Table II. Fluorophenylcyclopropanes from Reaction 1

alkene	product	yield,[a] %	purity,[b] %	t_R,[c] min
$Me_2C{=}CMe_2$	**3a**	49	98.5	4.49
$Me_2C{=}CHMe$	**3b**[d]	52	97.2	2.92, 3.19[e]
$Me_2C{=}CH_2$	**3c**	70	99.9	1.87
cis-MeCH=CHMe	**3d**[d]	76	99.3	2.68, 2.91[e]
trans-MeCH=CHMe	**3e**	42	99.2	2.16

[a] Isolated, purified product. [b] By GC. [c] GC conditions are given above. [d] Both isomers. [e] Isomeric cyclopropanes are separated by capillary GC.

in the absence of 18-crown-6 but free phenylhalocarbenes when a base/crown ether complex is employed. The latter species displays olefinic selectivities very similar to those of the phenylhalocarbenes photolytically generated from 3-halo-3-phenyldiazirines.[15]

Experimental Section

Materials and Equipment. Tetramethylethylene and Trimethylethylene were obtained from Aldrich Chemical Co. and distilled before use unless newly received. *cis*-2-Butene, *trans*-2-butene, and isobutene were obtained from Matheson Co. and used as received. Photolyses were carried out by using a focused Osram 200-W Xe mercury lamp (Pyrex filter). Capillary GC employed a Model 3700 Varian flame ionization unit with a Varian Model 4270 electronic integrator. The instrument was fitted with a BP-1, 50 ft, 20% SE-30 capillary column, operated at 100 °C (injector, 180 °C, detector, 300 °C, nitrogen pressure, 0.7 atm).

1-Fluoro-1-phenylcyclopropanes 3. General Procedure. 3-Bromo-3-phenyldiazirine[10] was converted to 3-fluoro-3-phenyldiazirine (1) by the procedure of ref 9. Diazirine **1** (2.5 mmol) and 25 mmol of alkene **2** were contained in a screw-top Pyrex Carius tube, stirred magnetically, and irradiated for 4 h at 25 °C. The tube was cooled to −70 °C (for gaseous alkenes), opened, and carefully warmed to evaporate excess alkene. Higher boiling alkenes were removed by aspiration. Crude products were purified by short column chromatography on EM Reagents silica gel 60 using *n*-hexane or *n*-pentane as eluents. The yields, GC purities and retention times of the adducts so obtained are shown in Table II. Complete spectroscopic and analytical characterizations of these compounds have previously been published.[12]

Competition Reactions. Photolytic Method. These reactions were carried out by using 1.5-mmol samples of diazirine **1** and carefully weighed binary mixtures of alkenes **2** (each present in at least 10-fold molar excess). The procedure followed the preparative method given above, except that excess $Me_2C{=}CMe_2$ or $Me_2C{=}CHMe$ was removed by distillation (1 atm, water bath).[17] The chromatography step was omitted. GC analysis employed the column and conditions described above, and the flame ionization detector was calibrated with weighed mixtures of pure products (three mixtures for each calibration). Relative reactivities were calculated from the standard relation:[13] $k_A/k_B = (P_A/P_B)(0_B/0_A)C_{A/B}$, where (P_A/P_B) is the GC integration ratio for products A and B, $(0_B/0_A)$ is the initial molar ratio of alkenes A and B, and $C_{A/B}$ is the appropriate calibration or detector response constant. Results appear in Table I.

α-Elimination Method. The competition reaction between $Me_2C{=}CHMe$ and $Me_2C{=}CH_2$ for PhCF was also carried out with PhCHBrF and KO-*t*-Bu (MSA Corp.) following the procedure described in ref 12 (Moss and Przybyla). GC analysis (present conditions) gave $k_{Me_2C=CHMe}/k_{Me_2C=CH_2} = 1.27 \pm 0.01$ for two reactions. The previous value was 1.2.[12] The same reaction was repeated using the (Thesis) procedure of ref 3. The base was a solution of 0.5 g (4.5 mmol) of KO-*t*-Bu and 1.7 g (6.4 mmol) of 18-crown-6 (Aldrich) in 20 mL of dry benzene. This was mixed at −70 °C with 38–70 mmol of each alkene and 0.34 g (1.8 mmol) of PhCHBrF,[12] originally diluted with 0.5 mL of benzene and contained in a small, breakable glass ampule. All reagents were sealed in a screw-top Carius tube and warmed to 25 °C. The ampule was broken by shaking, and the tube was rotated end-over-end for 24 h. The tube was then cooled and opened, and alkenes were evaporated. The residue was washed twice with 20-mL portions of water and once with saturated aqueous $NaHCO_3$. The organic phase was dried, benzene was removed by distillation, and the residue was analyzed by GC. Two runs gave $k_{Me_2C=CHMe}/k_{Me_2C=CH_2} = 1.6 \pm 0.1$. The previous value[3] was 3.0.

