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(7) The highest observed rotation for 2-pentanol in benzene solvent is 13.7°.[6a] However, a gas chromatographic study has determined that the absolute rotation of 2-pentanol is 18.8°.[8] Optically active 2-methoxypentane (**10**) having $[\alpha]_D$ +9.9° has been estimated[5a] to be 58% optically pure. We have prepared **10** having $[\alpha]_D$ +9.8° from **8** having $[\alpha]_D$ +12.2° which was presumed to be 65% optically pure, in fair agreement with the above value.
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Thermal Rearrangements of 4,5-Diphenyl-2*H*-imidazoles

John H. M. Hill,* Thomas R. Fogg,[1] and Harvey Guttmann

Department of Chemistry, Hobart and William Smith Colleges, Geneva, New York 14456

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Some time ago Weiss reported that 2,2,4,5-tetraphenyl- and 2,2-dibenzyl-4,5-diphenyl-2*H*-imidazoles (**3c, 5a**) thermally rearrange to the corresponding 1*H*-imidazoles with migration of a phenyl or benzyl group, respectively.[2] The apparent similarity of this rearrangement to the [1,5] sigmatropic shifts of geminal dimethylcyclopentadienes,[3] spirodienes,[4] and 2*H*-pyrroles[5] prompted us to investigate this reaction, particularly since Weiss had claimed that 2,2-dimethyl-4,5-diphenyl-2*H*-imidazole (**3a**) did not rearrange thermally and that 2,2-pentamethylene-4,5-diphenyl-2*H*-imidazole (**1c**) decomposed when heated.[6]

The 2*H*-imidazoles were prepared by condensing the appropriate ketone with benzil in refluxing acetic acid[2] or *N,N*-dimethylformamide containing excess ammonium acetate. Cyclobutanone yielded only rearranged product (**2a**) and cycloheptanone and cyclooctanone gave the required product together with large amounts of colored products.

We studied the rearrangement by heating samples of the 2*H*-imidazoles, with or without solvent, under nitrogen in sealed ampoules or NMR tubes in a thermostatted microtube furnace. Rate studies were generally carried out in the melt without solvent and measured by integration of the NMR signals of rearranged product relative to the signals of the aromatic protons or the unrearranged reactant. Under nitrogen the reaction showed first-order kinetics to about 5 half-lives at several temperatures. Failure to purge with nitrogen resulted in side reactions, indicated by darkening of the reaction and appearance of many additional peaks in the NMR spectra. The kinetic and activation data are presented in Table I.

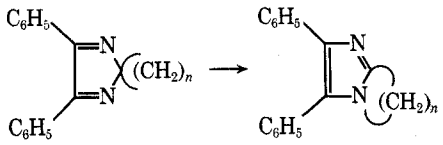
Three mechanisms have been documented for the thermal rearrangements of the analogous carbocyclic geminal dialkylcyclopentadienes and spirodienes. These are (a) a diradical route involving opening of a cycloalkane ring as observed for spiro[2,4]hepta-4,6-diene;[4b,7] (b) a suprafacial and stereospecific [1,5] alkyl shift as reported for *cis*- and *trans*-6,9-dimethylspiro[4,4]nona-1,3-diene;[8] and (c) a radical chain process, observed in geminal dimethyl cyclopentadienes, which competes with b, initiated by dissociation into cyclopentadienyl and methyl radicals.[9] Analogous stepwise and concerted processes are presumably available for 2*H*-imidazoles.

Table I
Kinetic and Activation Data for the Rearrangement of 2*H*-Imidazoles

Compd	Temp, K	k, sec^{-1}	E_a, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol	Rel rate at 550 K
1b	510	1.11×10^{-3}	44.1	+11	1000
	524	3.49×10^{-3}			
	545	1.90×10^{-2}			
1c	573	3.59×10^{-4}	49.4	+9	4
	582	6.68×10^{-4}			
	593	1.72×10^{-3}			
	601	2.70×10^{-3}			
1d	560	3.32×10^{-4}	45.9	+4	8
	573	8.07×10^{-4}			
	587	2.20×10^{-3}			
1e	555	4.50×10^{-3}	41.9	+3	140
	574	1.57×10^{-2}			
1f	564	5.71×10^{-3}	37.6	−5	100
	581	1.53×10^{-2}			
1g	543	1.87×10^{-3}	39.7	−1	120
	560	5.69×10^{-3}			
	576	1.54×10^{-2}			
3a	588	2.20×10^{-4}	40.5	−7	1
	603	6.66×10^{-4}			
3b	560	9.81×10^{-4}	41.2	−2	25
	573	2.40×10^{-3}			
	583	4.42×10^{-3}			
5a	498	9.33×10^{-5}	39.8	0	175
	513	2.79×10^{-4}			
	528	9.17×10^{-4}			
	543	2.58×10^{-3}			
5b	545	1.52×10^{-3}			
5c	543	6.24×10^{-3}			
5d	543	3.29×10^{-2}			
5e	543	5.92×10^{-4}			

