Acylation of Alkenes Generated in Situ by Hydride Transfer from Isoalkanes. Synthesis of Pentalenones, Hydrindenones, and Cyclopentenones[1]

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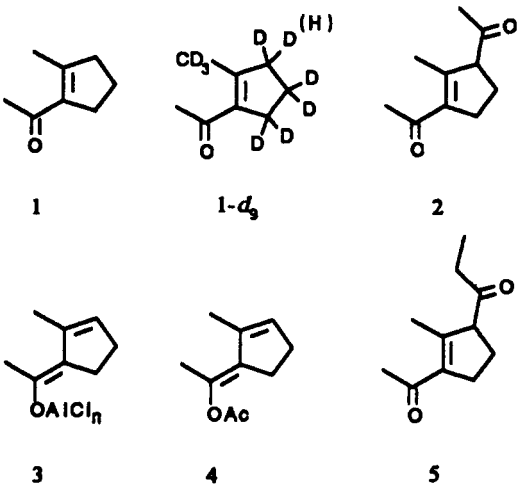
Abstract: Acylation, in the presence of $AlCl_3$ and hydride acceptor, of methylcyclopentane, methylcyclohexane, and 2-methylbutane by ethylenic acyl chlorides, in CH_2Cl_2 solution, respectively, leads to tetrahydropentalenones, tetrahydroindenones, and cyclopentenones in good yields. Hydride acceptor may be either acetyl chloride or the alkenoyl chloride itself. Better results are performed in the presence of nitromethane and $CuSO_4$. Overall yields are better than those obtained by the two-step process involving acylation of alkenes by alkenoyl chlorides and subsequent Nazarov cyclization of the resulting divinylketones. Methyl 1,4-migration is observed during the acylation of 2-methylbutane by sorboyl chloride. The mechanism of these conversions is discussed on the basis of results observed with cyclohexane-d_{12} and methylbutane-d_6 as well as stereochemical studies of the cyclization process.

Progress in modern organic synthesis currently requires the development of more economical methods. A crowning stage in this area is the functionalization of saturated hydrocarbons. A promising approach has been the selective substitution of unactivated tertiary hydrogens by hydride transfer.[2,3]

Acylation[4] and diacylation of alkanes,[5] involving hydride transfer[4b] to the acylating agent,[6] give either saturated or unsaturated ketones.[4] From cyclohexane in moist CH_2Cl_2, 1-acetyl-2-methylcyclopentene (**1**)[7,8] and 1,3-diacetyl-2-methylcyclopentene (**2**)[7b] are obtained, as a result of the rearrangement of the cyclohexyl cation.[9]

We have now shown that the use of inexpensive methylcyclopentane in CH_2Cl_2 leads in a very clean conversion to **1** and **2** in which 65–70% of the methylcyclopentane has been functionalized. The ratio of **1** to **2** depends on the proportions of acetyl chloride and $AlCl_3$.



1 **1-d_9** **2**

3 **4** **5**

Indeed, **2** is obtained only from the acylation of methylcyclopentene generated in situ from methylcyclopentane or cyclohexane; direct acylation of **1** leads to heavy products in which the proportion of **2** is very low. Consequently, we suggest that **2** comes from acylation of an intermediate on the way to the monoacylation product, such as the nonconjugated ketone 3-acetyl-2-methylcyclopentene[10] or enolate **3**. An acylation experiment with cyclohexane-d_{12} leads to **1**-d_9. The presence of about 33% hydrogen at the 3-position of **1**-d_9 could result from a protonation of dienolate **3** during hydrolysis.[11,12] Furthermore, the *O*-dienol-acetate **4** can react with either titanium tetrachloride or aluminum trichloride, leading quantitatively to diketone **2**. This reaction has an intermolecular character, since in the presence of propionyl chloride, the crossed product **5** is the main one.[7b] Therefore, dissociation of **4** with formation of aluminum enolate **3** and acetyl chloride can be assumed, followed by acylation of **3** at the γ-

(1) Preliminary aspects of this work were presented at the NATO Conference on *Selectivities in Lewis Acid-promoted Reactions*; Athens, Greece, October 2-7, 1988.

(2) (a) Nenitzescu, C. D.; Balaban, A. T. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience: New York, 1964; Vol. 3, Part 2, p 1033. (b) Nenitzescu, C. D. In *Carbonium Ions*; Olah, G. A., Schleyer, P. von R., Eds.; Wiley-Interscience: New York, 1970; p 463. (c) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985. (d) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; J. Wiley: New York, 1987.

(3) For leading recent references concerning the hydride-transfer reaction in solution, see: (a) Kramer, G. M. *Tetrahedron* **1986**, *42*, 1071. (b) Kramer, G. M.; McVicker, G. B. *Acc. Chem. Res.* **1986**, *19*, 78. (c) Farooq, O.; Marcelli, M.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1988**, *110*, 864. (d) Olah, G. A.; Prakash, G. K. S.; Fessner, W.-D.; Kobayashi, T.; Paquette, L. A. *J. Am. Chem. Soc.* **1988**, *110*, 8599. (e) Olah, G. A.; Farooq, O.; Wang, Q.; Wu, A. *J. Org. Chem.* **1990**, *55*, 1224. (f) Bagno, A.; Bukala, J.; Olah, G. A. *J. Org. Chem.* **1990**, *55*, 4284. (g) Culmann, J. C.; Sommer, J. *J. Am. Chem. Soc.* **1990**, *112*, 4057. For a discussion on the transition state, see: Karabatsos, G. J.; Tornaritis, M. *Tetrahedron Lett.* **1989**, *30*, 5733 and references therein.

(4) (a) Nenitzescu, C. D.; Ionescu, C. N. *Ann. Chem.* **1931**, *491*, 189. (b) Nenitzescu, C. D.; Cantuniari, I. P. *Ann. Chem.* **1934**, *510*, 269.

(5) Arnaud, M.; Pedra, A.; Roussel, C.; Metzger, J. *J. Org. Chem.* **1979**, *44*, 2972.

(6) Studies by ^{27}Al NMR have shown that the association of $AlCl_3$ with acetyl chloride in CH_2Cl_2 solution gives only the donor–acceptor complex and not an ion pair including acylium ion; see: Wilinski, J.; Kurland, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 2233.

(7) (a) Tabushi, I.; Fujita, K.; Oda, R. *Tetrahedron Lett.* **1968**, 4247. (b) Pardo, R.; Santelli, M. *Tetrahedron Lett.* **1981**, *22*, 3542. (c) Hardling, K. E.; Clement, K. S.; Gilbert, J. C.; Wiechman, R. *J. Org. Chem.* **1984**, *49*, 2049. (d) Ha, H.-J.; Park, K.-P. *Bull. Korean Chem. Soc.* **1988**, *9*, 411.

(8) Acetylation of excess cyclohexane in the presence of $AlCl_3$ results in the formation of 1-acetyl-2-methylcyclopentane as the main product; see: Vol'pin, M.; Akhrem, I.; Orlinkov, A. *New J. Chem.* **1989**, *13*, 771.

(9) 1-Methyl-1-cyclopentyl cation was generated in superacid medium from cyclohexyl- or cyclopentyl-type precursors, see: (a) Olah, G. A. *Top. Curr. Chem.* **1979**, *80*, 19. (b) Vancik, H.; Sunko, D. E. *J. Am. Chem. Soc.* **1989**, *111*, 3742. This tertiary cation shows high stability in strong acid solutions, although both carbon and hydrogen scrambling occurs; see ref 2c, p 84.

(10) Praill, P. F. G.; Whitear, A. L. *J. Chem. Soc.* **1961**, 3573.

(11) Three mechanisms have been invoked to account for the acylation of olefins. Electrophilic attack: (a) Beak, P.; Berger, K. R. *J. Am. Chem. Soc.* **1980**, *102*, 3848. (b) Song, Z.; Beak, P. *J. Am. Chem. Soc.* **1990**, *112*, 8126. Cyclic transfer of the γ-hydrogen to oxygen: Groves, J. K. *Chem. Soc. Rev.* **1972**, *1*, 73. Heteroene reaction: Hoffmann, H. M. R.; Tsuhima, T. *J. Am. Chem. Soc.* **1977**, *99*, 6008.

(12) Diacetylation of 1-methyl-1-cyclohexene by Ac_2O–$ZnCl_2$ occurs via acylation of the dienolate of 2-methyl-1-acetyl-1-cyclohexene; see: Dubois, M.; Cazaux, M. *Bull. Soc. Chim. Fr.* **1975**, 274. Diacetylation of acyclic alkenes leads to pyrylium salts; see: Balaban, A. T.; Schroth, W.; Fischer, G. In *Advances in Heterocyclic Chemistry*; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1969; Vol. 10, p 241.