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Registry No. 1, 87282-19-7; **2a**, 563-79-1; **2b**, 513-35-9; **2c**, 115-11-7; **2d**, 590-18-1; **2e**, 624-64-6; **3a**, 17815-89-3; **3b** (syn-F), 19294-50-9; **3b** (anti-F), 19294-51-0; **3c**, 17815-90-6; **3d** (syn-F), 19294-48-5; **3d** (anti-F), 19294-49-6; **3e**, 91423-75-5; fluorophenylcarbene, 17825-75-1.

(15) The crown ether PhCF selectivities[3] were previously used to calculate a carbene selectivity index,[16] $m_{PhCF} = 0.89$ for "free" PhCF. Using the photolytic data of Table I [column 1], including $k_{rel} = 4.98$ for $Me_2C{=}CMe_2$, we now calculate $m_{PhCF} = 0.89$ ($r = 0.993$), identical with the previous value.

(16) Moss, R. A.; Mallon, C. B.; Ho, C.-T. *J. Am. Chem. Soc.* **1977**, *99*, 4105.

(17) In several experiments, $Me_2C{=}CMe_2$ was not removed after reactions. Distillation of $Me_2C{=}CMe_2$ removes small quantities of products and inflates both the **3a**/**3c** product ratio and $k_{rel}(Me_2C{=}CMe_2)$. The lower values of $k_{rel}(Me_2C{=}CMe_2)$ in columns 1 and 3 of Table I are believed to be the more accurate ones.

Revised Structure of Zizanol[1]

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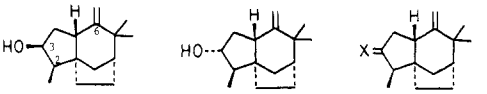
In the course of the total synthesis of the tricyclic sesquiterpene zizanol,[2] an analysis of the ^{13}C NMR chemical shifts for the C_2 methyl group in several zizaene derivatives suggested that the original assignment[3] of the relative stereochemistry of the C_3 hydroxyl group in zizanol as shown in structure **1** is in error. On the basis of both



1 **2** **3**, X = O **4**, H_2

chemical and spectroscopic evidence we report that the relative stereochemistry of the C_2 methyl and C_3 hydroxyl groups in zizanol is trans. Since the assignment of the stereochemistry of the C_2 methyl group is secure (X-ray analysis[4]), the correct structure for zizanol is that depicted in formula **2**.

An examination of the ^{13}C NMR chemical shift data shown in Table I reveals, as expected, a marked upfield shift, ca. 6.2 ppm, for the C_2 methyl group of ketone **3** compared with that of the hydrocarbon zizaene (**4**) due to the steric interaction between the sp^2 oxygen atom and the C_2 methyl group in ketone **3**.[5] For the two corresponding C_3 alcohols **1** and **2**, if the hydroxyl and methyl groups are cis as originally proposed for zizanol (e.g., **1**), the C_2 methyl group would be expected to be upfield relative to that in

(1) Financial support of this research by the Robert A. Welch Foundation is gratefully acknowledged.

(2) Kang, S. H.; Monti, S. A., to be published.

(3) (a) Homma, A.; Kato, M.; Wu, M.-D.; Yoshikoshi, A. *Tetrahedron Lett.* **1970**, 231. (b) Andersen, N. H. *Ibid.* **1970**, 1755.

(4) Coates, R. M.; Farney, R. F.; Johnson, S. M.; Paul, I. C. *J. Chem. Soc. D* **1969**, 999.