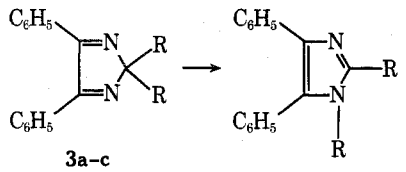
An approximate E_a for the stepwise processes of 67 kcal/mol is obtained, assuming that dissociation is rate determining, by subtracting the gain in stabilization energy in forming the delocalized imidazolyl radical (13 kcal/mol)[10] from the C–C bond dissociation energy (80 kcal/mol).[11a] Heterolytic dissociation would yield a higher value. This result is higher than the experimentally determined values for the 2*H*-imidazoles, which suggests that stepwise processes are not involved in the thermal rearrangements of these compounds. Nonetheless, significant differences in reaction rates (interpolated or extrapolated to 550 K) and activation parameters were observed as a possible consequence of ring strain differences in the polymethylene rings, delocalization and substituent effects in the migrating groups, and medium effects.

The inability of **1a** to withstand the conditions of synthesis and its consequent rearrangement to **2a** may be the result of the 27 kcal/mol strain energy of the cyclobutane ring.[12] Similarly **1b** rearranges 250 times faster than **1c** because of the 6.5 kcal/mol strain in cyclopentane compared with cyclohexane. The carbocyclic analogs show a similar effect: spiro[4,4]nona-1,3-diene rearranges 1000 times faster than spiro[4,5]deca-1,3-diene.[4c] On the other hand, the increased rearrangement rate of **1d–g** parallels the strain in the medium-sized rings. Although the strain in medium rings is generally greater than cyclopentane, the tenfold greater rate of **1b** compared to **1d–g** may be a consequence of differences in conformational rigidity in the transition states.



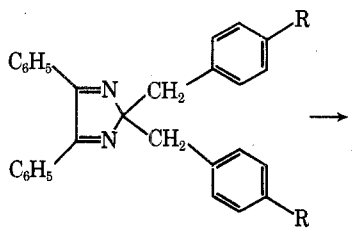
1a-g 2a-g

a, $n = 3$; b, $n = 4$; c, $n = 5$; d, $n = 6$; e, $n = 7$; f, $n = 9$; g, $n = 11$

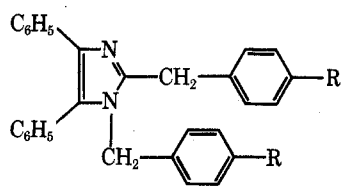


3a-c 4a-c

a, R = CH_3; b, R = C_2H_5; c, R = C_6H_5



5a-e



6a-e

a, R = H; b, R = Cl; c, R = CH_3; d, R = OCH_3; e, R = NO_2

The approximate limiting activation energy can be modified to reflect the ring strain in the reactants, but even this correction results in values of E_a higher than the experimental values. Thus increased ground-state energy due to ring strain does not result in intervention of a stepwise mechanism.

As concerted reactions are synchronous only if bond breaking and making occur at the same rate,[13] departures from synchronous reaction are to be anticipated if the reactants and products have different strain energies. The extent of this departure is difficult to determine in the absence of reliable methods for determining approximate activation energies for synchronous reactions of this kind. One approach has been to equate the extent of strain in the transition state with half of the difference in strain between the reactant and product.[4c] Results of this procedure are equivocal but application of this idea to the present work reveals a parallel between strain differences[14] and the values of $\Delta S^{\ddagger}$. As low values of $\Delta S^{\ddagger}$ are indicative of concerted processes and as strain differences between cycloalkanes and the next larger cycloalkenes decrease with increasing ring size,[12] a shift towards more synchronous reactions occurs as ring size increases.

