(7) Å for two crystallographic forms of **5** and 1.339 (6) Å for **6**. It seems therefore that in spite of the unrealistic input value, the calculation converges on a realistic C=C bond length, and the value clearly shows C=C elongation which reflects the relief of steric congestion. Similarly, all the calculated C(Aryl)–C(double bond) bond lengths are in the normal range 1.48–1.51 Å (the average bond length between single-bonded sp^2 carbons is 1.48 Å),[19] while the calculated C(1)–O bond length is 1.36 Å. Again, these values are similar to the corresponding distances found[7] for enols **6** and **7**.

Bond Angles. The calculated double bond angles are found to be in agreement with the crystallographic values for related enols (compare the α values in Table I with Table I in ref 7). Among the α values α_4 is unusual since it is calculated to be 121° (input 126.8°), lower than that expected by comparison with the crystallographic values for related enols (129–130°).[7] While the reason for this discrepancy is unclear to us, we note that α_4 values in 2,2-dimesityl-1-alkyl enols are linearly correlated with the bulk of the alkyl substituents.[20] Hence, the smaller α_4 value may be a consequence of the less severe repulsion between the α–mesityl and the less bulky β-aryl (as compared with the β-mesityl) groups. Moreover, a systematic analysis of double bond angles in tri– and tetraarylvinyl systems reveals that α_4 values as small as 122° occur in systems of the type Ar″Ar′C=C(Et)Ar.[21]

Torsional Angles. The torsional angles calculated for **1** are similar to those found by X-ray diffraction.[7] The values are closer for the β-mesityl and phenyl rings (calculated values 74° and 39°; experimental values 74° and 38°, respectively) than for the α-mesityl ring (67° vs. 72°). The difference may reflect the intervention of packing forces. A gratifying aspect is that our calculation stresses that the propeller conformation represents a minimum energy conformation, at least local, for an isolated triarylvinyl molecule in the gas phase. This is complementary of previous evidence in solution which is based on NMR[6] and on the analysis of the solid by X-ray diffraction.[7]

The OH Conformation. In addition to the input crystallographic syn conformation of the C=C—OH moiety, the positions of the lone pairs and proton on oxygen were permuted, resulting in two other input structures, both nonplanar anti conformations. On optimization, each of the three input structures relaxed into that planar conformation, syn or anti, that was closer to it. This is irremediable in the present version of the force field, since both planar conformations have one syn and one anti $C(sp^2)C(sp^2)OH$ combination, and the program takes C=C—OH and C(aryl)—C(=C)—OH to be torsionally equivalent. The geometry with anti C=C—OH came out higher by 0.1 kcal mol^{-1} in energy than the syn. Bond lengths and bond and dihedral angles (apart from C=C—OH) are similar in the two final structures. Since the program does not take hydrogen bonding into account, neither intramolecular to the aryl cis to OH nor to the external solvent, comparison with solution OH conformation, which is determined mainly by these interactions,[8] is of little value. However, we note that the planar conformations are more stable than the gauche conformation and that in the solid state the conformation of the OH is syn periplanar.[7]

Dipole Moment. The MM2 force field predicted for vinyl alcohol[13] a dipole moment of 1.24 D, in good agreement with the measured value of 1.016 ± 0.009 D.[16] Calculation for **1** afforded again 1.24 D, which is not unexpected since the $C(sp^2)$–$C(sp^3)$ bond moments for the two mesityl rings would roughly cancel on vectorial summation, due to their mutual trans arrangement. In order to check the prediction, the dipole moment of **1** was measured,[22] and the value obtained is 1.08 D.

Conclusions. The conformation and bond lengths and angles for (*Z*)-1,2-dimesityl-2-phenylethenol (**1**) were calculated by molecular mechanics. The results are complementary to previous findings on the structure and conformation in the solid state and in solution of crowded triarylethenols and provide structural parameters that seem more reliable than those obtained from the X-ray diffraction of the disordered crystals of **1**. The calculated dipole moment is in good agreement with the experimental value.