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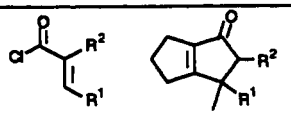
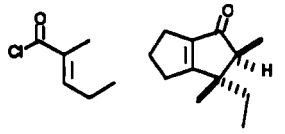
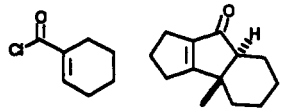
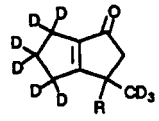
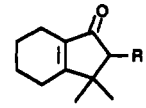
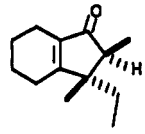
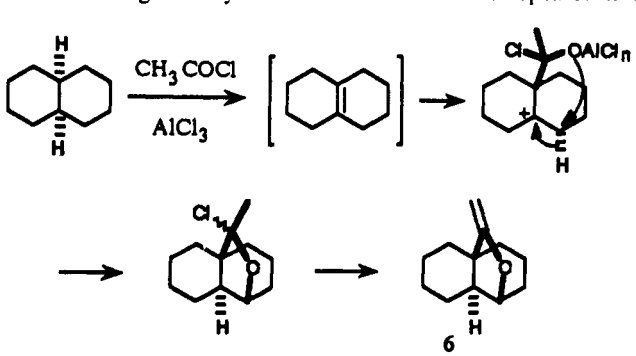
Table I. Preparation of Pentalenones and Hexahydroindenones

entry	alkane	acyl chloride	product	yield (%)	bp (°C/Torr)	ref
						
1	a	7a: R^1 = Me; R^2 = H	8a	60	55/0.4	16
2	a	7b: R^1 = n-Pr; R^2 = H	8b	60	63/0.4	-
3	a	7c: R^1 = R^2 = Me	8c	60	-	-
						
4	a	7d	8d	60	-	-
						
5	a	7e	8e	25	-	-
						
6	b	7a	8a-d_9: R = Me	45	-	-
7	b	7b	8b-d_9: R = n-Pr	40	-	-
						
8	c	7a	11a: R = H	60	-	17
9	c	7c	11c: R = Me	60	-	-
						
10	c	7c	11d	60	-	-

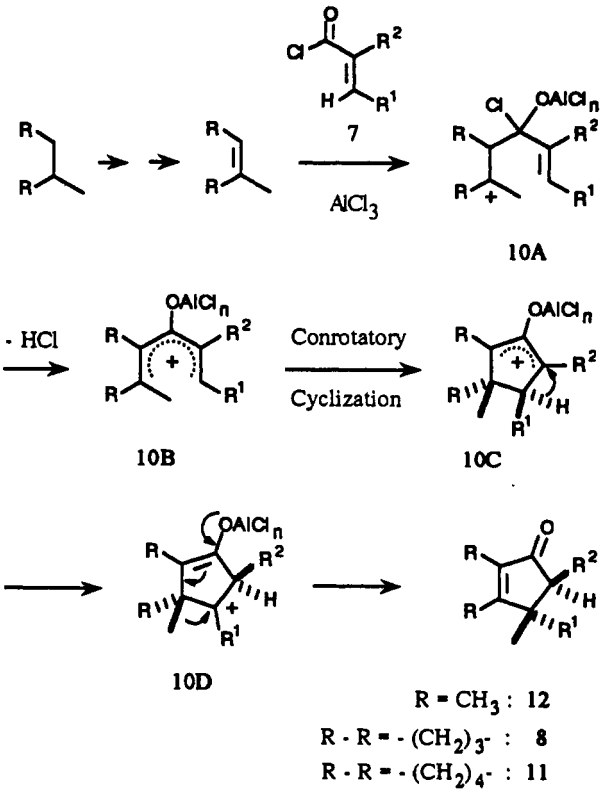
[a] Methylcyclopentane. [b] Cyclohexane-d_{12}. [c] Methylcyclohexane.

position.[13] Hydrogen chloride elimination can occur during acylation; for instance, Baddeley observed the formation of vinyl ether **6** during the acylation of decalin.[14] We repeated this



experiment and observed that only *cis*-decalin is acetylated, the trans isomer being recovered unchanged.[15] Acylation of octahydronaphthalene leads to the first intermediate that undergoes an axial hydride shift followed by cyclization and hydrochloric acid elimination. Although the precise reaction mechanism for the formation of **2** is not fully understood, we feel that the assumption of enolate **3** as an intermediate may account for the above-mentioned features.

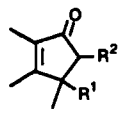
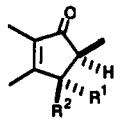
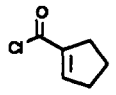
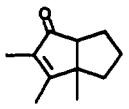
Scheme I. Synthesis of Pentalenones, Hydroindenones, and Cyclopentenones



In an attempt to expand the scope of the acylation reaction to the preparation of dienones, the reaction of alkenoyl chlorides **7** with methylcyclopentane was examined. Experiments in which the alkenoyl chloride was simply substituted for acetyl chloride were unsuccessful, apparently because of the poor hydride acceptor characteristics of these conjugated acyl halides. However, the slow addition of acetyl chloride to a solution of methylcyclopentane, alkenoyl chloride **7**, and $AlCl_3$ in CH_2Cl_2 promoted reaction. Under these conditions, the major product is a pentalenone with general structure **8** accompanied by a small amount (ca. 10–15%) of **1**. Several acyl halides (**7a–e**) were converted to the corresponding bicyclic ketones (**8a–e**) as summarized in Table I. The indicated yields are quite good considering the complexity of the overall conversion and prior experience with the preparation of similar compounds by related processes.[19] Pentalenones **8** were also obtained in a very clean reaction when anhydrous $CuSO_4$ and nitromethane were added in the reaction mixture instead of acetyl chloride.[20] Corresponding ethylenic

(13) The mechanism of acetyl group migration seems to be analogous to that of the Fries reactions; see: Martin, R. *Bull. Soc. Chim. Fr.* **1974**, 983.
(14) Baddeley, G.; Heaton, B. G.; Rasburn, J. W. *J. Chem. Soc.* **1960**, 4713.
(15) The alkylation of benzene also occurs selectively with *cis*-decalin; see: Ndandji, C.; Tsuchiya-Aikawa, L.; Gallo, R.; Metzger, J. *Nouv. J. Chim.* **1982**, *6*, 137.
(16) (a) Schostarez, H.; Paquette, L. A. *Tetrahedron* **1981**, *37*, 4431. (b) Oppolzer, W.; Battig, K. *Helv. Chim. Acta* **1981**, *64*, 2489. (c) Goure, W. F.; Wright, M. E.; Davies, P. D.; Labadie, S. S.; Stille, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 6417.
(17) (a) Ito, M.; Kodama, A.; Tsukida, K. *Chem. Pharm. Bull.* **1980**, *28*, 679; **1982**, *30*, 1194. (b) Kienzle, F.; Minder, R. E. *Chimia* **1985**, *39*, 100.
(18) Hart, H.; Huang, I.; Lavrik, P. *J. Org. Chem.* **1974**, *39*, 999.
(19) Pentalenone **8a** has been used in syntheses of propellane sesquiterpenes; see: (a) Schostarez, H.; Paquette, L. A. *J. Am. Chem. Soc.* **1981**, *103*, 722. (b) Tobe, Y.; Yamashita, S.; Yamashita, T.; Kakiuchi, K.; Odaira, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1259. (c) Mash, E. A.; Math, S. K.; Flann, C. J. *Tetrahedron* **1989**, *45*, 4945.

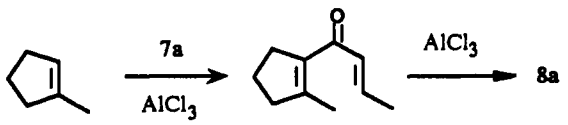
Table II. Preparation of Cyclopentenones and Pentalenone from 2-Methylbutane

entry	acyl chloride	product	yield (%)	bp (°C/Torr)	ref
					
11	7a	12a : R^1 = Me ; R^2=H	60	103/30	-
12	7b	12b : R^1 = n-Pr ; R^2= H	60	-	-
13	7c	12c : R^1 = R^2 = Me	60	-	18
					
14	7d	12d(S*,S*) : R^1= Et; R^2 = Me	47	-	-
14	7d	12d(S*,R*) : R^1= Me; R^2 = Et	14	-	-
					
15	7f	12f	25	-	-

aldehydes resulting from the reduction of acyl chlorides were obtained in low yield (ca. 20%), but no products resulting from the reduction of nitromethane were found.

This transformation is thought to proceed by acylation of methylcyclopentene generated in situ, followed by Nazarov conrotatory cyclization of the divinyl ketone intermediate as indicated in Scheme I.[21] With cyclic precursors, subsequent hydride shift in one face and methyl migration in the other face lead to the observed products **8** and **11** (vide infra).

Supporting evidence for this mechanism is provided by the preparation of **9** from 1-methylcyclopentene and crotyl chloride (**7a**) (65% yield) and its subsequent conversion to **8a** in moderate yield (40%) upon treatment with $AlCl_3$. The overall yield of this two-step synthesis is low compared with the hydride-transfer process starting from methylcyclopentane. The regulated, in situ



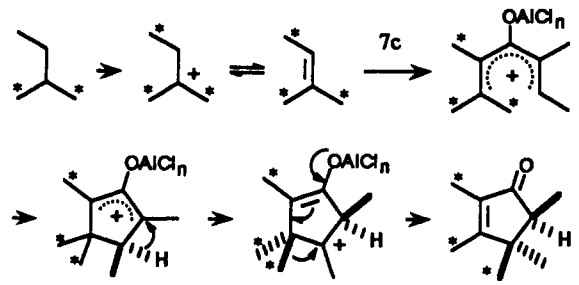
9

formation of 1-methylcyclopentene provides for a more efficient transformation by avoiding competing oligocondensation of the olefin. Moreover, Nazarov cyclization appears to take place more readily by way of the intermediate complex of the divinyl ketone and $AlCl_n$ **10B** when generated in situ from the first intermediate of the acylation reaction[11a] **10A** rather than by direct formation from $AlCl_3$ and ketone. Known Lewis acid mediated Nazarov cyclization of cross-conjugated dienones, even with formation of quaternary centers, occurs without methyl migration.[22]

The use of cyclohexane-d_{12} instead of methylcyclopentane gave **8a**-d_9 from **7a** (45% yield). The positions of the deuterium labels, especially the labeled methyl group, are consistent with the transformation of 1-methylcyclopentene-d_{10} (formed in situ from cyclohexane-d_{12}) into the indicated **8a**-d_9. A similar conversion of **7b** to **8b**-d_9 has also been demonstrated, albeit in low yield (Table I, entries 6 and 7).