(5) Weigert, F. J.; Roberts, J. D. *J. Am. Chem. Soc.* **1970**, *92*, 1347. Grant, D. M.; Paul, E. G. *Ibid.* **1964**, *86*, 2984.

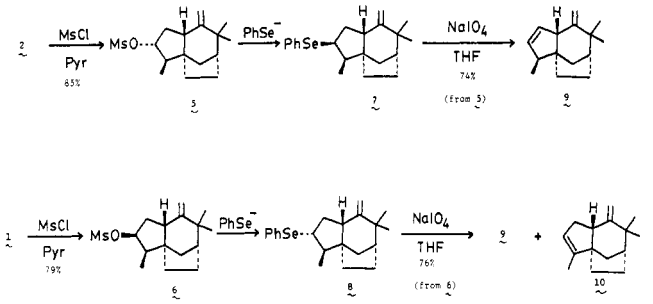
0022-3263/84/1949-3830$01.50/0

Table I. ^{13}C NMR Data for Some Zizaene Derivatives

compd	ppm[a]	compd	ppm[a]
1	11.03	5	16.31
2	17.02	6	12.08
3	13.78	7	15.88
4	20.00	8	18.89

[a] Chemical shift of the C_2 methyl group relative to internal Me_4Si.

Scheme I



ketone **3** since a cis sp^3 oxygen atom will exert a greater steric interaction than a sp^2 oxygen atom. Alternatively, if the C_2 methyl and C_3 hydroxyl groups are trans as in **2**, the reverse would be expected, the C_2 methyl group would be downfield from that of **3**. The data in Table I show that the ^{13}C NMR chemical shift for the C_2 methyl group in naturally occurring zizanol (**2**) is ca. 3.2 ppm downfield from that in ketone **3**. For epizizanol (**1**) the C_2 methyl group is ca. 2.8 ppm upfield. Both the C_3 mesylates **5** and **6** and the phenylselenyl derivatives **7** and **8** show similar chemical shift behavior.

Unambiguous chemical conformation of the hydroxyl group assignment in zizanol (**2**) was obtained as shown in Scheme I.[6] Treatment of mesylate **5**, derived from naturally occuring zizanol (**2**), with phenylselenyl anion[7] furnished the S_N2 substitution product **7** in which the C_2 methyl group and the C_3 phenylselenyl moiety are cis as judged by ^{13}C NMR data (Table I). Oxidation followed by syn elimination furnished tricyclic diene **9** as the only observed product. When epizizanol (**1**)[3] was subjected to the same sequence, a mixture (ca. 3.5 to 1) of dienes **9** and **10** was obtained. The exlusive formation of diene **9** from natural zizanol requires an initial trans disposition of the methyl and hydroxyl groups in this natural product and establishes the structure of zizanol as **2**.

Experimental Section

All reactions were performed under a nitrogen atmosphere. For small-scale reactions, the crude products were routinely passed through silica gel with the mixture of Skellysalve B (SKB) and ethyl acetate after aqueous quench and evaporation of solvents. For large-scale reactions, the workup included ether extraction, drying over anhydrous magnesium sulfate, and evaporation of solvents. Separations were carried out on a Waters Associates Model 6000 HPLC equipped with Poracil A (37-75) $^3/_8 \times 1.2$ m column and Prep LC/System 500 with silica gel. IR spectra were obtained on a Beckmann Model IR-10 spectrophotometer. Proton N spectra were measured on Varian Associates Models EM-390 or NT-200 and ^{13}C NMR spectra were measured on a Bruker WH 90 instrument or a Varian Associates Model FT-80A. Chemical shifts are reported in ppm downfield (δ) from internal Me_4Si. High resolution mass spectra were obtained on a CEC Model 21-100 mass spectrometer and GC–mass spectra in a Finnigan 4023 GC–mass spectrometer with SE-30 column.