Acknowledgment. We thank Prof. N. L. Allinger for his hospitality and generous contribution of computer time and Dr. H. Weiler-Feilchenfeld for measuring the dipole moments. This work was supported by a grant from the United States–Israel Binational Science Foundation (BSF), Jerusalem, Israel, for which we are indebted.

Registry No. 1, 77787-79-2.

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(22) Measurement was conducted in benzene at 30 °C, according to: Halverstadt, I. F.; Kumler, J. *J. Am. Chem. Soc.* **1942**, *64*, 2988. The measured molar refraction R_m is 116.592 cm^3 for 1 and 111.978 cm^3 for 2. The polarizations P are respectively 138.898 and 260.159 cm^3.

Synthesis of Carbocycles by the Interaction of Ambiphilic Reagents. Reactions of Cationic Oxyallyl-Iron(II) Complexes with η^1-Allyliron(II) Complexes and with *N*-Tosyl Enamines

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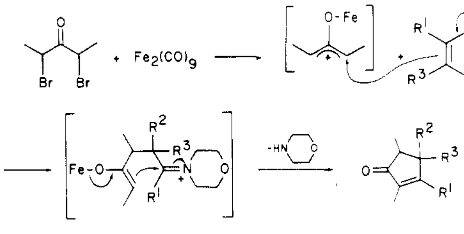
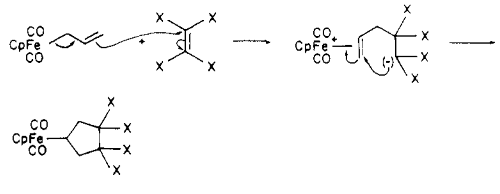
Received April 2, 1985

Ambiphilic reagents are useful for reactions involving the sequential formation of two bonds since they can alternately function as nucleophiles and electrophiles. Many organometallic complexes are ambiphilic and several that effect efficient carbocycle formation have been developed. For example, cationic oxyallyl–iron complexes, from the reaction of α,α'-dihalo ketones with $Fe_2(CO)_9$, react with enamines—first as an electrophile and then as a nucleophile—to annelate a five-membered ring to the enamine (eq 1).[1] Similarly, η^1-allyl(cyclopentadienyl)iron



(1)



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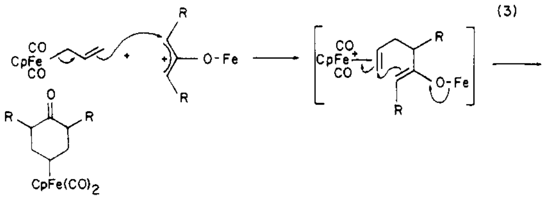
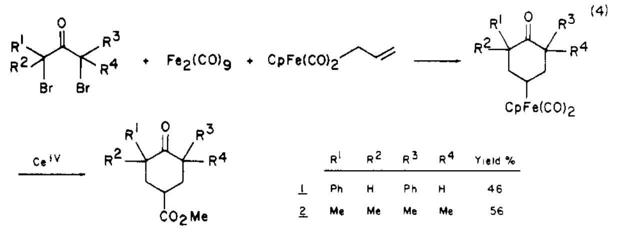
dicarbonyl reacts with electron-deficient olefins—first as a nucleophile and then as an electrophile—to form five-membered rings (eq 2).[2] Finally, "trimethylene methane" palladium complexes also annelate five-membered rings to electron-deficient olefins.[3] In all of these examples, a two-carbon ambiphile combines with a three-carbon ambiphile to produce a five-membered ring. However, both cationic oxyallyl–iron complexes and η^1-allyl(cyclopentadienyl)iron dicarbonyl are *three*-carbon ambiphiles, and reaction of these species with each other should lead to six-membered ring formation (eq 3). A study of this process as well as the results of the reactions of cationic oxyallyl–iron complexes with *N*-tosyl enamines is reported herein.