Similar conversions were found with methylcyclohexane as a source of in situ 1-methylcyclohexene and several alkenoyl halides **7**.[23] In this case, the hexahydroindenones **11a,c,d** were formed in acceptable yields as shown in Table I. No additional acetyl chloride was needed, but a slight excess of **7** (1.5 equiv) was used. Thus, methylcyclohexane appears to be a better hydride donor than methylcyclopentane. Again, a clean reaction occurred with 1 equiv of **7** in the presence of nitromethane and anhydrous $CuSO_4$.

The use of 2-methylbutane as the hydrocarbon component permitted the synthesis of simple cyclopentenones **12a–d** in comparable yields (Table II). With a view to probing the methyl migration, 1,1,1,3,3,3-hexadeuterio-2-ethylpropane (2-methylbutane-d_6) was acylated with **7c** to give **12c**-d_6 in which the



• = Trideuteromethyl **12c**-d_6

trideuteriomethyl groups were located on the C_2-, C_3-, and C_4-carbon atoms of the cyclopentenone. Integration of the ^1H NMR spectrum indicated a relative intensity of ca. 1 proton for each of these methyl groups. Furthermore, low-intensity signals for these methyl groups were observed in the ^{13}C NMR spectrum.[24] A rapid rearrangement that interchanges the three methyl groups of the *tert*-amyl cation before the acylation process can explain the presence of label at the C_2-position,[25] and the previously described hydride and methide shifts during the cyclization account for the presence of the trideuteriomethyl group at the C_4 cis position.

Information concerning the stereochemistry of the overall transformation is provided by the structure of products **8d** and **11d**, which have the two methyl substituents cis to each other (*S**,*S** isomers). These assignments are based on ^1H and ^{13}C NMR chemical shift data and NOESY experiments on the single diastereoisomer observed (Tables III–V). This stereochemistry is explained by the expected conrotatory mode for the Nazarov cyclization,[26] which gives an intermediate allyl cation (**10C**) with cis methyl and R^1 (ethyl) substituents (Scheme I). This ensures the stereochemistry of the final product pentalenone **8d** or hydrindenone **11d** derived from the ensuing hydride and methyl migrations. A remarkable feature of these acylation reactions

(20) Mixtures of $AlCl_3$ and cupric sulfate are known to be active for the isomerization of paraffins at room temperature; see ref 2c, p 56 and Ono, Y.; Yamaguchi, K.; Kitajima, N. *J. Catal.* **1980**, *64*, 13.

(21) For a review on the Nazarov cyclization, see: Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429.

(22) (a) See ref 21. (b) Ramaiah, M. *Synthesis* **1984**, 529. (c) Harding, K. E.; Clement, K. S. *J. Org. Chem.* **1984**, *49*, 3870. For an example of methyl migration during a protic catalyzed Nazarov cyclization, see: Ohloff, G.; Schulte-Elte, K. H.; Demole, E. *Helv. Chim. Acta* **1971**, *54*, 2913.

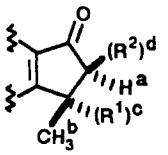
(23) Tertiary cycloalkyl cations frequently undergo ring expansion or contraction; see: Kirchen, R. P.; Sorensen, T. S.; Wagstaff, K. E. *J. Am. Chem. Soc.* **1978**, *100*, 5134. Nevertheless, the methylcyclohexyl cation is stable; see: Kirchen, R. P.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7811.

(24) It is well-known that the effect of the replacement of hydrogen by deuterium on the proton noise-decoupled ^{13}C NMR spectrum is to reduce the intensity of the signal due to the carbon bearing the deuterium; for examples, see: Brownstein, S.; Burton, G. W.; Hughes, L.; Ingold, K. U. *J. Org. Chem.* **1989**, *54*, 560.

(25) The 2-methyl-2-butyl cation shows degenerate properties with interchange of the two types of methyl group protons, not affecting the methylene group. For a review, see: Ahlberg, P.; Jonsäll, G.; Engdahl, C. *Adv. Phys. Org. Chem.* **1988**, *19*, 223.

(26) (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie-Academic Press: Weinheim, 1970; p 58. (b) Denmark, S. E.; Wallace, M. A.; Walker, C. B., Jr. *J. Org. Chem.* **1990**, *55*, 5543.

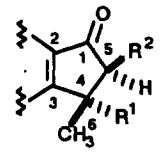
Table III. ^{1}H NMR Spectra Data[a] of Cyclopentenones **8**, **11**, and **12**



compd	δ,[b] [multiplicities][c] (J, Hz)[d]				
	H_a	H_b	H_c	H_d	miscellaneous
8a	2.59 [s]	1.22 [s]	1.22 [s] (3 H)	2.59 [s] (1 H)	2.47 (2 H, m), 2.38 (4 H, m)
8b	2.67 [$^1/_2$ AB] (18)	1.20 [s]		2.44 [$^1/_2$ AB] (18) (1 H)	2.40 (6 H, m), 1.6–1.0 (4 H, m), 0.91 (3 H, t, 7.4)
8c	2.45 [q] (7.6)	1.04 [s]	1.18 [s] (3 H)	1.10 [d] (7.6) (3 H)	2.45 (2 H, m), 2.36 (4 H, m)
8d	2.54 [q] (7.6)	1.02 [s]	0.84 [t] (7.5) (3 H)	1.09 [d] (7.6) (3 H)	2.37 (6 H, m), 1.51 (2 H, m)
8e	2.28 [m]	1.22 [s]	1.28 [m] (2 H)	1.36 [m] (2 H)	2.36 (5 H, m), 2.00 (1 H, m), 1.64 (2 H, m), 1.36 (2 H, m)
11a	2.23 [s]	1.15 [s]	1.15 [s] (3 H)	2.23 [s] (1 H)	2.25–1.46 (8 H, m)
11c	2.27 [m]	1.15 [s]	0.99 [s] (3 H)	1.07 [d] (7.5) (3 H)	2.25 (1 H, m), 2.11 (3 H, m), 1.67 (4 H, m)
11d	2.22 [q] (7.5)	0.99 [s]	0.78 [t] (3 H)	1.07 [d] (7.5) (3 H)	2.16 (4 H, m), 1.68 (4 H, m), 1.46 (2 H, m)
12a	2.33 [s]	1.20 [s]	1.20 [s] (3 H)	2.33 [s] (1 H)	2.03 (3 H, s), 1.72 (3 H, s)
12b	2.36 [$^1/_2$ AB] (18.5)	1.16 [s]		2.09 [$^1/_2$ AB] (18.5) (1 H)	1.90 (3 H, s), 1.67 (3 H, s), 1.40 (2 H, m); 1.0–0.8 (2 H, m), 0.88 (3 H, t, 6.2)
12c	2.11 [q] (7.5)	0.98 [s]	1.16 [s] (3 H)	1.07 [d] (7.5) (3 H)	1.85 (3 H, s), 1.67 (3 H, s)
12d (*S*,S**)	2.20 [q] (7.4)	0.98 [s]	1.54 [m] (2 H)	1.06 [d] (7.4) (3 H)	1.90 (3 H, s), 1.68 (3 H, s), 0.77 (3 H, t, 7.4)
12d (*R*,S**)[e]	2.05 [q] (7.4)	1.16 [s]	1.47 [m] (2 H)	1.09 [d] (7.4) (3 H)	1.90 (3 H, s), 1.71 (3 H, s), 0.46 (3 H, t, 7.4)
12f	2.65 (m)	1.27 [s]			2.3 (2 H, m), 2.0–1.1 (4 H, m), 1.98 (3 H, s), 1.70 (3 H, s)

[a] $CDCl_3$. [b] Chemical shifts relative to TMS (δ 0.00). [c] Multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [d] Coupling constants in hertz. [e] Hb and Hc are permuted.

Table IV. ^{13}C NMR Spectral Data[a] for Cyclopentenones **8**, **11**, and **12**



compd	C(1) (s)	C(2) (s)	C(3) (s)	C(4) (s)	C(5)	C(6) (q)	miscellaneous
8a	202.2	146.3	194.2	37.8	56.6 (t)	26.7	27.7 (t), 27.6 (t), 26.7 (q), 24.7 (t)
8b	202.7	147.1	193.7	41.5	53.8 (t)	25.4	41.4 (t), 28.2 (t), 27.6 (t), 24.6 (t), 18.4 (t), 14.6 (q)
8c	204.8	144.8	192.4	40.8	58.1 (d)	22.9	27.7 (t), 27.2 (t), 26.2 (q), 24.9 (t), 10.6 (q)
8d	205.5	145.7	192.2	44.5	54.3 (d)	20.8	31.7 (t), 28.3 (t), 27.2 (t), 24.7 (t), 11.4 (q), 9.1 (q)
8e	204.9	145.4	193.1	40.8	59.1 (d)	23.9	33.9 (t), 27.8 (t), 27.2 (t), 24.8 (t), 21.8 (t), 20.5 (t), 19.4 (t)
11a	207.4	136.4	180.2	40.6	51.2 (t)	26.8	26.8 (q), 22.8 (t), 22.3 (t), 21.6 (t), 19.9 (t)
11c	209.5	135.1	178.5	43.7	52.5 (d)	23.1	26.1 (q), 22.9 (t), 22.4 (t), 21.8 (t), 19.9 (t), 10.2 (q)
11d	210.7	137.4	178.7	47.1	48.0 (d)	21.3	31.2 (t), 23.3 (t), 22.4 (t), 21.8 (t), 20.0 (t), 11.3 (q), 8.9 (q)
12a	208.0	134.6	177.0	41.2	50.5 (t)	26.8	50.5 (t), 26.8 (q), 11.8 (q), 8.1 (q)
12b	208.2	135.7	176.0	44.6	47.3 (t)	25.8	41.0 (t), 18.1 (t), 14.6 (q), 12.0 (q), 8.0 (q)
12c	210.3	133.2	175.2	44.4	51.7 (d)	23.1	26.1 (q), 11.9 (q), 10.3 (q), 8.2 (q)
12d (*S*,S**)	210.8	134.4	174.7	47.9	47.1 (d)	21.4	31.0 (t), 12.1 (q), 11.4 (q), 8.8 (q), 8.1 (q)
12d (*S*,R**)[b]	209.6	135.1	171.6	48.0	51.5 (d)	25.0	28.6 (t), 12.08 (q), 10.2 (q), 9.1 (q), 8.0 (q)
12f	211.4	136.2	174.7	53.2	57.5 (d)	24.5	36.1 (t), 29.6 (t), 25.0 (t), 12.5 (q), 8.2 (q)

[a] δ, ppm, $CDCl_3$. Multiplicities: s, singlet; d, doublet; t, triplet; q, quartet. [b] CH_3 and R^1 are permuted.