Preparation of 3-Zizanone (3) from Vetiver Oil. Vetiver oil (100 g, Oil Vetiver Reunion Extra, Fritsche-D & O) was vacuum distilled to give a distillate with bp 90–160 °C at 0.5–1.0 mmHg. Separation of this mixture by HPLC (SKB/EtOAc = 6/1) furnished several fractions in which the R_f of the last peak was similar to those of the synthetic epizizanols. A 5-g sample of this last peak (11 g) in 80 mL of acetone was treated with Jones reagent in an ice–water bath until a reddish color persisted, and then the reddish mixture was stirred for 30 min. The excess Jones reagent was destroyed with isopropyl alcohol in the ice–water bath. Normal workup and separation of the crude product on HPLC (SKB/EtOAc = 25/1) yielded 400 mg of the desired ketone **3**:[3] ^1H NMR ($CDCl_3$) δ 1.10 (s, 3), 1.11 (d, 3, J = 8.5 Hz), 1.15 (s, 3), 1.3–2.6 (m, 10), 2.98 (t, 1, J = 9.5 Hz), 4.58 (d, 1, J = 2 Hz), 4.85 (d, 1, J = 2 Hz); IR ($CHCl_3$) 3085, 1735, 1635, 890 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 220.75, 154.84, 106.27, 52.30 (2 carbons), 48.51, 44.06, 40.55, 38.64, 35.83, 31.83, 28.33, 26.27, 26.03, 13.78; mass spectrum, m/e (relative intensity) 218 (35, M^+), 190 (19), 175 (23), 161 (22), 148 (56), 133 (22), 121 (59), 105 (41), 93 (57), 79 (58); M_r calcd for $C_{15}H_{22}O$ 218.1671, found 218.1667.

Zizanol (2) and 3-Epizizanol (1). Ketone **3** (400 mg, 1.83 mmole) was stirred with sodium borohydride (500 mg, 12.9 mmol) in 12 mL of THF and 12 mL of ethanol at room temperature for 5 h. The excess sodium borohydride was destroyed with water and the solvents were evaporated in vacuo. Normal workup and separation of the crude product on HPLC (SKB/EtOAc = 8/1) yielded 190 mg of zizanol[2] (**2**) (47%) and 95 mg of 3-epizizanol[2] (**1**) (24%). Zizanol (**2**): mp 58.5–60 °C; ^1H NMR ($CDCl_3$) δ 1.03 (d, 3, J = 6.4 Hz), 1.05 (s, 3), 1.07 (s, 3), 1.2–1.9, (m, 9), 2.11 (d, 1, J = 6.4 Hz), 2.53 (m, 1), 3.86 (dt, 1, J = 3.2 and 7.2 Hz), 4.57 (t, 1, J = 1.6 Hz), 4.74 (t, 1, J = 1.6 Hz); IR ($CHCl_3$) 3605, 3540–3250, 3085, 1635, 890 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 156.00, 105.28, 81.06, 53.70, 50.53, 48.90, 46.81, 40.23, 36.32, 36.18, 33.57, 28.40, 26.05, (2 carbons), 17.02; mass spectrum, m/e (relative intensity) 220 (4, M^+), 202 (18), 187 (9), 159 (21), 150 (46), 131 (30), 117 (9), 91 (14); M_r calcd for $C_{15}H_{24}O$ 220.1827, found 220.1836. 3-Epizizanol (**1**): mp 73–75 °C; ^1H NMR ($CDCl_3$) δ 0.98 (d, 3, J = 8 Hz), 1.06 (s, 3), 1.10 (s, 3), 1.2–2.4 (m, 10), 2.85 (7, 1), 4.35 (dt, 1, J = 3.5 and 7 Hz), 4.59 (t, 1, J = 1.5 Hz), 4.76 (t, 1, J = 1.5 Hz); IR ($CHCl_3$) 3615, 3550–3300, 3080, 1630, 890 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 156.41, 104.87, 73.75, 54.40, 48.91, 46.02, 45.35, 40.48, 36.44, 34.84, 32.66, 28.57, 26.17, 25.93, 11.03; mass spectrum, m/e (relative intensity) 220 (14, M^+), 202 (57), 187 (100), 159 (68), 146 (38), 131 (64), 95 (75), 83 (62); M_r calcd for $C_{15}H_{24}O$ 220.1827, found 220.1834.