(3)

Results and Discussion

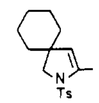
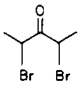
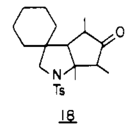
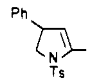
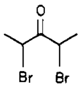
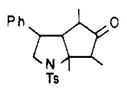
α,α'-Dibromo ketones, $Fe_2(CO)_9$, and η^1-allyl(cyclopentadienyl)iron dicarbonyl were heated at reflux in methylene chloride for 12 h and the resulting crude reaction product was oxidized with ceric ammonium nitrate in methanol, producing 4-carbomethoxycyclohexanones in modest yield (eq 4). The yields of the reaction depended strongly on the substitution pattern on the dihalo ketone. Tetrasubstituted, trisubstituted, and α,α'-disubstituted ketones underwent this cyclization reaction smoothly. In contrast, tetrabromoacetone and monosubstituted ketones failed to lead to cyclic material. This parallels the behavior observed in the reactions of enamines with cationic oxyallyl–iron complexes.[1a] α,α'-Dibromocycloheptanone also failed to produce any cyclic product, although it was consumed in the reaction and converted to uncharacterized products. This may have been due to steric strain in the expected bicyclic ketone and, again, parallels the behavior of this substrate in other cycloaddition reactions.[1a]



(4)

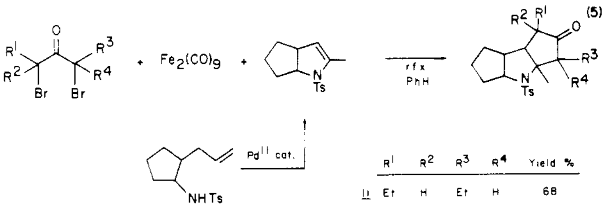
	R^1	R^2	R^3	R^4	Yield %
1	Ph	H	Ph	H	46
2	Me	Me	Me	Me	56
3	i-Pr	H	i-Pr	H	43
4	Et	H	Et	H	38
5	Me	H	Et	H	37
6	Me	H	Me	H	30
7	Me	Me	H	Me	31
8	Br	H	Br	H	--
9	H	H	Et	H	--
10	H	$-(CH_2)_4-$		H	--

Table I

substrate	ketone	product	yield, %
		 **18**	58
		 **19**	51

The yields of the reaction were also dependent on the reaction conditions employed, since it was necessary to find conditions compatible with two rather different organometallic species. The optimum conditions reflect this compromise. The isolated yields of the initially formed 4-(cyclopentadienyliron dicarbonyl)cyclohexanones were substantially higher than those of the final ester product, indicating that the efficiency of the carbon–carbon bond-forming steps was high and that there was substantial loss of material in the oxidation step. However, these organoiron complexes proved impossible to purify and difficult to handle, depositing small amounts of paramagnetic iron species upon any manipulation. Thus, direct oxidation to the free organic product, without purification of the organoiron intermediate, was carried out. As is usual with these σ-alkyliron species, oxidation promoted a carbonyl insertion, and esters resulted.

Electron-rich olefins other than enamines also undergo reaction with cationic oxallyl–iron complexes, resulting in the formation of cyclopentanones.[1] *N*-tosyl enamines have recently become available by the palladium(II)-catalyzed cyclization of *N*-tosyl aliphatic aminoolefins.[4] The fundamental chemistry of this unusual class of compounds remains relatively unexplored, and the inherent nucleophilicity of *N*-tosyl enamines is not known. Reaction of the bicyclic *N*-tosyl enamine in eq 5 with cationic oxyallyl–iron complexes produced tricyclic amino ketones 11–14 in fair yield. Again, tetrabromoacetone and α,α'-dibromocycloheptanone failed to lead to cyclic products,



(5)