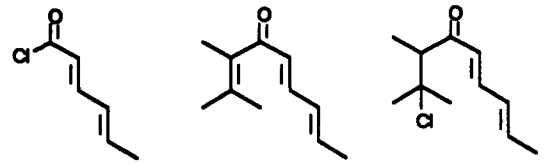
Table V. Physical Data of Cyclopentenones **8**, **11**, and **12**

compd	IR (neat) (cm^{-1})	mass (*m/z*)	formula	HRMS calcd	HRMS found
8a-d_9	2220, 2150, 1705, 1640	159 (34), 158 (32), 143 (63), 141 (100)	$C_{10}H_5D_9O$	159.1609	159.1614
8b	1695, 1635	178 (22), 163 (22), 135 (100)	$C_{12}H_{18}O$	178.1357	178.1355
8b-d_9	2220, 1700, 1640	186 (10), 185 (10), 145 (72), 144 (100)	$C_{12}H_{10}D_8O$	187.1923	187.1922
8c	1690, 1640	164 (32), 149 (100), 136 (9), 121 (17)	$C_{11}H_{16}O$	164.1201	164.1202
8d	1690, 1640	178 (27), 163 (30), 149 (100)	$C_{12}H_{18}O$	178.1357	178.1368
8e	1700, 1635	190 (30), 175 (100)	$C_{13}H_{18}O$	190.1357	190.1368
11c	1700, 1650	178 (20), 163 (100), 137 (20), 135 (20)	$C_{12}H_{18}O$	178.1357	178.1351
11d	1700, 1645	192 (27), 163 (90), 135 (100)	$C_{13}H_{20}O$	192.1514	192.1510
12a	1705, 1650	138 (47), 123 (100)	$C_9H_{14}O$	138.1044	138.1049
12b	1700, 1645	166 (16), 123 (100)	$C_{11}H_{18}O$	166.1357	166.1346
12c	1705, 1650	152 (29), 137 (100), 109 (44)	$C_{10}H_{16}O$	152.1201	152.1215
12d	1705, 1655	166 (39), 137 (97), 109 (100), 67 (35)	$C_{11}H_{18}O$	166.1357	166.1363
12f	1700, 1650	164 (100), 149 (82), 136 (69), 121 (81)	$C_{11}H_{16}O$	164.1201	164.1194

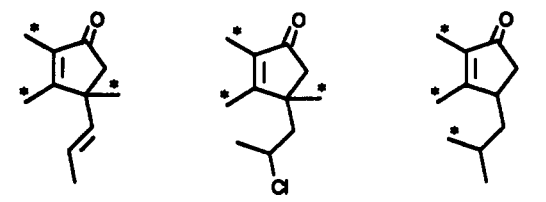
was the complete absence of epimerization of the ketones **8d** and **11d** in the reaction medium. The same result was observed during the formation of the tricyclic ketone **8e** (6/5 trans junction). In contrast, the formation of a mixture of cyclopentenones **12d** (4*S**,5*S** isomer/4*R**,5*S** isomer = 3/1) could result in epimerization of the methyl α to the carbonyl or/and nonconcerted

hydride and methyl migrations.

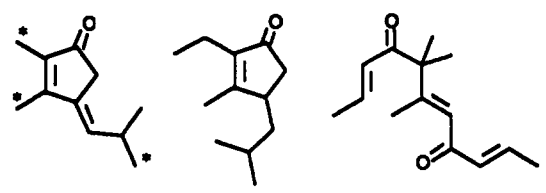
Condensation of sorboyl chloride (**13**) with isoalkanes was a complex reaction. Because of the intriguing nature of the condensation with 2-methylbutane, we first studied the reaction with 2-methyl-2-butene. The products were depending on the reaction temperature. Thus, at −80 °C, the main products were ketones



13 **14** **15**



16 **17a,b** **18**



19 **20** **21**

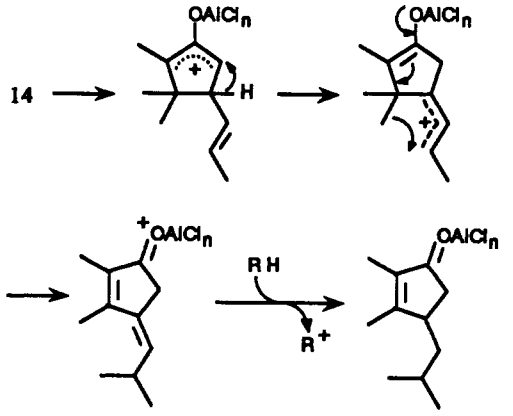
* = Trideuteromethyl

14 (ca. 10% yield) and **15** (ca. 20% yield), but when the reaction mixture was refluxed, cyclopentenones **16** (ca. 6% yield) and **17a,b** (two diastereoisomers) (ca. 20% yield) were isolated. The conversion observed upon heating could be rationalized by conjugate addition of hydrochloric acid to trienone **14** and then cyclization according to Scheme I. Confirmation of the methyl shift was possible by the use of 1,1,1-trideuterio-2-(trideuteriomethyl)-2-butene (2-methyl-2-butene-d_6). The labeled methyl groups were located at the C_2-, C_3-, and C_4-carbon atoms of the cyclopentenone moiety as expected.

Acylation of 2-methylbutane also depends on the reaction conditions. At 0 °C (or better, by addition of nitromethane), cyclopentenone **17a,b** was the main product (42% yield). In contrast, at room temperature cyclopentenone **18** was isolated in 50% yield. To understand the formation of **18**, 2-methylbutane-d_6 was used, giving **18**-d_6 in which the trideuteriomethyl groups were located on C_2- and C_3-carbon atoms of the cyclopentenone moiety and on the isobutyl chain (as determined by ^1H, ^2H, and ^{13}C NMR). Integration indicated a slightly higher intensity of the deuterium label at the C_2-carbon atom (area ratio 1.1:1:1). As in the above experiments, a rearrangement interchanging the three methyl groups of the *tert*-amyl cation before the acylation process might account for the label at the C_2-position. The pathway indicated in Scheme II involves Nazarov cyclization and hydride shift leading to an allylic cation, and then a 1,4-shift of methyl takes place. From the dienone **19**, an intermolecular hydride transfer with 2-methylbutane generated the isobutyl chain of **18** with formation of the *tert*-amyl cation, the precursor of 2-methyl-2-butene. Thus, the entire process constituted a cycle. Formation of dienone **19** when the reaction is performed with a deficiency of isoalkane (0.66 equiv) confirms this process.

However, the apparent methyl 1,4-shift was a puzzling fact. A variety of known reactions show this apparent methyl 1,4-migration, but it is not known whether or not any of these are

Scheme II. Formation of **18** by Acylation of 2-Methylbutane with Sorboyl Chloride



sigmatropic 1,4-shifts[27] or proceed by a series of 1,2-migrations or more complex process. For example, the extensive deuterium scrambling in the 1-*tert*-butyl-1,3,3-trimethylallyl cation has been accounted for by a cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement.[28] However, the exchange of the C_1-methyl group with one of the methyls in the *tert*-butyl group could arise from direct methyl 1,4-shift with inversion.[26a,29] Formation of **19** could simply be described as resulting from a direct methyl 1,4-migration, favored by the stabilization of the charge in the rearranged ketone.

The reaction mixtures resulting from the acylation of isohexanes (2-methylpentane, 3-methylpentane, or 2,3-dimethylbutane) by sorboyl chloride yielded two cyclopentenones (**18** (major product) and **20**). Better yields were obtained with 2,3-dimethylbutane. The interconversion of tertiary hexyl cations in superacid media is a well-known process,[30] facilitated by the presumably low reactivity of sorboyl chloride. Consequently, the corresponding isohexenes were obtained, and the formation of a single cyclopentenone with 12 carbon atoms (**20**) resulted from the faster acylation reaction with 2-methyl-2-pentene. The striking presence of **18**, which corresponds to the acylation of 2-methyl-2-butene, can be rationalized by a combination of oligomerization, isomerization, and cracking, leading to 2-methyl-2-butene and 2-methyl-2-pentene,[31] which are acylated faster than the other alkenes. Thus, the low reactivity of sorboyl chloride along with its sensitivity to steric hindrance accounts for the kinetic separation

(27) (a) See ref 26a, p 128. (b) Epiotis, N. D. *J. Am. Chem. Soc.* **1973**, *95*, 1206.

(28) (a) Poulter, C. D.; Winstein, S. *J. Am. Chem. Soc.* **1969**, *91*, 3649, 3650. (b) Sorensen, T. S.; Ranganayakulu, K. *Tetrahedron Lett.* **1970**, 659. (c) Poulter, C. D.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2297. In the same way, the chain elongation observed by treatment in acidic medium of 2,3-dimethyl-4-penten-2-ol could result from a methyl 1,4-migration; see: Deno, N. C.; Lastomirsky, R. R. *J. Org. Chem.* **1975**, *40*, 514.