Mesylate 5. Zizanol (**2**) (190 mg, 0.86 mmol) was stirred with mesyl chloride (0.8 mL, 10.3 mmol) in 12 mL of pyridine at room temperature for 11 h. After the volatile material was evaporated in vacuo, normal workup and separation of the crude product on HPLC (SKB/EtOAc = 8/1) yielded 220 mg of mesylate **5** (85%): ^1H NMR ($CDCl_3$) δ 1.07 (s, 6), 1.10 (d, 3, J = 5 Hz), 1.25–2.80 (m, 11), 2.99 (s, 3), 4.61 (7, 1), 4.73 (7, 1), 4.82 (m, 1); IR ($CHCl_3$) 3080, 1635, 1355, 1330, 1170, 890 cm^{-1}; ^{13}CMR ($CDCl_3$) δ 155.04, 105.90, 89.27, 53.50, 48.66, 47.75, 46.00, 40.23, 38.36, 35.97, 33.43, 32.81, 28.30, 25.95 (2 carbons), 16.31; mass spectrum, m/e (relative intensity) 298 (weak, M^+), 202 (28), 159 (34), 145 (19), 131 (78), 119 (22), 105 (37), 91 (45), 79 (47); M_r calcd for $C_{16}H_{26}O_3S$ 298.1603; found 298.1610.

Zizaene (4). Mesylate **5** (99 mg, 0.33 mmol) was heated at reflux with lithium aluminum hydride (200 mg, 5 mmol) in 18 mL of ether for 10 h. After the reaction was quenched sequentially with 0.2 mL of water, 0.2 mL of 15% aqueous sodium hydroxide, and 0.6 mL of water, the white precipitate was filtered and the ether was evaporated in vacuo. The residue was passed through silica gel and separated by HPLC (SKB/EtOAc = 30/1) to yield 67 mg of zizaene[8] (**4**) (99%); ^1H NMR ($CDCl_3$) δ 0.94 (d, 3, J = 6 Hz), 1.04 (s, 3), 1.08 (s, 3), 1.2–2.4 (m, 12), 2.53 (mt, 1, J = 9 Hz), 4.61 (t, 1, J = 1.5 Hz), 4.75 (t, 1, J = 1.5 Hz); IR ($CHCl_3$) 3080, 1630, 885 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 157.32, 104.94, 54.84, 49.27, 47.27, 40.47, 40.38, 36.19, 31.77, 28.63, 26.09, 26.01, 24.90, 20.00; mass spectrum, m/e (relative intensity) 204 (13, M^+), 161 (13), 134 (90), 119 (38), 107 (23), 91 (46), 79 (30); these spectral data are the same as for natural zizaene and clearly different from

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(8) Coates, R. M.; Sowerby, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 5396.

those for 2-epizizaene[9] (e.g., in 2-epizizaene the C-2 methyl group is at δ 0.87; M_r calcd for $C_{15}H_{24}$ 204.1878, found 204.1874.

Mesylate 6. 3-Epizizanol (1) (95 mg, 0.43 mmol) was treated with mesyl chloride (0.4 mL, 5.17 mmol) in pyridine (8 mL) as described for the preparation of mesylate **5**. Separation of the crude product on HPLC yielded 102 mg of mesylate **6** (79%): ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 3), 1.06 (d, 3, J = 7 Hz), 1.10 (s, 3), 1.25–2.55 (m, 10), 2.88 (mt, 1, J = 9 Hz), 3.01 (s, 3), 4.60 (br s, 1), 4.82 (br s, 1), 5.17 (dt, 1, J = 3.5 and 9 Hz); IR ($CHCl_3$) 3085, 1630, 1350, 1325, 1170 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 155.25, 105.58, 83.95, 53.87, 48.70, 45.35, 45.09, 40.45, 38.16, 36.15, 32.49, 32.41, 28.44, 26.06, 25.84, 12.08; mass spectrum, m/e (relative intensity) 298 (weak, M$^+$), 202 (16), 187 (23), 159 (29), 145 (19), 131 (37), 119 (16), 105 (22), 91 (30), 79 (23); M_r calcd for $C_{16}H_{26}O_3S$ 298.1603; found 298.1613.