	R^1	R^2	R^3	R^4	Yield %
11	Et	H	Et	H	68
12	Me	H	Me	H	61
13	Ph	H	Ph	H	42
14	Me	Me	Me	Me	44
15	Br	Br	Br	Br	--
16	i-Pr	H	i-Pr	H	--
17	H	$-(CH_2)_4-$		H	--

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as did 2,6-dimethyl-3,5-dibromo-4-heptanone. Thus, although *N*-tosyl enamines were sufficiently nucleophilic to undergo cycloaddition with cationic oxyallyl–iron complexes, they shared the substrate limitations experienced by enamines themselves, and hence, only α-alkylated cyclopentanones could by synthesized.

Other N-tosylated enamines also reacted with 2,4-dibromopentane and $Fe_2(CO)_9$ to yield the adducts shown in Table I.

Experimental Section

General. All articles of glassware used in reactions done under an inert atmosphere were oven-dried prior to use. Nuclear magnetic resonance spectra were recorded on an IBM WP-270 SY (270 MHz) or Nicolet NTC-FT 1180 (360 MHz) instrument in $CDCl_3$ using tetramethylsilane as an internal standard. Melting points were recorded on a Laboratory Devices Mel-Temp apparatus in a sealed tube and are uncorrected. Infrared spectra were recorded on a Beckman Model 4200 spectrometer. Preparative thin-layer chromatography was performed on 20 cm × 20 cm plates, with a layer of Kieselgel 60 PF-254 silica gel 1.5 mm thick, and visualization was accomplished with I_2 or UV light. Compounds were then removed from the silica gel with ethyl acetate. The use of a Chromatotron refers to the device marketed by Harrison Research, Palo Alto, CA. In vacuo distillation refers to the use of a Kugelrohr apparatus. Preparative gas chromatography (GC) was performed at the indicated oven temperature on a Hewlett-Packard Model 5890 gas chromatograph equipped with a Hewlett-Packard Model 3390A recorder using a $^1/_4$-in. 10% SE-30 on Chromasorb W column 12 ft in length. Analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Materials. (Allyl)Fp was stored as its tetrafluoroborate salt *and regenerated according to the method of Baker.*[2c] *N*-Tosyl enamines,[4] diiron nonacarbonyl,[5] and polybromo ketones[6] were prepared by known methods. Methylene chloride was dried with 4A molecular sieves, distilled and stored under argon in the dark. Methanol was fractionally distilled and stored over molecular sieves. Benzene was distilled and stored over sieves under argon. Other materials were obtained from commercial sources and used as obtained.

Formation of 4-Carbomethoxycyclohexanones. General Procedure. The indicated amounts of reactants were heated at reflux in 8 mL of methylene chloride for 12 h under an argon atmosphere. The reaction mixture was filtered through a pad of Celite 545 and the solvent removed in vacuo. The residue was taken up in 20 mL of methanol which had been previously saturated with CO by passage of a slow stream of the gas through the solvent for 2 h. A large excess of ceric ammonium nitrate (4.384 g, 8.0 mmol) was added in one portion, and the mixture was stirred for 4 h while a slow stream of CO was passed through the reaction mixture. The solvent was removed in vacuo and the residue taken up in 100 mL of H_2O. This was extracted with 3 × 100 mL of H_2O, and the combined ethereal layers were washed with 50 mL of H_2O and then 50 mL of saturated brine. The organic layer was dried (Na_2SO_4), shaken with decolorizing charcoal, and filtered and solvent removed in vacuo to yield the crude product as an orange semisolid. The products were purified by evaporative distillation followed by preparative TLC using 7:3 hexane/ethyl acetate.