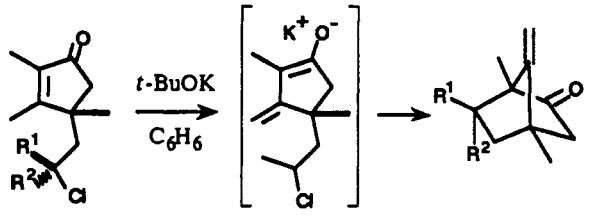
(29) Methyl 1,4-migrations have been invoked in Fischer indole cylizations; see: (a) Miller, B.; Matjeka, E. R. *J. Am. Chem. Soc.* **1980**, *102*, 4772. In rearrangement of 10,10-dibenzyl-9-anthranols, see: (b) Beckwith, A. L. J.; Renfrow, W. B.; Teubner, J. K. *Tetrahedron Lett.* **1968**, 3468. (c) Miller, B.; Saidi, M. R. *J. Am. Chem. Soc.* **1976**, *98*, 2227. (d) Miller, B.; Lin, W.-O. *J. Org. Chem.* **1979**, *44*, 887. In rearrangement of β-naphtalenones, see: (e) Miller, B.; Saidi, M. R. *J. Am. Chem. Soc.* **1976**, *98*, 2227. (f) Miller, B.; Lin, W.-O. *J. Org. Chem.* **1979**, *44*, 887. In rearrangement of 4,4-disubstituted-2-cyclohexenols, see: Vittorelli, P.; Peter-Katalinić, J.; Mukherjee-Müller, G.; Hansen, H. J.; Schmid, H. *Helv. Chim. Acta* **1975**, *58*, 1379. In rearrangements of bicyclo[3.1.0]hexenyl carbonium ions, see: Sorensen, T. S.; Rauk, A. In *Pericyclic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. II, p 59.

(30) Brouwer, D. M.; Oelderik, J. M. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 721.

(31) For examples of fragmentation reactions in superacid medium, see: Karabatsos, G. J.; Vane, F. M.; Meyerson, S. *J. Am. Chem. Soc.* **1963**, *85*, 733.

between the various alkenes in equilibrium. A spectacular illustration of this process is the acylation of "diesel" fuel, which leads to a mixture of **18** (ca. 10–15% yield) and **20** (ca. 5% yield). In contrast, acylation of 2,3-dimethylbutane by crotonyl chloride occurs very slowly and without rearrangement. A single ketone (**21**), resulting of the double acylation of 2,3-dimethyl-2-butene, is obtained in low yield (ca. 15%).

The stereochemistry of the chlorocyclopentenone **17a** or **b** was determined by conversion into the bicycloketone **22a** or **b**, respectively, after treatment with *t*-BuOK. The exo isomer **22a** (respectively endo isomer **22b**) can be correlated with the 4*R**,2′*S** isomer **17a** (respectively 4*R**,2′*R** isomer **17b**).



17a : R^1 = Me ; R^2 = H **22a** : R^1 = Me ; R^2 = H

17b : R^1 = H ; R^2 = Me **22b** : R^1 = H ; R^2 = Me

Conclusions

We have shown that the in situ formation of branched alkenes increases the yield of the acylation reaction. The slow delivery of reagents in a steady-state concentration is a known procedure,[32] but not used as a source of alkene. Nazarov cyclization of intermediate divinyl ketones occurs with a mechanism that includes two 1,2-shifts. Some bi- or tricyclic cyclopentenones are available from this process. The low reactivity of sorboyl chloride allowed the alkene to isomerize and even to undergo fragmentation reactions before the acylation.

Experimental Section

General Methods. ^{1}H NMR spectra were determined on Bruker AC 200 (200 MHz) and Bruker AM-500 (500 MHz) spectrometers. ^{13}C NMR spectra of $CDCl_3$ solutions were recorded on a Varian XL 200 (50.309 MHz) with Me_4Si as the internal standard. Mass spectra were obtained on a Varian MAT 311 mass spectrometer. All reactions were performed under an argon atmosphere. CH_2Cl_2 was distilled from P_2O_5. 1,1,1-Trideuterio-2-(trideuteriomethyl)-2-butene (2-methylbutene-d_6) (contaminated by ca. 12% of 1,1-deuterio-2-(trideuteriomethyl)-1-butene) was obtained by dehydration of 1,1,1,3,3,3-hexadeuterio-2-ethyl-2-propanol. 1,1,1,3,3,3-Hexadeuterio-2-ethylpropane (2-methylbutane-d_6) was prepared by dehydroxylation of 1,1,1,3,3,3-hexadeuterio-2-ethyl-2-propanol according to Barton procedure.[33] $CuSO_4 \cdot 5H_2O$ was dried by heating at 150 °C for 24 h and at 350 °C for 3 h.

1-Acetyl-2-methyl-1-cyclopentene (1) and 1,3-Diacetyl-2-methyl-1-cyclopentene (2). A solution of $AlCl_3$ (16 g, 0.12 mol or 20 g, 0.15 mol), acetyl chloride (9.5 g, 0.12 mol or 15.7 g, 0.2 mol), and methylcyclopentane (8.4 g, 0.1 mol) in CH_2Cl_2 (125 or 150 mL) was refluxed for 2 h. After cooling to room temperature, the solution was poured on ice and extracted twice with CH_2Cl_2. The organic layers were washed with water, stirred for 0.5 h with a saturated solution of $NaHCO_3$, washed with brine, dried ($MgSO_4$), and concentrated. Subsequent fractional distillation yielded 7.5 g (60%) or 1.2 g (10%) of **1** (lit.[7b]) and 1.7 g (10%) or 8.3 g (50%) of **2**. Data for compound **2**: bp 90–120 °C (1 Torr); ^{1}H NMR δ 3.57 (1, t, J = 7 Hz), 2.85 (2, m), 2.22 (3, br s), 2.12 (3, s), 2.10–1.80 (2, m), 2.00 (3, br s); ^{13}C NMR δ 208.7 (s), 198.3 (s), 149.5 (s), 138.8 (s), 65.5 (d), 33.4 (t), 30.4 (q), 28.4 (q), 25.7 (t), 15.9 (q); mass spectrum m/z 166 (4) (HRMS 166.1003, calcd for $C_{10}H_{14}O_2$ 166.0993), 124 (42), 43 (100); IR (film) 1710, 1680, 1615, 1160 cm^{-1}.

1-Acetyl-2-methyl-3-(1-oxopropyl)-1-cyclopentene (5). To a stirred solution of $TiCl_4$ (1.9 g, 10 mmol) in CH_2Cl_2 (10 mL) at −40 °C were added enol acetate **4** (1.66 g, 10 mmol) in CH_2Cl_2 (5 mL) and propionyl chloride (1.02 g, 11 mmol). After stirring for 18 h, the usual workup and flash chromatography led to 1.35 g (75%) of **5** and 250 mg (15%) of **2**. Data for compound **5**: ^{1}H NMR δ 3.64 (1, m), 2.67 (2, m), 2.46 (2, q, J = 7.25 Hz), 2.22 (3, s), 2.2–1.8 (2, m), 1.97 (3, d, J = 0.8 Hz), 1.02 (3, t, J = 7.25 Hz); ^{13}C NMR δ 210.4 (s), 197.8 (s), 149.1 (s), 137.8 (s), 63.6 (d), 34.2 (t), 32.7 (t), 29.6 (q), 25.3 (t), 15.0 (q), 6.7 (q); IR (film) 1710, 1680, 1660, 1625, 1615, 1355, 1115 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.12; H, 8.80.

Acylation of *cis*-Decahydronaphthalene. To a stirred suspension of $AlCl_3$ (4 g, 30 mmol) in CH_2Cl_2 (50 mL) at 8–10 °C was added acetyl chloride (3.75 g, 48 mmol). After 15 min, a mixture of *cis*-decahydronaphthalene (2.76 g, 20 mmol) and CH_2Cl_2 (20 mL) was added. After stirring for 10 h at the same temperature, the mixture was poured into an excess of ice and vigorously stirred. After the usual workup, the crude product was distilled and purified by flash chromatography (ether/pentane, 1/4) to give 1.64 g (46%) of **6** (lit.[14]): bp 105–110 °C (8 Torr); ^{1}H NMR δ 4.10 (1, s), 3.92 (1, d, J = 4 Hz), 3.53 (1, s), 2.01 (1, m), 1.45 (14, m); ^{13}C NMR δ 165.9 (s), 80.4 (d), 76.9 (t), 50.1 (d), 46.3 (s), 39.6 (t), 31.5 (t), 30.3 (t), 26.7 (t), 25.0 (t), 22.2 (t), 19.1 (t); IR (film) 1670, 1600, 1105, 1030, 1005 cm^{-1}.

General Procedure for the Preparation of Pentalenones 8a–e from Methylcyclopentane. To a stirred suspension of $AlCl_3$ (4.4 g, 33 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added a solution of alkenoyl chloride **7** (20 mmol) in CH_2Cl_2 (15 mL). After 30 min, methylcyclopentane (1.68 g, 20 mmol) was added. Acetyl chloride (1.42 mL, 20 mmol) in CH_2Cl_2 (15 mL) was added over 1 h. The solution was refluxed (**8a**, 2 h; **8b**, 5 h; **8c**, 10 h; **8d**, 4 h; **8e**, 3.5 h) and then cooled to room temperature, poured on ice, diluted with ether, and extracted twice with ether. The organic layers were vigorously stirred with saturated $NaHCO_3$ for 1 h, washed with brine, dried ($MgSO_4$), and concentrated. Subsequent distillation or flash chromatography on silica gel yielded **1** (ca. 10–15%) and pentalenones **8a–e**.

General Procedure for Acylation in the Presence of Cupric Sulfate. To a stirred suspension of $AlCl_3$ (4.0 g, 30 mmol) and $CuSO_4$ (1.0 g, 6.25 mmol) in CH_2Cl_2 (15 mL) at room temperature was added nitromethane (1 mL) and 20 μL of water. After 15 min of stirring, a mixture of alkane (20 mmol) and acyl chloride (20 mmol) in CH_2Cl_2 (8 mL) was added. The suspension was stirred for 16 h and then refluxed for 8 h. The solution was cooled to room temperature, worked up as described above, and purified by subsequent fractional distillation or flash chromatography on silica gel to yield the corresponding cyclopentenone.

