Anal. Calcd for $C_{18}H_{16}N_4O_4$ (DNP): C, 61.36; H, 4.58. Found: C, 61.15; H, 4.68.

2-Methyl-3-*n*-propylindenone (entry 5): yellow liquid; IR (neat) 2900, 1705, 1625, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 4 H), 2.5 (t, J = 7 Hz), 1.80 (s, 3 H, C-2 methyl), 1.4–1.9 (m, 2 H), 1.0 (t, J = 7 Hz, 3 H); DNP, mp 230–231 °C (from chloroform–methanol).

Anal. Calcd for $C_{19}H_{18}N_4O_4$ (DNP): C, 62.28; H, 4.95. Found: C, 62.20; H, 5.00.

2-*n*-Propyl-3-methylindenone (entry 5): yellow liquid; IR (neat) 2900, 1705, 1625, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 4 H), 2.26 (t, J = 7 Hz, 2 H), 2.11 (s, 3 H, C-3 methyl), 1.2–1.7 (m, 2 H), 0.93 (t, J = 7 Hz, 3 H); DNP, mp 195.5–197 °C (from chloroform–methanol).

Anal. Calcd for $C_{19}H_{18}N_4O_4$ (DNP): C, 62.28; H, 4.95. Found: C, 62.20; H, 5.09.

2-Methyl-3-*tert*-butylindenone (entry 6): yellow solid; mp 33–34.5 °C (from petroleum ether); IR ($CHCl_3$) 2910, 1705, 1605, 1580, 1565 cm^{-1}; NMR ($CDCl_3$) δ 7.0–7.4 (m, 4 H), 2.0 (s, 3 H, C-2 methyl), 1.46 (s, 9 H); DNP, mp 239–240 °C (from chloroform–methanol).

Anal. Calcd for $C_{20}H_{20}N_4O_4$ (DNP): C, 63.15; H, 5.30. Found: C, 62.05; H, 5.24.

Satisfactory analytical data could not be obtained for this compound; however, all spectral data are consistent with the assigned structure.

2-*tert*-Butyl-3-methylindenone (entry 6): yellow solid; mp 58–59 °C (from petroleum ether); IR ($CHCl_3$) 2925, 1705, 1605, 1580 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.4 (m, 4 H), 2.25 (s, 3 H, C-3 methyl), 1.36 (s, 9 H).

Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 84.19; H, 8.15.

2-Methyl-3-phenylindenone (entry 7):[18] orange solid; mp 83–84 °C (from ethanol) (lit.[18] mp 83.5–85 °C); IR ($CHCl_3$) 2990, 1705, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.4 (m, 4 H), 7.46 (s, 5 H), 1.90 (s, 3 H, C-2 methyl).

2-Phenyl-3-methylindenone (entry 7):[19] orange solid; mp 69–70 °C (from ethanol) (lit.[19] mp 69–70 °C); IR ($CHCl_3$) 2990, 1705, 1598 cm^{-1}; NMR ($CDCl_3$) δ 7.0–7.5 (m, 4 H), 7.36 (s, 5 H), 2.26 (s, 3 H, C-3 methyl).

2-*n*-Butylindenone (entry 8):[8] yellow solid; mp 32.5–33 °C (from petroleum ether) (lit.[8] mp 35–36 °C); IR ($CHCl_3$) 2990, 1705, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 5 H), 2.1–2.3 (m, 2 H), 1.1–1.7 (m, 4 H), 0.95 (t, 3 H).

2-*tert*-Butylindenone (entry 9): yellow liquid; IR (neat) 2990, 1705, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.8–7.5 (m, 5 H), 1.25 (s, 9 H); DNP, mp 272.5–273.5 °C (from chloroform–methanol).

Anal. Calcd for $C_{19}H_{18}N_4O_4$ (DNP): C, 62.28; H, 4.95. Found: C, 61.97; H, 5.07.

2-Cyclohexylindenone (entry 10): yellow solid; mp 48–49 °C (from petroleum ether); IR ($CHCl_3$) 2990, 1705, 1605 cm^{-1}; NMR ($CDCl_3$) δ 6.9–7.5 (m, 5 H), 2.2–2.5 (m, 1 H), 1.2–2.1 (m, 10 H); DNP, mp 225.5–227 °C (from chloroform–methanol).

Anal. Calcd for $C_{21}H_{20}N_4O_4$ (DNP): C, 64.27; H, 5.14. Found: C, 64.02; H, 5.25.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to Research Corp., and to the National Cancer Institute, DHEW (Grant No. CA 26374), for support of this research.