The rearrangement of **3a** to **4a** and **3b** to **4b**, where considerations of ring strain do not apply, are about 100 times and 5 times slower than, for example, **1g** to **2g**. These differences in rate may be the consequence of anchoring the migrating terminus by the flexible polymethylene chain. Similar differences in migratory aptitudes of methyl and ethyl groups have been observed recently in the case of 2,2-dialkyl-2*H*-indene rearrangements.[15]

We find that the rearrangement of 2*H*-imidazoles is rather insensitive to solvent, so measuring the reaction rates in the melt appears to be a valid procedure. The rearrangement of **1b** and **5a** in a variety of solvents of differing polarity and dielectric constant was carried out and the results are in Table II. In addition the clean first-order kinetics observed while the composition of the melt is changing during a reaction is consistent with a minimal medium effect.

Table II
Effect of Solvent on Rearrangement Rate

Solvent	k_1, sec^{-1} at 470 K: 1b → 2b	5a → 6a
Melt	5.12×10^{-5}	1.50×10^{-5}
Diphenyl ether	4.46×10^{-5}	8.9×10^{-6} [b]
Triphenylmethane		1.4×10^{-5} (8.8×10^{-5})[a]
Benzyl alcohol	8.5×10^{-5} [b]	3.2×10^{-5} [b]
Nitrobenzene	1.37×10^{-4}	5.8×10^{-5} [b]
1,3,5-Trichlorobenzene		4.9×10^{-5}

[a] At 498 K. [b] Followed to about 1 half-life.

We carried out a Hammett $\sigma^{+}\rho$ investigation of the rearrangement of **5a–e** to **6a–e** at 543 K. The ρ value was −1.15, though the linear correlation was not particularly good ($r = 0.92$) with marked upward curvature. The small value of ρ obtained here when compared with the large values found for reactions known to involve benzylic carbonium ions[16] argues, at least for this series of compounds, for a concerted mechanism, though the negative slope implies some charge development.

These results do not totally rule out a stepwise mechanism involving radicals, though the greater rate of rearrangement of **5a** compared to, for example, **3a** does not appear to be a consequence of dissociation into resonance-stabilized benzylic and imidazolyl radicals (the benzylic resonance energy is 13 kcal/mol[11b]), as the E_a values are quite similar for these compounds. We have carried out both trapping and crossover experiments to expose the intervention of radicals. Reactions of **3b** and **5a** run in triphenylmethane (molar ratio 1:2) to about 3 half-lives at 560 K failed to reveal any 2-methyl-4,5-diphenylimidazole in the former and any toluene in the latter case. Crossovers between **3a** and **3b** and between **3b** and **5a** were attempted. The disparity in reaction rates was compensated for by

Table III
2*H*-Imidazoles[e]

Compd	% yield	Mp, °C	NMR,[f] δ
1b	73	105–108	2.11 (8 H, s)
1c	66	107–108[a]	1.78 (10 H, s)
1d	60	141–143	1.92 (12 H, s)
1e	38	136–138	1.94 (14 H, s)
1f	48	146–148	1.73 (18 H, s)
1g	80	143–144	1.60 (22 H, s)
3a	75	78–79[b]	1.62 (6 H, s)
3b	50	105–106	0.81 (6 H, t), 2.20 (4 H, q)
5a	60	88–89[c]	2.88 (4 H, s)
5b	80	126–128	2.87 (4 H, s)
5c	40[d]	109–110	2.30 (6 H, s), 2.85 (4 H, s)
5d	30[d]	127–128	2.84 (4 H, s), 3.76 (6 H, s)
5e	40	151–152	2.96 (4 H, s)

[a] Reference 2, 107–108°. [b] Reference 2, 78–79°. [c] Reference 2, 88–89°. [d] *N,N*-Dimethylformamide as reaction solvent. [e] Satisfactory analytical data (±0.3% for C, H, N) were obtained for all compounds in table except **1c**, **3a**, and **5a**, which were not new. Ed. [f] Aryl proton signals omitted.