4,4,5,5,6,6-Hexadeuterio-3-methyl-3-(trideuteriomethyl)-3,4,5,6-tetrahydro-1(2*H*)-pentalenone (8a-d_9). The procedure described for **8a** was used with cyclohexane-d_{12} (1 g, 10 mmol) instead of methylcyclopentane and 0.8 g (10 mmol) of acetyl chloride, 1.6 g (15 mmol) of **7a** and 3.40 g (25 mmol) of anhydrous $AlCl_3$ in CH_2Cl_2 (30 mL). The mixture was heated for 8 h, and the crude product was purified by flash chromatography (ether/pentane, 1/20) to yield 0.2 g (15%) of **1-acetyl-3,3,4,4,5,5-hexadeuterio-2-(trideuteriomethyl)cyclopentene (1-d_9)** and 0.73 g (45%) of **8a-d_9**. Data for compound **1-d_9**: ^{1}H NMR δ 2.15 (s); ^{13}C NMR δ 198.4 (s), 154.3 (s), 136.0 (s), 40.9 (low intensity signal) (see ref 24), 30.3 (q); mass spectrum m/z 133 (52) (HRMS 133.1462, calcd for $C_8H_3D_9O$ 133.1453), 132 (27), 118 (100), 117 (59), 90 (61), 89 (29), 58 (31), 43 (54); IR (film) 2220, 2190, 2100, 1670, 1650, 1605 cm^{-1}. Data for compound **8a-d_9**: ^{1}H NMR δ 2.60 (2, s), 1.22 (3, s); ^{13}C NMR δ 202.4 (s), 194.6 (s), 146.7 (s), 56.6 (t), 37.6 (s), 26.6 (q).

4,4,5,5,6,6-Hexadeuterio-3-propyl-3-(trideuteriomethyl)-3,4,5,6-tetrahydro-1(2*H*)-pentalenone (8b-d_9). Using the procedure described for **8a-d_9** with **7b** (2.02 g, 15 mmol) instead of **7a** gave a crude oil, which was purified by flash chromatography (ether/pentane, 1/20) to yield 0.2 g (15%) of **1-d_9** and 0.76 g (40%) of **8b-d_9**: ^{13}C NMR δ 202.8 (s), 193.7 (s), 147.2 (s), 53.8 (t), 41.3 (s), 41.3 (t), 28.0 (low intensity signal) (see ref 24), 18.4 (t), 14.6 (q).

1-Crotonyl-2-methyl-1-cyclopentene (9). Anhydrous $AlCl_3$ (1.33 g, 10 mmol) and **7a** (1.04 g, 10 mmol) in CH_2Cl_2 (30 mL) at room temperature were stirred until a homogeneous solution was obtained. The mixture was cooled to −90 °C, and 1-methyl-1-cyclopentene (15 mmol, 1.23 g) in CH_2Cl_2 (15 mL) was slowly added. The mixture was allowed to warm to −40 °C after 3 h, on ice, and extracted with CH_2Cl_2. After the usual workup, the crude product was purified by flash chromatography (ether/pentane, 1/30) to give 1 g (65%) of **9** (lit.[7b]): bp 80–85 °C (1 Torr); ^{1}H NMR δ 6.95 (1, d, q, J = 15.3, 6.9 Hz), 6.48 (1, d, q, J = 15.3, 1.5 Hz), 2.75 (2, m), 2.55 (2, m), 2.10 (3, br s), 1.98 (3, d, q, J = 6.9, 1.5 Hz), 1.90 (2, m); ^{13}C NMR δ 191.4 (s), 152.9 (s), 142.5 (d), 136.0 (s), 130.7 (d), 40.8 (t), 34.4 (t), 21.8 (t), 18.3 (q), 16.8 (q); IR (film) 1710, 1670, 1640 cm^{-1}.

Isomerization of 9 to 8a. To a stirred solution of $AlCl_3$ (0.67 g, 5 mmol) in CH_2Cl_2 (5 mL) was slowly added **9** (0.5 g, 3.3 mmol) in CH_2Cl_2 (5 mL). After refluxing for 4 h, the usual workup and flash

(32) For examples of the slow delivery of bromine from NBS, see: March, J. *Advanced Organic Chemistry*; J. Wiley & Sons: New York, 1985; p 625. For examples of the in situ preparation of Grignard reagents (Barbier reaction), see: Blomberg, C.; Hartog, F. A. *Synthesis* **1977**, 18. For examples of the in situ formation of methyl vinyl ketone in the Robinson annulation reaction, see: Jung, M. E. *Tetrahedron* **1976**, *32*, 1.

(33) Barton, D. H. R.; Crich, D. *J. Chem. Soc., Chem. Commun.* **1984**, 774.

chromatography afforded 0.2 g (40%) of **8a**.

General Procedure for the Preparation of Compounds 11a,c,d and 12a–d,f. To a stirred suspension of $AlCl_3$ (4 g, 30 mmol) in CH_2Cl_2 (15 mL) at 0 °C was added alkenoyl chloride **7** (22.5 mmol) in CH_2Cl_2 (5 mL). After 30 min of stirring, alkane (15 mmol) in CH_2Cl_2 (10 mL) was slowly added. After a reflux time (**11d**, **12a–d**, 4 h; **11a,c**, 6h; **12f**, 12 h), the procedure was the same as for the preparation of **8** from methylcyclopentane.

Acylation of 1,1,1,3,3,3-Hexadeuterio-2-ethylpropane (2-Methylbutane-d_6) by 7c. The same procedure using 1,1,1,3,3,3-hexadeuterio-2-ethylpropane gave **12c**-d_6: ^1H NMR, analogous spectrum to that of **12c** with low intensity signals (ca. 1 proton) at 1.85, 1.67, and 0.98 ppm; ^{13}C NMR, comparable spectrum to that of **12c** with a reduced intensity at δ = 26.1 ppm, a low intensity at δ = 23.1 ppm (multiplet), and very low intensities at δ = 11.9 and 8.2 ppm (m) (see ref 24); mass spectrum m/z 158 (24) (HRMS 158.1582, calcd for $C_{10}H_{10}D_6O$ 158.1577); IR (film) 2200 cm^{-1}.

Acylation of 2-Methyl-2-butene by Sorboyl Chloride (13). To a stirred suspension of $AlCl_3$ (3.50 g, 26 mmol) in CH_2Cl_2 (125 mL) at −40 °C was added **13** (3.26 g, 25 mmol) in CH_2Cl_2 (50 mL). After stirring for 1 h, the solution was cooled to −90 °C, and 2-methyl-2-butene (1.75 g, 25 mmol) in CH_2Cl_2 (50 mL) was added. The solution was warmed to −10 °C over 2 h and hydrolyzed, or refluxed for 30 min and then hydrolyzed. In the first case, after usual workup, the crude product was flash-chromatographed on silica gel (CH_2Cl_2/pentane) to give **2,3-dimethyl-2,5,7-nonatrien-4-one (14)** (ca. 10% yield) and **2-chloro-2,3-dimethyl-5,7-nonadien-4-one (15)** (ca. 20% yield) (unstable product). Data for **14**: ^1H NMR δ 7.15 (1, d, q, J = 15.4, 5.22 Hz), 6.23 (2, m), 6.11 (1, d, J = 15.4 Hz), 2.17 (3, s), 1.92 (3, s), 1.86 (3, d, J = 5.22 Hz), 1.86 (3, s); IR 1700, 1650, 975 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.18; H, 9.73. Data for **15**: ^1H NMR δ 7.19 (1, d, q, J = 15.4, 5.0 Hz), 6.25 (2, m), 6.18 (1, d, J = 13.3 Hz), 3.22 (1, q, J = 7.0 Hz), 1.88 (3, d, J = 5.0 Hz), 1.66 (3, s), 1.62 (3, s), 1.26 (3, d, J = 7.0 Hz); ^{13}C NMR δ 200.7 (s), 143.1 (d), 140.6 (d), 130.3 (d), 127.8 (d), 71.5 (s), 55.4 (d), 30.9 (q), 29.6 (q), 18.5 (q), 13.8 (q); IR 1680, 1595 cm^{-1}. In the second case, the crude product was distilled; the main product of the fraction with bp 50–65 °C (0.15 Torr) was **2,3,4-trimethyl-4-propenyl-2-cyclopenten-1-one (16)** (ca. 8% yield), and for the fraction with bp 80–105 °C (0.15 Torr), the main products were **(4*R**)-2,3,4-trimethyl-4-((2′*S**)-2′-chloropropyl)-2-cyclopenten-1-one (17a)** (ca. 12% yield) and **(4*R**)-2,3,4-trimethyl-4-((2′*R**)-2′-chloropropyl)-2-cyclopenten-1-one (17b)** (ca. 12% yield). Each fraction was further purified by flash chromatography (ether/pentane). Data for **16**: ^1H NMR δ 5.50 (1, $^1/_2$ AB, q, J = 15.6, 5.9 Hz), 5.31 (1, $^1/_2$ AB, q, J = 15.6, 0.9 Hz), 2.42 (1, $^1/_2$ AB, J = 18.5 Hz), 2.25 (1, $^1/_2$ AB), 1.86 (3, s), 1.69 (3, d, d, J = 5.9, 0.9 Hz), 1.69 (3, s), 1.25 (3, s); mass spectrum m/z 164 (65) (HRMS 164.1201, calcd for $C_{11}H_{16}O$ 164.1198), 149 (15), 126 (100). Data for **17a**: ^1H NMR δ 3.82 (1, m), 2.73 (1, $^1/_2$ AB, J = 18.6 Hz), 2.16 (1, $^1/_2$ AB), 2.17 (1, $^1/_2$ AB, J = 15.0 Hz), 1.84 (1, $^1/_2$ AB), 1.92 (3, s), 1.70 (3, s), 1.48 (3, d, J = 6.6 Hz), 1.22 (3, s); ^{13}C δ 207.3 (s), 173.7 (s), 136.8 (s), 54.8 (d), 48.0 (t), 47.3 (t), 44.5 (s), 27.1 (q), 26.3 (q), 12.1 (q), 8.2 (q); mass spectrum m/z 202 (3), 200 (8) (HRMS 200.0974, calcd for $C_{11}H_{17}O^{35}Cl$ 200.0967), 123 (100), 95 (44), 84 (22); IR (film) 1705, 1650 cm^{-1}. Data for **17b**: ^1H NMR δ 3.88 (1, m), 2.57 (1, $^1/_2$ AB, J = 18.75), 2.20 (1, $^1/_2$ AB), 1.97 (2, m), 1.95 (3, s), 1.69 (3, s), 1.51 (3, d, J = 6.6 Hz), 1.2 (3, s); ^{13}C NMR δ 207.3 (s), 175.2 (s), 136.5 (s), 54.4 (d), 48.3 (t), 47.8 (t), 44.0 (s), 27.3 (q), 25.6 (q), 12.8 (q), 8.2 (q); mass spectrum m/z 202 (5), 200 (16) (HRMS 200.0976, calcd for $C_{11}H_{17}O^{35}Cl$ 200.0967), 123 (100), 95 (50), 67 (14); IR (film) 1690, 1645, 1250, 1105 cm^{-1}.

