reactive zerovalent copper has been produced which reacts readily with functionalized organic halides at low temperature to form the corresponding functionalized organocopper reagents. These organocopper reagents cross-couple with acid chlorides and undergo conjugate addition in high yields to afford highly functionalized ketones. The isolation of these compounds has been greatly simplified since the use of phosphines has been circumvented. Significantly, this active copper allows the direct formation of allylic organocopper species from allyl chlorides and acetates. The nature of these organocopper reagents and additional cross-coupling reactions are currently under investigation.

Acknowledgment. We gratefully acknowledge the financial support provided by the National Institutes of Health (Grant GM 35153).

Registry No. A, 930-68-7; B, 2497-21-4; C, 14371-10-9; CuCN, 544-92-3; LiBr, 7550-35-8; $Br(CH_2)_7CH_3$, 111-83-1; $Br(CH_2)_6Cl$, 6294-17-3; $Br(CH_2)_3CO_2Et$, 2969-81-5; $Br(CH_2)_2CO_2Et$, 539-74-2; $Br(CH_2)_3CN$, 5332-06-9; C_6H_5Br, 108-86-1; *p*-BrC_6H_4CN, 623-00-7; *o*-BrC_6H_4CN, 2042-37-7; *o*-$BrC_6H_4CO_2Et$, 6091-64-1; *p*-BrC_6H_4Cl, 106-39-8; $PhCO(CH_2)_7CH_3$, 6008-36-2; $PhCO(CH_2)_6Cl$, 17734-41-7; $PhCO(CH_2)_3CO_2Et$, 73172-56-2; $PhCO(CH_2)_2CO_2Et$, 6270-17-3; $PhCO(CH_2)_3CN$, 10413-00-0; PhCOPh, 119-61-9; *p*-NcC_6H_4COPh, 1503-49-7; *o*-NcC_6H_4COPh, 3717-78-0; *o*-$EtO_2CC_6H_4COPh$, 604-61-5; *p*-ClC_6H_4COPh, 134-85-0; $Cl(CH_2)_7CH_3$, 111-85-3; BrC_6H_{11}, 108-85-0; $ClCH_2CH{=}C(CH_3)_2$, 503-60-6; $ClCH_2CH{=}CH_2$, 107-05-1; $AcOCH_2CH{=}CH_2$, 591-87-7; $ClCH_2C(CH_3){=}CH_2$, 563-47-3; $CH_3CH(Cl)CH{=}CH_2$, 563-52-0; $PhCOCH_2CH{=}CH_2$, 6249-80-5; $PhCOCH_2C(CH_3){=}CH_2$, 52813-35-1; $PhCOCH(CH_3)CH{=}CH_2$, 50599-02-5; $PhCOC(CH_3)_2CH{=}CH_2$, 62894-04-6; PhCOCl, 98-88-4; naphthalene, 91-20-3; 3-octylcyclohexanone, 57242-85-0; ethyl 4-(cyclohexanon-3-yl)butyrate, 100315-21-7; ethyl 5-methyl-7-oxononanoate, 132514-88-6; ethyl 6-formyl-5-phenylhexanoate, 118744-16-4; 3-(3-cyanopropyl)cyclohexanone, 110718-80-4; 1-cyano-4-methyl-6-oxooctane, 132514-89-7; 3-(6-chlorohexyl)cyclohexanone, 110718-81-5; 3-(cyclohexyl)cyclohexanone, 7122-93-2; 3-phenylcyclohexanone, 20795-53-3; 3-(3-methyl-2-butenyl)cyclohexanone, 29843-83-2.