Table IV
1*H*-Imidazoles[d]

Compd	Mp, °C	NMR, δ[f]
2a	154–155	2.58 (2 H, m), 2.92 (2 H, m), 3.87 (2 H, t)
2b	137–138	1.87 (4 H, m), 2.76 (2 H, m), 3.62 (2 H, m)
2c	138–140[a]	1.81 (6 H, m), 2.80 (2 H, m), 3.56 (2 H, m)
2d	146–148	1.80 (8 H, m), 2.80 (2 H, m), 3.58 (2 H, m)
2e	140–143	1.68 (10 H, m), 2.76 (2H, m), 3.65 (2 H, m)
2f	146–147	1.46 (14 H, m), 2.74 (2 H, m), 3.68 (2 H, m)
2g	146–148	1.37 (18 H, m), 2.68 (2 H, t), 3.72 (2 H, t)
4a	121–122[b]	2.38 (3 H, s), 3.32 (3 H, s), 7.30 (10 H, m)
4b	126–128	1.09 (3 H, t), 1.41 (3 H, t), 2.52 (2 H, q), 3.70 (2 H, q)
6a	147–148[c]	3.88 (2 H, s), 4.46 (2 H, s)
6b	131–134	3.87 (2 H, s), 4.50 (2 H, s)
6c	117–119	2.31 (6 H, s), 3.80 (2 H, s), 4.40 (2 H, s)
6d	131–133	3.72 (2 H, s), 3.81 (6 H, s), 4.38 (2 H, s)
6e	159–161	4.06 (2 H, s), 4.68 (2 H, s)

[a] 138–140°. [b] 121–122°. P. Beak and J. L. Meisels, *J. Am. Chem. Soc.*, **89**, 2375 (1967). [c] 147–148°, ref 2. [d] Satisfactory analytical values were reported for all compounds in table except **2c**, **4a**, and **6d**, which were not new. Ed. [e] Aryl proton signals omitted.

using a reactant ratio favoring the less reactive component. Inside the limits of the analytical methods no crossover was detected. Trapping of radicals, however, has not been realized in those cases where their intervention has been proved in similar rearrangements.[3,9]

We conclude that thermal rearrangement of 2*H*-imidazoles is concerted but not necessarily synchronous.

Experimental Section

General. NMR spectra were obtained on Varian T-60 or Jeol Minimar 100 spectrometers in carbon tetrachloride or deuteriochloroform with tetramethylsilane as internal standard. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. GLC was done with an Aerograph 600C with flame ionization and mass spectra were obtained on a Varian EM-600 with direct inlet.

Reactants. These were prepared as described by Weiss.[2] A molar ratio of benzil, ketone, and ammonium acetate of 1:1:10 in glacial acetic acid (2.5 *M* in ammonium acetate) gave optimum yields. Products were purified by recrystallization from aqueous methanol or benzene–petroleum naphtha. Colored by-products occurred in all preparations. For **1d** and **1e** these constituted a significant portion of the crude reaction product. Table III contains data for the 2*H*-imidazoles.

Products. Samples of the appropriate 2*H*-imidazoles (0.5–1.0 g) were heated in nitrogen-purged, evacuated ampoules for about 30–90 min at about 550 K followed by recrystallization from aqueous methanol. The products were isolated in 70–80% yield. Data for the 1*H*-imidazoles are in Table IV.

Kinetic Procedure. Approximately 50 mg of the 2*H*-imidazole was placed in each of six NMR tubes which were purged with nitrogen and capped. The tubes were inserted in a multiposition thermostatted microtube furnace to within 0.5 cm of the cap. Tubes were withdrawn at noted times and quenched in ice water and the contents were dissolved in a suitable solvent. NMR spectra were recorded and the integrals of the signals were carefully and reproducibly determined. Reactions in solution were carried out in nitrogen-purged, evacuated ampoules at about 1 *M* concentration. The contents of the ampoules were diluted with deuteriochloroform and the NMR spectra were recorded as previously.

Calculations. The first-order rate constants were determined from plots of $\log a/(a-x)$ vs. time, where x is the normalized integral of the downfield protons on the methylene groups at positions 1 and 2 ($>NCH_2-$ and $=CCH_2$) in the product and a is 4 (6 in the case of **3a**), the number of protons on the methylene groups at position 2 [$>C(CH_2)_2$] of the reactant. The phenyl protons served as an internal standard of ten protons. Alternatively for **3a** and **5a–e**, a was the integral of the total aliphatic protons and x was the integral of those due to the product, occurring at lower field. All runs were replicated and the rate constants showed a precision of ±3%. E_a and $\Delta S^{\ddagger}$ were determined as described by Bunnett[17] and were judged to be within ±0.5 kcal/mol and ±2 cal/deg mol, respectively.