Phenylselenyl Compound 7 and Diene 9. Sodium borohydride (35 mg, 0.9 mmol) was stirred with diphenyl diselenide (140 mg, 0.45 mmol) in 15 mL of ethanol to generate the colorless phenylselenide anion. Mesylate **5** (270 mg, 0.91 mmol) was added to the phenylselenide anion and then heated at reflux for 12 h. After 0.5 mL of water was added to the mixture, the ethanol was evaporated in vacuo. The residue was passed through silica gel and separated by HPLC (SKB/EtOAc = 30/1) to yield 38 mg of starting material **5** and the phenylselenyl compound **7** which was a little contaminated with PhSeX (presumably, X = H). Without further purification, the phenylselenyl compound **7** was heated at reflux with sodium periodate (2.00 g, 9.35 mmol) and sodium bicarbonate (400 mg, 4.76 mmol) in 20 mL of THF and 2 mL of water for 13 h. Normal workup and separation of the crude product on HPLC (SKB/EtOAc = 30/1) yielded 118 mg of a colorless oil, diene **9** (64%). Compound **7**: ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 6), 1.08 (d, 3, J = 6 Hz), 1.2–2.6 (m, 10), 2.86 (mt, 1, J = 9 Hz), 3.88 (td, 1, J = 6.5 and 9 Hz), 4.60 (m, 1), 4.79 (m, 1), 7.1–7.4 (m, 3), 7.4–7.8 (m, 2); ^{13}C NMR ($CDCl_3$) δ 156.15, 132.60, 131.59, 129.15, 128.93, 127.70, 126.47, 105.41, 55.27, 49.00, 45.63 (3 carbons), 40.49, 36.42, 33.40, 31.99, 28.66, 26.27, 26.05, 15.88; mass spectrum, m/e (relative intensity) 360 (weak, M$^+$), 289 (1), 202 (2), 187 (1), 159 (2), 131 (3), 91 (2), 73 (2); M_r calcd for $C_{21}H_{28}Se$ 360.1356; found 360.1354. Compound **9**: ^{1}H NMR ($CDCl_3$) δ 0.94 (d, 3, J = 6.5 Hz), 1.07 (s, 3), 1.11 (s, 3), 1.2–2.7 (m, 8), 3.47 (br s, 1), 4.73 (m, 2), 5.6–6.0 (m, 2); IR ($CHCl_3$) 3080, 1635, 885 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 154.36, 137.82, 128.77, 103.67, 55.27, 53.20, 49.64, 47.49, 40.62, 35.13, 33.76, 27.78, 25.96, 25.62, 14.89; mass spectrum, m/e (relative intensity) 202 (26, M$^+$) 187 (33), 159 (74), 145 (34), 131 (100), 119 (55), 105 (66), 91 (98), 77 (52).

Phenylselenyl Compound 8 and Dienes 9 and 10. Mesylate **6** (250 mg, 0.84 mmol) was treated with sodium borohydride (45 mg, 1.16 mmol) and diphenyl diselenide (150 mg, 0.48 mmol) in 15 mL of ethanol as described for the preparation of the phenylselenyl compound **7**. The resulting phenylselenyl compound **8** was subjected to the same treatment as in oxidative elimination reaction of the phenylselenyl compound **7**. Separation of the crude product on HPLC gave 129 mg of an unseparable mixture of dienes **9** and **10** (76%), of which GC–mass spectroscopic analysis showed the ratio of **9**:**10** = 3.5:1. The major product **9** of the mixture was identical with the product derived from mesylate **5** as judged by ^{1}H NMR, ^{13}C NMR, and mass spectrum. Compound **8**: ^{1}H NMR ($CDCl_3$) δ 0.95–1.10 (d, 3), 1.04 (s, 6), 1.2–2.9 (m, 11), 3.10 (m, 1), 4.53 (m, 1), 4.71 (m, 1), 7.2–7.5 (m, 3), 7.5–7.8 (m, 2); ^{13}C NMR ($CDCl_3$) 155.48, 134.19, 131.57, 129.14, 128.81, 127.69, 127.07, 105.47, 54.37, 48.86, 48.70, 48.43, 47.78, 40.21, 36.36, 35.38, 33.50, 28.33, 25.90 (2 carbons), 18.99; mass spectrum, m/e (relative intensity) 360 (2, M$^+$), 289 (3), 234 (7), 202 (16), 159 (14), 131 (27), 91 (18), 77 (20); M_r calcd for $C_{21}H_{28}Se$ 360.1356; found 360.1364. Compound **10** (as the minor isomer of the mixture): ^{1}H NMR ($CDCl_3$) δ 5.36 (m); ^{13}C NMR ($CDCl_3$) δ 123.37, 104.79; GC–mass spectrum, m/e (relative intensity) 202 (20, M$^+$), 187 (5), 159 (22), 147 (17), 131 (100), 119 (25), 105 (45), 91 (63), 77 (38).