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Novel Imido– and Phosphorane–Imido–Nickel(II) Complexes. Crystal and Molecular Structure of $(\mu_3\text{-NH})(\mu_3\text{-NPMe}_3)(\text{NiClPMe}_3)_3$

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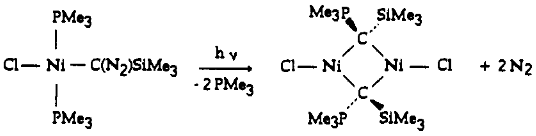
Received December 31, 1990

Up to now, the chemistry of nitrene or imido ligands coordinated to late transition metals (groups 8 to 10) has been little developed whereas numerous complexes of the early transition metals have been reported.[1-3]

We recently described the synthesis of the phosphine ylide bridged complex $[NiCl\{C(PMe_3)(SiMe_3)\}]_2$ by photoactivation of the diazomethyl precursor $(PMe_3)_2ClNi[C(N_2)(SiMe_3)]$[4]



(1)

Diazoalkanes and azido derivatives are isoelectronic, and both react with a wide range of organic substrates in the same way.[5] It was thus of interest to investigate the photoactivation of the isoelectronic azido $(PMe_3)_2ClNi(N_3)$ complex **1**. In contrast to diazo complexes, azido compounds are well-known and several nickel–azido species have been prepared.[6a] However, no description of their photochemical reactivity has been reported.

We observed that the photochemical activation of $(PMe_3)_2ClNi(N_3)$ resulted in the formation of new trimetallic and tetrametallic diamagnetic nickel clusters **2** and **3**, with phosphorane–imido and imido ligands in capping positions (eq 2). This result is interesting because only one trimetallic cluster with Ni–imido bonds, $[Ni_3Cp_3(\mu_3\text{-NR})]$, exists in this class, but as a 49e paramagnetic cluster,[7] and because no phosphorane–imido

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‡ Laboratoire de Chimie Inorganique, Université P. Sabatier.

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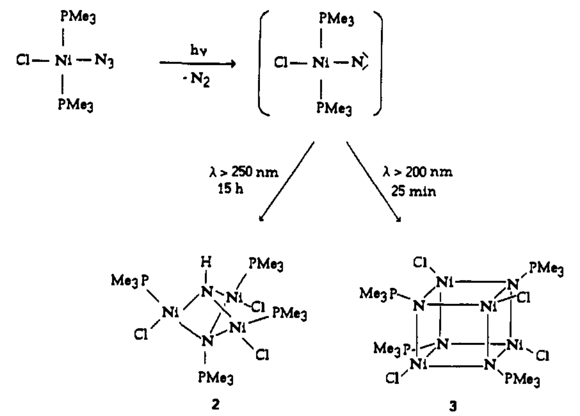


(2)

complex has been reported in the nickel group.

When the azido chloro complex **1**[8] was dissolved in toluene and exposed to UV light, evolution of N_2 was observed. If the reaction was performed in a glass flask, the solution turned dark red and dark-red crystals of **2** precipitated in 31% yield.[9] They were stable in air for brief periods and started decomposing above 225 °C under argon. In solution, **2** rapidly reacted with moist air, giving trimethylphosphine oxide and a dark material containing nickel.

Characterization of **2** was accomplished by X-ray crystallography.[10] The ORTEP drawing with the atomic numbering scheme is displayed in Figure 1. The molecule presents an equatorial plane in which are located the three nickel atoms forming a regular triangle, each bearing a phosphine and a chloride ligand pointing above and below the plane, respectively. Isomers with different orientations of ligands have not been detected. As μ_3 bridging ligands below and above the center of the Ni3 triangle are Me_3PN^- (average Ni–N2 = 195.3 pm; P4–N2 = 160.9(7) pm) and, for reasons of charge and electron count, HN^{2-} (ν(NH) at 2048 cm^{-1}; average Ni–N = 184.4 pm); this trimer is diamagnetic. Formally, it belongs to the 48e-cluster family $[M_3P_3Cl_3(\mu_3\text{-}NPR_3)(\mu_3\text{-}NH)]$, together with $[Co_3Cp_3(\mu_3\text{-}NH)(\mu_3\text{-}CO)]$, $Rh_3Cp_3(\mu_3\text{-}NH)(\mu_3\text{-}CO)$, and $[Ni_3Cp_3(\mu_3NR)]^+$. However, with a 16-electron count for all valence shells of nickel in square-planar coordination, metal–metal bonding need not be invoked although, at an average Ni–Ni distance of 263.9 pm, the interactions could provide additional stabilization of the trimer.[11] These distances are significantly longer than those found in $[Ni_3Cp_3(\mu_3NR)]$: Ni–Ni (2.21, 2.34, and 2.27 Å). The Ni–P and Ni–Cl distances are as usual. Analytical data of the bulk samples were consistent with the structure of **2**.