Trapping and Crossover Experiments. Mixtures of **3b** or **5a** in triphenylmethane (molar ratio 1:2) were heated in evacuated ampoules at 560 K for about 3 half-lives (10–30 min). For **3b** the contents were examined by TLC (SiO_2 or Al_2O_3 with benzene, methylene chloride, or ethyl acetate elution). Only **3b**, **4b**, and triphenylmethane were detected; no 2-ethyl-4,5-diphenylimidazole was found. An independent test showed that it could have been detected if present in <5% concentration. For **5a** examination of the contents of the ampoule by GLC (6 ft × 0.125 in., 5% XF-1150 on Gaskrom Q at 125°) or MS failed to reveal any toluene.

Mixtures of **3a** and **3b** (molar ratio 5:1) and **3b** and **5a** (molar ratio 4:1) were ground in a mortar and loaded into ampoules which were purged with nitrogen, evacuated, and sealed. After heating at about 590 K for 30–90 min the contents of the ampoules were examined by TLC (SiO_2 with elution by benzene or methylene chloride). Only reactants and expected products were detected in each case. Independent tests showed that the crossover products, 1-methyl-2-ethyl-4,5-diphenylimidazole and 1-ethyl-2-benzyl-4,5-diphenylimidazole, were separable from the other products and could be detected if present in < 5% concentration.

Registry No.—**1b**, 55682-24-1; **1c**, 5396-98-5; **1d**, 55682-25-2; **1e**, 55682-26-3; **1f**, 55682-27-4; **1g**, 55682-28-5; **2a**, 55682-29-6; **2b**, 55682-30-9; **2c**, 16340-54-8; **2d**, 55682-31-0; **2e**, 55682-32-1; **2f**, 55682-33-2; **2g**, 55682-34-3; **3a**, 31839-62-0; **3b**, 55682-35-4; **4a**, 16340-59-3; **4b**, 55682-36-5; **5a**, 55682-37-6; **5b**, 55682-38-7; **5c**, 55682-39-8; **5d**, 55682-40-1; **5e**, 55682-41-2; **6a**, 55682-42-3; **6b**, 55682-43-4; **6c**, 55682-44-5; **6d**, 55682-45-6; **6e**, 55682-46-7.

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(12) Data for ring strain is from P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970), and E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, p 180.

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On the Regioselectivity of Lewis Acid Catalyzed Diels–Alder Reactions of Methylcyclopentadiene[1]

Harlan L. Goering* and Chiu-Shan Chang

Department of Chemistry, University of Wisconsin Madison, Wisconsin 53706

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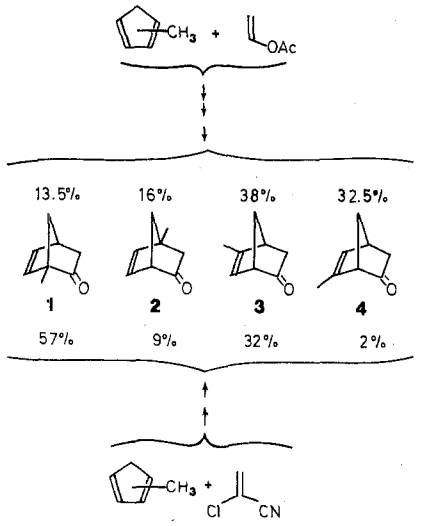
In connection with our investigation of bicyclic systems, 1-methyl-5-norbornen-2-one (**1**) was of interest as a precursor for 1,2-dimethyl-5-norbornen-2-yl derivatives. This compound had been obtained earlier, together with 4- (**2**), 5- (**3**), and 6-methyl-5-norbornen-2-one (**4**), by the Diels–Alder reaction of methylcyclopentadiene and vinyl acetate at 180° followed by a two-step conversion of the adduct to the ketone mixture (lithium aluminum hydride reduction followed by oxidation).[2] However, as shown by the upper part of Chart I, the desired isomer is the minor component of the mixture and thus this did not appear to be a suitable approach for preparing large amounts of **1**. From the **1:2** and **3:4** ratios it is clear that very little regioselectivity is observed for the uncatalyzed Diels–Alder addition of 1- and 2-methylcyclopentadiene.