Registry No. **1**, 28624-26-2; **2**, 28102-79-6; **3**, 28051-97-0; **4**, 18444-94-5; **5**, 91466-52-3; **6**, 91548-24-2; **7**, 91466-53-4; **8**, 91548-25-3; **9**, 91466-54-5; **10**, 91466-55-6.

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Friedel-Crafts Reactions of Tetramethylphenyl Ketones with Tetramethylbenzenes

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In a previous article we reported a novel reaction of the hindered ketones acetomesitylene and propiomesitylene with mesitylene which results in the formation of 1,1-dimesitylethene and 1,1-dimesitylpropene, respectively.[1] In this paper we extend our study to the reaction of the tetramethylbenzenes with the corresponding tetramethylphenyl ketones in order to see the effect of increasing the nucleophilicity of the aromatic hydrocarbon and the steric hindrance of the ketone upon the course of the reaction leading to 1,1-diarylalkenes.

We describe here the reactions of durene (1,2,4,5-tetramethylbenzene, **1**), isodurene (1,2,3,5-tetramethylbenzene, **2**), and prehnitene (1,2,3,4-tetramethylbenzene) with acetyl and propionyl chloride and also the reactions of the acetyl and propionyl derivatives of each of these tetramethylbenzenes with the parent hydrocarbons.

Durene. Heating a mixture of durene, acetyl chloride, and $AlCl_3$ at 100 °C for 6 h in a molar ratio of 2:1:0.25, respectively, gave acetyldurene (**3a**, 18%) and 1,1-didurylethene (**7a**, 25%).[2] Similarly, the reaction of durene with propionyl chloride gave propiodurene (**3b**, 12%) and 1,1-didurylpropene (**7b**, 40%).

Isodurene. Heating a mixture of isodurene, acetyl chloride, and $AlCl_3$ in a molar ratio of 2:1:0.25, respectively, at 100 °C for 6 h gave acetoisodurene (**4a**) and 1,1-diisodurylethene (**8a**) in 13% and 50% yields, respectively. Similarly, the use of propionyl chloride in place of acetyl chloride led to the formation of propioisodurene (**4b**) and 1,1-diisodurylpropene (**8b**) in 12% and 78% yields, respectively.

The intermediacy of the ketones **3a**, **3b**, **4a**, and **4b** was confirmed by preparing them by acylation at low temperature and then heating them with durene or isodurene and $AlCl_3$ at 150–160 °C to yield the diarylalkenes **7a**, **7b**, **8a**, and **8b**.

Prehnitene. Unlike the reactions of durene and isodurene, the reaction of prehnitene with acetyl chloride and propionyl chloride gave only the acyl prehnitenes. No 1,1-diprehnitylalkenes could be isolated from these reactions, nor could they be obtained by reaction of the acylprehnitenes with prehnitene.

It is clear from these results that the three tetramethylbenzenes are acylated normally by acetyl and propionyl chlorides to give the corresponding tetramethylphenyl ketones, but whereas the acyldurenes and acylisodurenes react further with another hydrocarbon molecule to give the corresponding 1,1-diarylalkenes, as in the case of the trimethylbenzenes,[1] the acylprehnitenes fail to react further to give the 1,1-diarylalkenes.

This different behavior of the acylprehnitenes can be explained in terms of combined steric and electronic effects. As in the case of acylmesitylenes,[1] the two ortho methyl groups in acyldurene and acylisodurene prevent coplanarity of the carbonyl group with the aromatic ring. A positive charge on the carbonyl carbon cannot be dissipated into the ring as it can be in an acylprehnitene, which has only one ortho methyl group. This leads to the

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