The phosphorane–imido ligand is able to give two to six electrons to one, two, or three metal centers (Scheme I). End-on coordination occurs with early transition metals, but interestingly, no bridging modes (IV or V) have been observed so far.[6b,12] Consequently, the structure of **2** describes the first example of the triply bridging mode V of the phosphorane–imido ligand, and this is in agreement with the Ni–N bond length which lies in the upper range of the values usually observed. Triply bridging and end-on bonded organoimido ligands, RN^{2-}, on the contrary are well-known with electron-deficient metal centers.[2a,13,14]

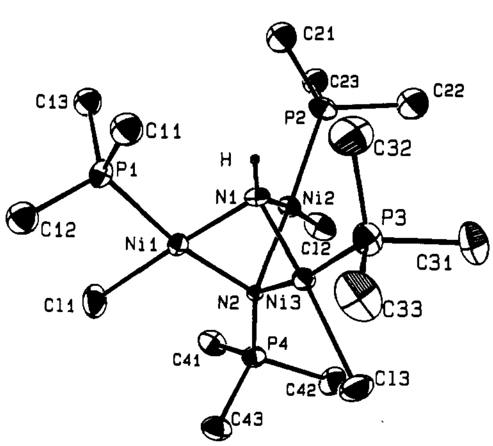
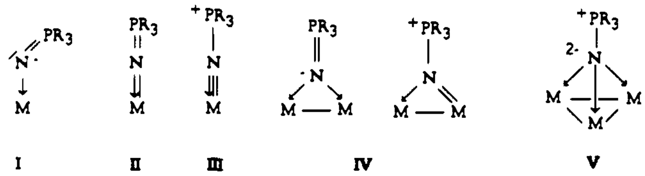
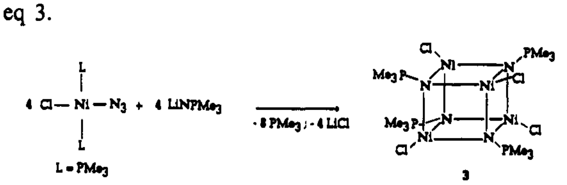


Figure 1. ORTEP view of $(\mu_3\text{-}NH)(\mu_3\text{-}NPMe_3)(NiClPMe_3)_3$. Important bond distances (pm) and angles (deg) are as follows: Ni1–Ni2, 263.1 (1); Ni1–Ni3, 265.4 (1); Ni2–Ni3, 263.3 (1); Ni1–N1, 183.8 (6); Ni2–N1, 184.0 (7); Ni3–N1, 185.5 (6); Ni1–N2, 194.9 (6); Ni2–N2, 195.7 (5); Ni3–N2, 195.8 (6); Ni1–Cl1, 221.6 (2); Ni2–Cl2, 221.5 (3); Ni3–Cl3, 223.9 (2); Ni1–P1, 216.3 (3); Ni2–P2, 216.5 (2); Ni3–P3, 215.5 (3); N1–N2, 226.3 (9); N2–P4, 160.9 (7); Ni1–N1–Ni2, 91.4 (4); Ni1–N1–Ni3, 92.0 (3); Ni2–N1–Ni3, 91.0 (3); Ni1–N2–Ni2, 84.7 (2); Ni1–N2–Ni3, 85.6 (3); Ni2–N2–Ni3, 84.5 (2); P4–N2–Ni1, 128.9 (3); P4–N2–Ni2, 129.7 (4); N1–Ni1–N2, 73.3 (3); N1–Ni1–P1, 95.9 (2); Cl1–Ni1–N2, 101.2 (2); Cl1–Ni1–P1, 89.6 (2).