Chart I



The equilibrium composition of the three isomeric methylcyclopentadienes is 45% 1-methyl-, 54% 2-methyl-, and 1% 5-methylcyclopentadiene.[3] The formation of over twice as much **3** + **4** as **1** + **2** shows that there is considerable isomerization of 1-methyl- to 2-methylcyclopentadiene which leads to unwanted isomers.

From various reports in the literature [4–6] it appeared that regioselectivity as well as rate should be increased by Lewis acid catalysts, and we now report that this is indeed the case. As shown by the lower part of Chart I, the cupric fluoroborate[7] catalyzed Diels–Alder reaction of the equilibrium mixture of the isomeric methylcyclopentadienes and α-chloroacrylonitrile in benzene at 0–5°, followed by hydrolysis, gives a mixture containing 57% of the desired ketone (**1**) together with 9% **2**, 32% **3**, and 2% **4**. Only trace amounts of unidentified contaminants were detected by GC. Satisfactory yields of pure **1** could be obtained by careful fractionation.

Comparison of the **1:2** and **3:4** ratios for the catalyzed and uncatalyzed reactions shows that cupric fluoroborate causes a remarkable increase in regioselectivity as well as in rate. Similar results have been reported for other dienes and the earlier interpretations[4,6] appear adequate for the present case.

It is noteworthy that the (**1** + **2**):(**3** + **4**) ratios show that 2-methylcyclopentadiene is more reactive than the 1-methyl isomer for the high-temperature uncatalyzed reaction whereas the reverse is true for the catalyzed reaction. Also, the amount of **1** + **2** obtained from the catalyzed reaction, relative to the amount of the 1-methyl isomer in the diene, suggests that there is isomerization of 2-methylcyclopentadiene to the 1-methyl isomer under the conditions of the catalyzed Diels–Alder reaction.

Experimental Section

1-Methyl-5-norbornen-2-one (1). Monomeric methylcyclopentadiene was prepared just before use by distillation of methylcyclopentadiene dimer. In a typical experiment a solution of 40 g (0.50 mol) of methylcyclopentadiene, 175 g (2 mol) of α-chloroacrylonitrile, and 75 ml of benzene[8] was cooled to 0–5° and 35.6 g (0.15 mol) of dry cupric fluoroborate was added slowly. The reaction mixture was stirred for 4 hr at 0–5°, after which brine containing sodium potassium tartrate was added. The resulting mixture was extracted with ether. After concentration of the ether extract under reduced pressure 500 ml of dimethyl sulfoxide was added to the residual oil. A hot solution of 1.25 mol of potassium hydroxide in 50 ml of water was added to the dimethyl sulfoxide solution and the resulting mixture was stirred at room temperature for 10 hr, after which the mixture was washed with water and extracted with ether. The ether extract was dried ($MgSO_4$) and the ether was removed under reduced pressure. Capillary GC (SE-30, 100 ft, 80°) showed that the residual oil consisted of **1**, 4- (**2**), 5- (**3**), and 6-methyl-5-norbornen-2-one (**4**) in a ratio of 57:9:32:2. Only trace amounts of unidentified contaminants were present. Distillation of the crude product, 46–53° (10 mm), gave 50 g (82%) of a colorless mixture of the four products. All ketones were isolated in pure form by preparative GC (10% Carbowax, 10 ft, 80°) and identified by the NMR spectra, which corresponded in detail to the NMR data reported earlier.[2b] The desired ketone (**1**) is the most volatile isomer and can be separated and purified by fractionation with a spinning band column, bp 46–47° (10 mm), NMR (CCl_4) δ 6.46 (q, 1 H), 5.72 (d, 1 H), 3.05 (s, 1 H), 1.68–2.24 (m, 4 H), 1.2 (s, 3 H).

Registry No.—**1**, 19740-13-7; **2**, 22405-38-5; **3**, 22405-40-9; **4**, 19740-15-9; methylcyclopentadiene, 26519-91-5; α-chloroacrylonitrile, 920-37-6.

References and Notes

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