Registry No. 3-Hexyne, 928-49-4; 2-butyne, 503-17-3; diphenylacetylene, 501-65-5; 2-pentyne, 627-21-4; 2-hexyne, 764-35-2; 4,4-dimethyl-2-pentyne, 999-78-0; (1-propynyl)benzene, 673-32-5; 1-hexyne, 693-02-7; 3,3-dimethyl-1-butyne, 917-92-0; ethynylcyclohexane, 931-48-6; 2,3-diethylindenone, 75421-58-8; 2,3-dimethylindenone, 2887-89-0; 2,3-diphenylindenone, 1801-42-9; 2-methyl-3-ethylindenone, 59046-71-8; 2-ethyl-3-methylindenone, 75421-59-9; 2-methyl-3-*n*-propylindenone, 75421-60-2; 2-*n*-propyl-3-methylindenone, 75421-61-3; 2-methyl-3-*tert*-butylindenone, 75421-62-4; 2-*tert*-butyl-3-methylindenone, 75421-63-5; 2-methyl-3-phenylindenone, 13304-52-4; 2-phenyl-3-methylindenone, 10408-73-8; 2-*n*-butylindenone, 24741-71-7; 2-*tert*-butylindenone, 75421-64-6; 2-cyclohexylindenone, 75421-65-7; 2,3-diethylindenone DNP, 75421-66-8; 2-ethyl-3-methylindenone DNP, 75421-67-9; 2-methyl-3-*n*-propylindenone DNP, 75421-68-0; 2-*n*-propyl-3-methylindenone DNP, 75421-69-1; 2-methyl-3-*tert*-butylindenone DNP, 75421-70-4; 2-*tert*-butylindenone DNP, 75421-71-5; 2-cyclohexylindenone DNP, 75421-72-6; *o*-diiodobenzene, 615-42-9; $Ni(CO)_4$, 13463-39-3; $Pd(PPh_3)_4$, 14221-01-3.

(18) H. E. Zimmerman, *J. Am. Chem. Soc.*, **78**, 1168 (1956).
(19) C. F. Koelsch and R. V. White, *J. Am. Chem. Soc.*, **65**, 1639 (1943).

Communications

Base-Induced Conversions of [8 + 2]π Cycloadducts from Azaheptafulvenes and Monosubstituted Ketenes to (*Z*)-α-Substituted Cinnamamides

Summary: The [8 + 2]π cycloadducts from azaheptafulvenes and monosubstituted ketenes rearrange upon treatment with base to give in good yields the amide derivatives of the (*Z*)-α-substituted cinnammic acids.

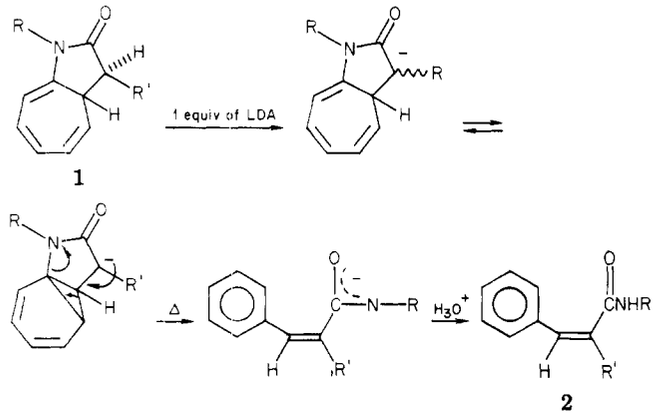
Sir: Substituted ketenes and 8-azaheptafulvenes, generated (not isolated) from the corresponding acyl chlorides and 8-azaheptafulvenium fluoroborates by use of triethylamine as a base, react to give [8 + 2] cycloadducts.[1,2] The cycloadducts, tentatively assigned trans (exo) stereochemistry,[1,3] when treated with LDA at 0 °C and warmed (refluxed), rearrange to the corresponding amide of (*Z*)-α-aryl(or alkyl)cinnammic acid in good yields (Scheme I, Table I). The rearrangement presumably proceeds through a norcaradiene intermediate.[4-6]

The *Z* configuration was confirmed by comparison with authentic *N*-(*p*-bromophenyl)-α-methylcinnamamide.[7-9]

(1) K. Yamamoto, S. Kajigaeshi, and S. Kanemasa, *Chem. Lett.*, 91 (1977).
(2) *N*-Aryl adducts are obtained in 70–80% yield and *N*-alkyl adducts in 40–45% yield.
(3) Treatment of the adduct (R = *p*-C_7H_7, R' = C_6H_5) in THF at −78 °C with 1 equiv of LDA followed by quenching at the same temperature resulted in no isomerization. Inspection of models confirms that the trans (exo) isomer is less strained.
(4) W. von E. Doering and D. B. Denney, *J. Am. Chem. Soc.*, **77**, 4619 (1955).
(5) W. E. Truce and J. P. Shepherd, *J. Am. Chem. Soc.*, **99**, 6453 (1977).
(6) S. W. Staley, M. A. Fox, and A. Cairncross, *J. Am. Chem. Soc.*, **99**, 4524 (1977).
(7) Y. Kishi and M. R. Johnson, *Tetrahedron Lett.*, 4347 (1979).
(8) R. J. DeFeoand and P. D. Strickler, *J. Org. Chem.*, **28**, 2915 (1963).
(9) L. A. Singer and N. P. Kong, *J. Am. Chem. Soc.*, **88**, 5213 (1966).