Scheme I



Upon exposure to shorter wavelength light in a quartz flask, the red color of the toluene solution of **1** became green. The sparingly soluble compound **3** deposited as the final product in about 77% yield.[15] While both transformations in eq 2 are still poorly understood, **3** may be obtained through a more rational and straightforward synthesis using [(trimethylphosphoranylidene)amido]lithium salt[16] in 20% yield according to eq 3.



(3)

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(8) $NiCl_2(PMe_3)_2$ (1.50 g, 5.32 mmol) and 0.35 g (5.32 mmol) of NaN_3 in 60 mL of THF were stirred for 40 h at 20 °C. The volatiles were removed in vacuo, and the residue was extracted with 20 mL of toluene over a sintered glass disk (G3). Condensing 10 mL of pentane upon the red solution kept a 0 °C precipitated violet needles, which were isolated by decantation, washed with refluxing solvent, and dried in vacuo: yield, 1.03 g (3.56 mmol, 67%); decomposition >110 °C; stable in air for 5 min, slightly soluble in pentane, moderately soluble in ether or toluene, freely soluble in THF; ^{1}H NMR (C_6D_6, 298 K, external TMS) δ 0.09 s (PMe_3); IR (Nujol) 2040 cm^{-1} vs ($\nu_{as}(N_3)$). Anal. Calcd for $C_6H_{18}ClN_3NiP_2$ (288.3): C, 24.99; H, 6.29. Found: C, 24.28; H, 6.22.

(9) A typical experiment: A 50-mL glass flask filled with 245 mg (0.85 mmol) of **1** in 30 mL of toluene and sealed under vacuum was placed under a mercury lamp (low pressure, 15 W) for 15 h at a distance of 5 cm. The dark mixture was filtered, and red crystals deposited from the resulting red solution kept at 0 °C: yield, 55 mg (0.09 mmol; 31%); decomposition >225 °C; air sensitive, slightly soluble in toluene or THF, better in CH_2Cl_2. Anal. Calcd for $C_{12}H_{37}Cl_3N_2Ni_3P_4$ (615.8): C, 23.41; H, 6.06; N, 4.55. Found: C, 23.30; H, 6.04; N, 4.10.

(10) Crystal structure data: monoclinic, space group $P2_1/c$, $a = 16.228$ (5) Å, $b = 16.370$ (5) Å, $c = 10.566$ (4) Å, $\beta = 108.18$ (3)°, $V = 2663$ Å^3, $Z = 4$, $d_{calcd} = 1.536$ g cm^{-3}, μ(Mo kα) = 25.27 cm^{-1}, Enraf-Nonius CAD-4 diffractometer, $T = 20 \pm 2$ °C; 6894 reflections measured; 5962 selected with $I < 3\sigma(I)$; $R = 0.0513$; $R_w = 0.0568$. Resolution: SHELX 86 and 76.

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(15) Forty milliliters of a toluene solution of **1** (0.630 g, 2.18 mmol) was poured into a 50-mL quartz ampule and irradiated for 25 min as previously described. A dark green solution was produced with dark microcrystals covering the wall. They were isolated by reducing the volume of the solution to 20 mL in vacuo and then cooling to −30 °C. Washing with ether and drying in vacuo gave dark green crystals: yield, 310 mg (0.42 mmol, 77%); decomposition >240 °C; sensitive to air and moisture, slightly soluble in THF or toluene, better in CH_2Cl_2; ^{1}H NMR (CD_2Cl_2, 298 K, external TMS) δ 1.45 (d, PMe_3, $^2J_{PH} = 13.0$ Hz); ^{31}P NMR (CD_2Cl_2, 298 K, external H_3PO_4) δ 34.54 (s); MS (EI, 70 eV, 373 K), m/z (I_{rel} found/calcd with ^{58}Ni, ^{60}Ni, ^{35}Cl, ^{37}Cl) 732 (22/28), 734 (78/80), 736 (100/100), 738 (86/71), 740 (58/31), 742 (28/9), 744 (6/2). Anal. Calcd for $C_{12}H_{36}Cl_4N_4Ni_4P_4$ (736.9): C, 19.56; H, 4.92; N, 7.60. Found: C, 19.67; H, 5.31; N, 7.46.