Acylation of 1,1,1-Trideuterio-2-(trideuteriomethyl)-2-butene by Sorboyl Chloride (13). The procedure described above (second case) was used with 1,1,1-trideuterio-2-(trideuteriomethyl)-2-butene (1.9 g, 25 mmol) (contaminated by ca. 12% of 1,1-dideuterio-2-(trideuteriomethyl)-1-butene) instead of 2-methyl-2-butene. The crude product was distilled (60–90 °C (0.15 Torr)) to give 1.3 g of product, which was flash-chromatographed on silica gel (ether/pentane, 1/4 to 1/2). Data for **14**-d_6: ^1H NMR spectrum, signals of three methyl groups were diminished, δ 2.17 (rel intens (ri) 0.75 proton, s), 1.92 (ri 0.8 p, s), 1.86 (ri 0.9 p, s). Data for **16**-d_6: ^1H NMR δ 1.86 (ri 0.75 p, s), 1.69 (ri 1.34 p, s), 1.25 (ri 0.75 p, s). Data for **17a**-d_6: ^1H NMR δ 1.92 (ri 0.75 p, s), 1.70 (ri 1.30 p, s), 1.22 (ri 0.72 p, s); ^{13}C NMR (methyl groups) δ 27.14 (q), 26.33 (q, low intens), 12.10 (q, low intens), 8.15 (q, low intens). Data for **17b**-d_6: ^1H NMR δ 1.95 (ri 0.70 p, s), 1.69 (ri 1.35 p, s), 1.20 (ri 0.75 p, s); ^{13}C NMR (methyl groups) δ 27.36 (q), 25.70 (q, low intens), 12.70 (q, low intens), 8.17 (q, low intens).

Acylation of 2-Methylbutane by Sorboyl Chloride (13) in the Presence of Nitromethane. To a stirred suspension of $AlCl_3$ (13.3 g, 100 mmol) in CH_2Cl_2 (40 mL) at 0 °C were added nitromethane (4 mL) and 100 μL of water. After 15 min of stirring, **13** (6.5 g, 50 mmol) and 2-methylbutane (5.80 mL, 3.6 g, 50 mmol) in CH_2Cl_2 (22 mL) were added. The mixture was warmed to room temperature over 1 h, and then refluxed for 3 h. After usual workup, the organic layers were stirred for 3 h with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated. Subsequent distillation yielded **17a,b** (4.5 g, 46% yield).

Acylation of 2-Methylbutane by Sorboyl Chloride (13). To a stirred suspension of $AlCl_3$ (13.3 g, 100 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added 200 μL of ethanol. After 0.25 h of stirring, **13** (7.85 g, 60 mmol) in CH_2Cl_2 (16 mL) was added and the mixture was stirred for 15 min. A solution of 2-methylbutane (7.1 mL, 4.40 g, 61 mmol) in CH_2Cl_2 (24 mL) was added. The mixture was warmed to room temperature over 1 h and then stirred for 28 h. After the usual workup, the organic layers were stirred for 3 h with saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated. Distillation and subsequent flash chromatography on silica gel (ether/pentane, 1/10) yielded **2,3-dimethyl-4-(2′-methylpropyl)-2-cyclopenten-1-one (18)** (4.15 g, 42%). Data for **18**: bp 60–64 °C (0.4 Torr); ^1H NMR (500 MHz) δ 2.67 (1, m), 2.51 (1, $^1/_2$ AB, d, J = 18.5, 6.4 Hz), 2.04 (1, $^1/_2$ AB, d, J = 18.5, 1.7 Hz), 2.0 (3, s), 1.68 (3, q, J = 0.9 Hz), 1.65 (1, d, d, q, J = 10.0, 3.9, 6.5 Hz), 1.55 (1, $^1/_2$ AB, d, d, J = 13.6, 10.0, 2.9 Hz), 1.04 (1, $^1/_2$ AB, d, d, J = 13.6, 11.5, 3.9 Hz), 0.942 (3, d, J = 6.5 Hz), 0.939 (3, d, J = 6.5 Hz); ^{13}C NMR δ 208.5 (s), 173.2 (s), 135.6 (s), 42.6 (t), 40.8 (d), 40.6 (t), 26.6 (d), 23.7 (q), 21.2 (q), 14.9 (q), 7.7 (q); mass spectrum m/z 167 (3), 166 (31) (HRMS 166.1363, calcd for $C_{11}H_{18}O$ 166.1357), 124 (5), 123 (18), 111 (11), 110 (100), 109 (51), 95 (33), 81 (36); IR (film) 1700, 1645 cm^{-1}.

In a comparable experiment utilizing only 2.88 g (40 mmol) of 2-methylbutane, the mixture was stirred at room temperature for 7 h and refluxed for 1.5 h. The crude oil was flash-chromatographed on silica gel (ether/pentane, 1/10) to give **18** (20% yield) and **2,3-dimethyl-4-(2′-methylpropylidene)-2-cyclopenten-1-one (19)** (8% yield): ^1H NMR δ 5.51 (1, d, J = 9.6 Hz), 2.87 (2, s), 2.46 (1, d, sept, J = 9.6, 6.6 Hz), 2.03 (3, s), 1.77 (3, s), 1.02 (6, d, J = 6.6 Hz); ^{13}C NMR δ 205.1 (s), 163.8 (s), 138.8 (s), 134.9 (s), 131.8 (d), 36.7 (t), 29.5 (d), 22.7 (q) (2C), 11.9 (q), 8.4 (q); mass spectrum m/z 164 (32) (HRMS 164.1210, calcd for $C_{11}H_{16}O$ 164.1201), 149 (21), 122 (100), 107 (21), 91 (23), 79 (40); IR 1700, 1645 cm^{-1}.

Acylation of 1,1,1,3,3,3-Hexadeuterio-2-ethylpropane by Sorboyl Chloride (13). The same procedure as above (first case) was used with 1,1,1,3,3,3-hexadeuterio-2-ethylpropane instead of 2-methyl-2-butane. The crude product was distilled and then flash-chromatographed on silica gel (ether/pentane). Data for **18**-d_6: ^1H NMR spectra, signals of four methyl groups were shortened, δ 2.00 (rel intens (ri) ca. 1 proton, s), 1.68 (ri ca. 0.9 p, d, J = 1.2 Hz), 0.940 (ri ca. 4 p, d, J = 6.11 Hz); ^2H NMR (CCl_4) δ 1.91, 1.55, 0.88 (ri 1:1.1:1); ^{13}C NMR δ (in part) 42.96 (t), 41.3 (d), 41.04 (t), 26.94 (mult, low intens) (see ref 24), 23.96 (q), 21.55 (q), 15.22 (q, low intens), 7.99 (q, low intens); mass spectrum m/z 173 (20), 172 (25) (HRMS 172.1743, calcd for $C_{11}H_{12}D_6O$ 172.1734), 171 (13), 129 (12), 128 (16), 127 (14), 116 (40), 115 (56), 114 (83), 113 (100), 112 (56); IR (film) 2210, 2200–2125, 2065 cm^{-1}.

Acylation of Isohexanes by Sorboyl Chloride (13). This reaction was carried out via the same procedure as for the preparation of **18**, with 5.16 g (60 mmol) of 2,3-dimethylbutane, 2-methylpentane, or 3-methylpentane. After the usual workup, the crude product was distilled and the fraction with bp 60–80 °C (0.4 Torr) was flash-chromatographed on silica gel (ether/pentane, 1/20). The first-eluted ketone was **2-ethyl-3-methyl-4-(2′-methylpropyl)-2-cyclopenten-1-one (20)** followed by **18** (yields with 2,3-dimethylbutane: **20**, 35%; **18**, 15%. With 2-methylpentane or 3-methylpentane: **20**, 15–20%; **18**, 20–30%). Data for **20**: ^1H NMR δ 2.67 (1, m), 2.54 (1, $^1/_2$ AB, d, J = 18.4, 6.4 Hz), 2.18 (2, m), 2.05 (1, $^1/_2$ AB, J = 18.4 Hz), 2.01 (3, s), 1.8–1.5 (2, m), 1.05 (1, m), 0.99 (3, t, J = 7.5 Hz), 0.94 (6, d, J = 6.1 Hz); ^{13}C NMR δ 208.1 (s), 172.4 (s), 141.9 (s), 43.2 (t), 41.4 (t), 41.2 (d), 27.0 (d), 23.9 (q), 21.7 (q), 16.4 (t), 14.9 (q), 12.8 (q); mass spectrum m/z 180 (6) (HRMS 180.1520, calcd for $C_{12}H_{20}O$ 180.1514), 165 (10), 137 (30), 124 (100); IR (film) 1700, 1645 cm^{-1}.