0022-3263/80/1945-5429$01.00/0

Scheme I



All rearrangement products exhibit a vinylic proton signal at δ 6.57–6.58 except when R′ = phenyl (δ 7.05).

The time and temperature required to effect rearrangement show a dependency on the nature of the group attached to nitrogen. Rearrangement occurs at room temperature when the substituent group is alkyl or mesityl; however, with other aryl substituents on nitrogen, the temperature required to effect complete rearrangement is increased. This may bear some analogy to the π-electron-donor effect on the cycloheptatriene–norcaradiene equilibrium.[6]

The general procedure for rearrangement was as follows. The reaction was carried out in a 50-mL round-bottomed flask equipped with a nitrogen inlet tube, reflux condenser, and a Teflon magnetic stirring bar. The glassware was assembled cold, flame-dried, and allowed to cool under a stream of nitrogen. The ketene–azaheptafulvene cycloadduct (6–8 mmol) was added to the cooled apparatus. DME (15–20 mL, previously dried over sodium ribbon and freshly distilled) was added via syringe and the cycloadduct brought into solution by stirring. This solution was cooled to between −5 and 0 °C with the aid of an ice–salt bath.

Lithium diisopropylamide was prepared in the following manner. To a 50-mL round-bottomed flask equipped with nitrogen inlet tube, rubber stopper, and a Teflon magnetic stirring bar was added 1 equiv of diisopropylamine (previously dried and distilled over sodium ribbon) via syringe. DME (5–10 mL) was added via syringe, and stirring was initiated. The solution was cooled to −5 °C with an ice–salt bath. An equimolar amount of *n*-BuLi/hexane was added via syringe in a dropwise fashion. The solution was then stirred at −5 °C for 45 min.

A double-ended needle was used to transfer the LDA solution dropwise to the original flask containing the cycloadduct. One hour after the addition of LDA, the ice–salt bath was removed, and the reaction mixture was either allowed to warm to room temperature or brought to reflux (depending upon consumption of starting material as monitored by NMR). After quenching with 2% CH_3CO_2H/THF, the reaction mixture was diluted with water (25 mL) and extracted with methylene chloride (2 × 50 mL). The organic extracts were dried ($MgSO_4$), the CH_2Cl_2 was removed in vacuo, and the crude product was purified by column chromatography (silica gel eluted with benzene).

Table I.[a,d] (*Z*)-α-Aryl(or Alkyl)cinnamamides

R	R′ (mp, °C)	% yield[b,c]
$CH_3C_6H_4$	CH_3 (113–114), $C_6H_5CH_2$ (158–160), $(CH_3)_2CH$ (164–166), $(CH_3)_3C$ (170–172), C_6H_5 (189–191.5)	71.0–76.0
$CH_3OC_6H_4$	CH_3 (114–115.5), $C_6H_5CH_2$ (155–157), $(CH_3)_2CH$ (177–179.5), $(CH_3)_3C$ (175–176.5), C_6H_5 (198.5–200)	69.0–86.2
ClC_6H_4	CH_3 (140–141.5), $C_6H_5CH_2$ (173–175), $(CH_3)_2CH$ (169.5–171.5), $(CH_3)_3C$ (174–175.5), C_6H_5 (190–192.5)	70.1–77.0
BrC_6H_4	CH_3 (135–136.5), $C_6H_5CH_2$ (165–167), $(CH_3)_2CH$ (182.5–184), $(CH_3)_3C$ (163–165), C_6H_5 (195–196.5)	68.0–78.0
CH_3	$(CH_3)_3C$ (139–141.5)	86.8
$(CH_3)_3C$	C_6H_5 (152–153.5)	85.7
mesityl	C_6H_5 (179–180.5)	83.7

[a] Reactions carried out in DME. [b] Yields are actual isolated yields. [c] All products were purified by column chromatography. [d] Products were characterized by nuclear, IR, and mass spectroscopic data.