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The dark green crystals of 3 were sensitive to moisture but were stable up to 240 °C under argon. Their mass spectrum (EI, 373 K) confirmed the presence of $NPMe_3$ ligands, showing a pattern of peaks consistent with isotope distributions as calculated for tetrameric units and their fragment ions. Therefore μ_3-$NPMe_3$ units and a cubane-type molecular structure with Ni and N atoms in alternating corners are the most likely.

Formation of phosphorane–imido ligand under photochemical conditions suggests the existence of a nitrene intermediate. Such a reaction has been previously proposed to explain the photochemical reactivity of azido complexes.[17,18] Thus the chemistry of this azido Ni complex presents an interesting parallel with the chemistry of the related diazo complex. In both cases, there is formation of an electrophilic species: a carbene or nitrene, which reacts with PMe_3 giving rise to ylide-type adducts.

These results could be indicative of an interesting parallel between the chemistry of this low-valent-metal nitrene and that of the related carbene. Work is now in progress in that direction.

Acknowledgment. H.-F.K. and H.K. thank the Fonds der Chemischen Industrie and Deutscher Akademischer Austauschdienst for financial support. Material support through the Centre National de la Recherche Scientifique and the Université P. Sabatier are also gratefully acknowledged. Special mention is made of the PROCOPE Programm (MAF France and DAAD), which allowed this joint research to be possible.

Supplementary Material Available: Tables 1–4 containing crystal data for $(\mu_3\text{-NH})(\mu_3\text{-NPMe}_3)(\text{NiClPMe}_3)_3$, positional parameters and their estimated standard deviations, bond distances, and bond angles (5 pages); Table 5 containing observed and calculated structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Chiral Pathways in the Thermal Rearrangement of 3,7-Dimethylene-1-ethyltricyclo[4.1.0.0^{2,4}]heptane to 2,5-Dimethylene-3-ethylbicyclo[4.1.0]hept-3-ene. Decyclization of a Pair of 2,2′-Linked Methylenecyclopropanes Avoids a Symmetrical 2,5-Dimethylenecyclohept-3-ene-1,6-diyl Biradical Intermediate

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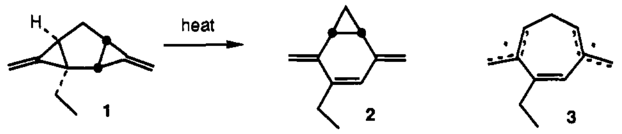
Thermal rearrangement of a 2,2′-linked di(methylenecyclopropyl) to a 1,4-dimethylenecyclohex-2-ene presents subtle problems in the description of the covalency changes. Do the two rings cleave simultaneously or sequentially? Is a disjoint[1] 2,5-dimethylenecyclohept-3-ene-1,6-diyl biradical an intermediate? This paper reports a rare example[2] of this rearrangement and the first examination of the mechanistic questions by the use of a stereochemical probe.