Acylation of 2,3-Dimethylbutane by Crotonyl Chloride (7a). The general procedure of acylation in the presence of cupric sulfate was used with **7a** (2.09 g) and 2,3-dimethylbutane (1.72 g). After 6 h of heating and usual workup, the crude product was distilled and flash-chromatographed on silica gel (ether/pentane) to give **5,5,6-trimethyl-2,6,9-undecatriene-4,8-dione (21)** (ca. 15% yield). Data for **21**: bp 110 °C (0.2 Torr); ^1H NMR δ 7.05–6.79 (2, m), 6.37 (1, d, J = 0.8 Hz), 6.24 (2, d, q, J = 15.1, 1.8 Hz), 2.01 (3, d, J = 0.8 Hz), 1.93 (3, d, d, J = 6.8, 1.5 Hz), 1.86 (3, d, d, J = 6.9, 1.6 Hz), 1.29 (6, s); ^{13}C NMR δ 199.4 (s), 190.2 (s), 158.3 (s), 143.1 (d), 142.0 (d), 133.3 (d), 128.0 (d), 121.9 (d), 54.2 (s), 22.9 (q) (2 C), 17.8 (q), 17.7 (q), 16.7 (q). Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.26; H, 9.11.

Obtention of 1,4,6-Trimethyl-7-methylenebicyclo[2.2.1]heptan-2-one (22) from 17. To a stirred suspension of potassium *tert*-butoxide (300 mg, 2.7 mmol) in anhydrous benzene (10 mL) was added **17** (430 mg,

2.15 mmol). After 6 h of stirring, the mixture was filtered on silica gel, which was washed with ether. The filtrate was concentrated in vacuo and flash-chromatographed on silica gel (pentane → ether/pentane, 1/10) to give **22** (250 mg, 70%). Data for **22**: IR (film) 3090, 1755, 1685, 895 cm^{-1}; mass spectrum *m/z* 164 (18) (HRMS 164.1209, calcd for $C_{11}H_{16}O$ 164.1201), 149 (5), 122 (60), 107 (100). Data for exo isomer **22a** (from **17a**): ^1H NMR δ 4.90 (1, s), 4.73 (1, s), 2.29 (1, $^1/_2$ AB, J = 17.4 Hz), 2.1 (1, $^1/_2$ AB, d, J = 3.2 Hz), 2.04–1.87 (3, m), 1.31 (3, s), 1.10 (3, s), 0.88 (3, d, J = 6.6 Hz); ^{13}C NMR δ 214.58 (s), 159.11 (s), 99.12 (t), 60.12 (s), 53.40 (t), 44.82 (t), 43.34 (s), 34.42 (q), 17.61 (d), 16.99 (q), 7.74 (q). Data for endo isomer **22b** (from **17b**): ^1H NMR δ 4.66 (1, s), 4.58 (1, s), 2.08 (1, $^1/_2$ AB, J = 17.4 Hz), 1.97 (1, $^1/_2$ AB, d, J = 1.96 Hz), 1.96–1.74 (3, m), 1.19 (3, s), 1.05 (3, s), 0.82 (3, d, J = 6.84 Hz); ^{13}C NMR δ 212.6 (s), 162.0 (s), 95.6 (t), 61.2 (s), 54.1 (t), 44.6 (t), 43.1 (s), 38.6 (q), 16.8 (q or d), 16.6 (d or q), 8.9 (q).

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Registry No. **1**, 3168-90-9; **1**-d_9, 135773-75-0; **2**, 80638-72-8; **4**, 135773-67-0; **5**, 135773-68-1; **6**, 4752-31-2; **7a**, 625-35-4; **7b**, 97943-16-3; **7c**, 35660-94-7; **7d**, 83841-91-2; **7e**, 36278-22-5; **7f**, 59253-90-6; **8a**, 72233-31-9; **8a**-d_9, 135773-74-9; **8b**, 135773-69-2; **8b**-d_9, 135773-76-1; **8c**, 135773-70-5; **8d**, 135773-71-6; **8e**, 135773-72-7; **9**, 135773-73-8; **11a**, 30434-75-4; **11c**, 135773-77-2; **11d**, 135773-78-3; **12a**, 30434-70-9; **12b**, 135773-79-4; **12c**, 50506-54-2; **12c**-d_6, 135773-83-0; (*S**,*S**)-**12d**, 135773-80-7; (*S**,*R**)-**12d**, 135773-81-8; **12f**, 135773-82-9; **13**, 2614-88-2; **14**, 135773-84-1; **15**, 135773-88-5; **16**, 135773-85-2; **17a**, 135773-86-3; **17b**, 135773-87-4; **18**, 135773-89-6; **19**, 135773-90-9; **20**, 135773-91-0; **21**, 135773-92-1; **22a**, 135773-93-2; **22b**, 135773-94-3; $AlCl_3$, 7446-70-0; CH_3COCl, 75-36-5; $TiCl_4$, 7550-45-0; EtCOCl, 79-03-8; $CuSO_4$, 7758-98-7; $MeNO_2$, 75-52-5; $(CH_3)_2CHEt$, 78-78-4; $(CD_3)_2CHEt$, 77734-77-1; methylcyclopentane, 96-37-7; *cis*-decahydronaphthalene, 493-01-6; 1-methylcyclopentene, 693-89-0; cyclohexane-d_{12}, 1735-17-7; methylcyclohexane, 108-87-2; 2-methyl-2-butene, 513-35-9; 2,3-dimethylbutane, 79-29-8; 2-methylpentane, 107-83-5; 3-methylpentane, 96-14-0.

A Carbene to Biradical Rearrangement: Reaction Paths from (8-Methyl-1-naphthyl)carbene to Acenaphthene

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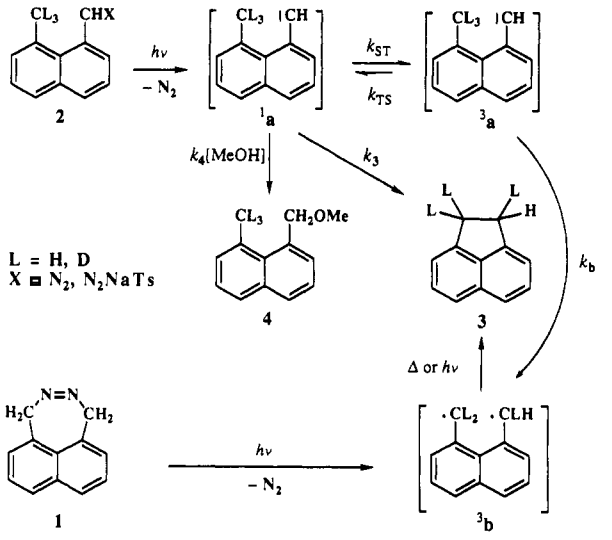
Abstract: Photochemical nitrogen elimination from 1-(diazomethyl)-8-methylnaphthalene (**2**) yields acenaphthene (**3**) via the reactive intermediates (8-methyl-1-naphthyl)carbene (a) and 1,8-naphthoquinodimethane (b). The triplet biradical b was observed by absorption spectroscopy at 77 K and by laser flash photolysis at room temperature. The cyclization of triplet b to triplet **3** is forbidden by state symmetry. Two pathways for the reaction b → **3** have been identified: (1) intersystem crossing to the singlet ground state is rate-determining in the thermal decay of b, and (2) an adiabatic reaction yielding **3** in the lowest excited triplet state was observed upon photolysis of triplet b at 77 K. The carbene precursor of b was intercepted by methanol. This resulted in a reduced yield of transient b in acetonitrile. The trapping reaction did not obey a linear Stern–Volmer relationship.

1,8-Naphthoquinodimethane (b, IUPAC name: 1,8-naphthalenediylbismethyl) has been identified by ESR spectroscopy as a non-Kekulé conjugated hydrocarbon biradical with a ground state of triplet multiplicity (^{3}b). It was generated by low-temperature photolysis of the azo compound 1,4-dihydronaphtho[1,8-*de*][1,2]diazepine (**1**)[1] and of the diazo compound 1-(diazomethyl)-8-methylnaphthalene (**2**, X = N_2).[2] The high photochemical reactivity of 1,8-naphthoquinodimethane (^{3}b) has largely prevented its detection by spectroscopic techniques other than ESR when **1** was used as a precursor,[1b] but several derivatives of ^{3}b have been extensively characterized by a variety of spectroscopic methods, both as transient intermediates at room temperature and as persistent species at low temperature.[3] The hypothetical precursor of ^{3}b in the photolysis of the diazo compound (**2**, X = N_2), (8-methyl-1-naphthyl)carbene (a), has remained elusive.[2b,4]

We now report that the electronic absorption of the triplet biradical b is readily observed both by low-temperature photolysis and by room temperature flash photolysis of the diazo compound **2** (X = N_2). Moreover, we have trapped the precursor carbene a with methanol in fluid solution, proving that it is a true intermediate (Scheme I).

Scheme I



Results

Room Temperature Photolyses; Trapping of the Carbene a. Solutions of the diazo compound **2** were stable indefinitely at ambient temperature when kept in the dark. Irradiation of 10^{-4} M solutions of **2** (X = N_2) in degassed hexane or acetonitrile with

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(1) (a) Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 1972. (b) Gisin, M.; Rommel, E.; Wirz, J.; Burnett, M. N.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216.

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