Registry No. 1 (R = $CH_3C_6H_4$; R′ = CH_3), 75234-12-7; 1 (R = $CH_3C_6H_4$; R′ = $C_6H_5CH_2$), 75234-13-8; 1 (R = $CH_3C_6H_4$; R′ = $(CH_3)_2CH$), 75247-64-2; 1 (R = $CH_3C_6H_4$; R′ = $(CH_3)_3C$), 75247-65-3; 1 (R = $CH_3C_6H_4$; R′ = C_6H_5), 62515-90-6; 1 (R = $CH_3OC_6H_4$; R′ = CH_3), 75247-66-4; 1 (R = $CH_3OC_6H_4$; R′ = $C_6H_5CH_2$), 75247-67-5; 1 (R = $CH_3OC_6H_4$; R′ = $(CH_3)_2CH$), 75247-68-6; 1 (R = $CH_3OC_6H_4$; R′ = $(CH_3)_3C$), 75247-69-7; 1 (R = $CH_3OC_6H_4$; R′ = C_6H_5), 62515-89-3; 1 (R = ClC_6H_4; R′ = CH_3), 75247-70-0; 1 (R = ClC_6H_4; R′ = $C_6H_5CH_2$), 75247-71-1; 1 (R = ClC_6H_4; R′ = $(CH_3)_2CH$), 75247-72-2; 1 (R = ClC_6H_4; R′ = $(CH_3)_3C$), 75247-73-3; 1 (R = ClC_6H_4; R′ = C_6H_5), 62515-91-7; 1 (R = Br C_6H_4; R′ = CH_3), 75247-74-4; 1 (R = BrC_6H_4; R′ = $C_6H_5CH_2$), 75247-75-5; 1 (R = BrC_6H_4; R′ = $(CH_3)_2CH$), 75247-76-6; 1 (R = BrC_6H_4; R′ = $(CH_3)_3C$), 75247-77-7; 1 (R = BrC_6H_4; R′ = C_6H_5), 75247-78-8; 1 (R = CH_3; R′ = $(CH_3)_3C$), 75247-79-9; 1 (R = $(CH_3)_3C$; R′ = C_6H_5), 75247-80-2; 1 (R = mesityl; R′ = C_6H_5), 75247-81-3; 2 (R = $CH_3C_6H_4$; R′ = CH_3), 75234-14-9; 2 (R = $CH_3C_6H_4$; R′ = $C_6H_5CH_2$), 75234-15-0; 2 (R = $CH_3C_6H_4$; R′ = $(CH_3)_2CH$), 75234-16-1; 2 (R = $CH_3C_6H_4$; R′ = $(CH_3)_3C$), 75234-17-2; 2 (R = $CH_3C_6H_4$; R′ = C_6H_5), 75234-18-3; 2 (R = $CH_3OC_6H_4$; R′ = CH_3), 75247-82-4; 2 (R = $CH_3OC_6H_4$; R′ = $C_6H_5CH_2$), 75234-15-0; 2 (R = $CH_3OC_6H_4$; R′ = $(CH_3)_2CH$), 75234-19-4; 2 (R = $CH_3OC_6H_4$; R′ = $(CH_3)_3C$), 75234-20-7; 2 (R = $CH_3OC_6H_4$; R′ = C_6H_5), 75247-83-5; 2 (R = ClC_6H_4; R′ = CH_3), 75234-21-8; 2 (R = ClC_6H_4; R′ = $C_6H_5CH_2$), 75234-22-9; 2 (R = ClC_6H_4; R′ = $(CH_3)_2CH$), 75234-23-0; 2 (R = ClC_6H_4; R′ = $(CH_3)_3C$), 75234-24-1; 2 (R = ClC_6H_4; R′ = C_6H_5), 75234-25-2; 2 (R = BrC_6H_4; R′ = CH_3), 75234-26-3; 2 (R = BrC_6H_4; R′ = $C_6H_5CH_2$), 75234-27-4; 2 (R = BrC_6H_4; R′ = $(CH_3)_2CH$), 75247-84-6; 2 (R = BrC_6H_4; R′ = $(CH_3)_3C$), 75247-85-7; 2 (R = BrC_6H_4; R′ = C_6H_5), 75234-28-5; 2 (R = CH_3; R′ = $(CH_3)_3C$), 75234-29-6; 2 (R = $(CH_3)_3C$; R′ = C_6H_5), 75247-86-8; 2 (R = mesityl; R′ = C_6H_5), 75234-30-9.

Barry D. Dean, William E. Truce*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received June 17, 1980

Total Synthesis of (−)-Prezizaene and (−)-Prezizanol

Summary: An 18-step total synthesis of the novel zizaane sesquiterpenes, (−)-prezizaene (**1**) and (−)-prezizanol (**2**), from (+)-pulegone is described; the key step of the synthesis is the intramolecular ring expansion of (diazoethyl)hydrindanone **12** to the isomeric methanoperhydroazulenones **13** and **14**.

Sir: The tricyclic sesquiterpene prezizaene was first iso-

0022-3263/80/1945-5430$01.00/0