The tricyclic 2,2′-linked di(methylenecyclopropyl) 1 was synthesized in five steps from the known[3] 6-chloro-6-methylbicyclo[3.1.0]hexan-2-one. Heating 1 in the gas phase[4] caused clean rearrangement to 2,5-dimethylene-3-ethylbicyclo[4.1.0]hept-3-ene (2). An Arrhenius treatment of the first-order rate constants (k) determined at seven temperatures spanning the range 132–180 °C gave the equation $\log (k \text{ in s}^{-1}) = (13.9 \pm 0.4) - (35900 \pm 800)/2.3RT$ cal/mol.[5,6]



Plausibly, one might postulate the vinylogous tetramethyleneethane 3 as the key intermediate in the rearrangement. A test for such an achiral species would employ enantiomerically enriched 1[7-9] as the reactant, from which product 2, although chiral, necessarily would be racemic if formed via 3. Reaction mixtures from separate pyrolyses of either enantiomer of 1 (85.6% ee in one enantiomer and 79.3% in the other) were analyzed enantiospecifically on a 50-m 2,3,6-tri-*O*-methyl-β-cyclodextrin (10% in OV-1701) fused silica capillary gas chromatography (GC) column.[10] Recovered from partial conversion, reactant 1 had essentially undiminished ee. Product 2 was *partially* but incompletely racemized. The ee of the product was independent of the duration of pyrolysis but varied monotonically with reaction temperature. Temperatures (and percentage of original reactant ee retained) were as follows: 115.0 °C (54.6%); 140.3 °C (52.4%); 159.7 °C (50.4%); 177.0 °C (48.6%); 195.6 °C (46.0%); 208.0 °C (43.8%). The slope of an Arrhenius plot of the ratio of the rate constants k_1 and k_2 for the competitive formation of the two product enantiomers gives the value of 1120 ± 230 cal/mol for the difference in activation enthalpy between these two processes.

These results rule out any mechanistic pathway passing exclusively through an equilibrated achiral intermediate such as 3. Attempts to gain access to this species by heating product 2 at higher temperatures did result in slow racemization, but the rates were erratic due to surface effects. From these data, a lower limit of 42 kcal/mol may be assigned to $\Delta G^{\ddagger}$ for this reaction.

Bond additivity[11] and strain energy[12] estimates suggest that product 2 is thermodynamically more stable than reactant 1 by ~45 kcal/mol, whereas biradical 3 lies ~33 kcal/mol above 2 but ~12 kcal/mol *below* 1. In view of the behavior of the analogous cases of 6-methylenebicyclo[3.1.0]hex-2-ene pyrolyses (4 → 6),[3] where rearrangement occurs exclusively through a metastable biradical intermediate 5, it is remarkable that the reaction pathway descending from the 1 → 2 transition state avoids the deep energy hole in the region of biradical 3. We suggest that

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[1] Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

[2] (a) We are not aware of previous examples, and no citations of the reaction are given in reference works.[2b,c] (b) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981. (c) Berson, J. A. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Essay 5.

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[4] The kinetic methods and equipment used were similar to those described elsewhere: (a) Getty, S. J.; Berson, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 1652. (b) Getty, S. J.; Berson, J. A. *J. Am. Chem. Soc.*, in press.

[5] Compare the values $\log A = 14.26$, $E_a = 40400$ cal/mol, for 2-methylmethylenecyclopropane: Chesick, J. P. *J. Am. Chem. Soc.* **1963**, *85*, 2720.

[6] Attempts to trap hypothetical intermediates in solution-phase reactions of 1 with neat diethyl fumarate or with maleic anhydride in triglyme were unsuccessful and gave only the rearranged hydrocarbon 2.

[7] Synthesized from enantiomerically enriched 6-chloro-6-methylbicyclo[3.1.0]hexan-2-one, which was resolved by the sulfoximine method of Johnson and Zeller.[8,9] The relative and absolute configurations of reactant 1 and product 2 are as yet unknown but are not necessary for the conclusions of this paper. Reactant 1 was enriched in the GC later emergent enantiomer when prepared from (+) ketone and gave product enriched in the earlier emergent enantiomer of 2.

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[9] See also: Parziale, P. A.; Berson, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 1650.

[10] (a) Preparation based on work of Schurig and Nowotny[10b] and available commercially from Chrompack International BV. (b) Schurig, V.; Nowotny, H.-P. *Angew. Chem.* **1990**, *29*, 939.

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