4-Carbomethoxy-2,6-diphenylcyclohexanone (1). (Allyl)Fp (469 mg, 2.15 mmol), 1,3-dibromo-1,3-diphenylpropan-2-one (368 mg, 1.00 mmol), and diiron nonacarbonyl (400 mg, 1.10 mmol) were combined to yield, upon demetalation and purification, 141 *mg (46%) of 1 as a white solid (R_f 0.26). Recrystallization from* acetone/ether gave the analytical sample as white crystals: mp 173–174 °C; ^{1}H NMR (360 MHz) δ 2.37 (2, q, J = 13.2 Hz, *H*CH), 2.61–2.67 (2, m, HC*H*), 2.23 (1, t of t, J = 12.0, 3.4, 3.4 Hz, MeO_2CCH), 3.72 (3, s, CO_2CH_3), 3.86 (2, d of d, J = 13.6, 4.8 Hz, PhCH), 7.16 (4, m, Ar H), 7.32 (6, m, Ar H); IR (KBr) 1733 (CO_2Me), 1716 (C=O) cm^{-1}. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.73; H, 6.82.

4-Carbomethoxy-2,2,6,6-tetramethylcyclohexanone (2). (Allyl)Fp (488 mg, 2.24 mmol), 2,4-dibromo-2,4-dimethylpentan-3-one (272 mg, 1.00 mmol), and diiron nonacarbonyl (400 mg, 1.10 mmol) were combined to yield, upon demetalation and purification, 119 mg (56%) of **2** as a white solid (R_f 0.59). The analytical sample was obtained by sublimation [60 °C (0.05 mm)] as a white crystalline solid: mp 74–75 °C; ^{1}H NMR (360 MHz) δ 1.11 (6, s, CH_3), 1.20 (6, s, CH_3), 1.84 (2, t, J = 12.9 Hz, *H*CH), 1.96–2.02 (2, m, HC*H*), 2.99 (1, t of t, J = 12.4, 3.7, 3.7 Hz), 3.71 (3, s, CO_2CH_3); IR (KBr) 1735 (CO_2CH_3), 1698 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.49. Found: C, 68.03; H, 9.66.

4-Carbomethoxy-2,6-diisopropylcyclohexanone (3). (Allyl)Fp (493 mg, 2.26 mmol), 3,5-dibromo-2,6-dimethylheptan-4-one (300 mg, 1.00 mmol), and diiron nonacarbonyl (400 mg, 1.10 mmol) were combined to yield, upon demetalation and purification, 103 mg (43%) of **3** as a white solid (R_f 0.52). The analytical sample was obtained by sublimation [53 °C (0.10 mm)] as white crystals: mp 57–60 °C; ^{1}H NMR (360 MHz) δ 0.86 (6, d, J = 6.7 Hz, CH_3), 0.91 (6, d, J = 6.7 Hz, CH_3), 1.56 (2, m, Me_2CH), 2.04–2.35 (6, m, CH, CH_2), 2.82 (1, t of t, J = 12.6, 3.5, 3.5 Hz, MeO_2CCH), 3.71 (3, s, CO_2CH_3); IR (KBr) 1732 (CO_2Me), 1703 (C=O) cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 69.71; H, 9.90.

4-Carbomethoxy-2,6-diethylcyclohexanone (4). (Allyl)Fp (563 mg, 2.58 mmol), 3,5-dibromoheptan-4-one (272 mg, 1.00 mmol), and diiron nonacarbonyl (400 mg, 1.10 mmol) were combined to yield, upon demetalation and purification, 77 mg (38%) of **4** as a clear oil (R_f 0.53). The analytical sample was obtained by preparative GC at 190 °C: ^{1}H NMR (360 MHz) δ 0.90 (6, t, J = 7.5 Hz, CH_2CH_3), 1.24 (2, m, MeCH*H*), 1.52 (2, q, J = 12.9 Hz, COCH), 1.83 (2, m, MeC*H*H), 2.19–2.29 (2, m, HC*H*), 2.32–2.42 (2, m, *H*CH), 2.89 (1, t of t, J = 12.5, 3.6, 3.6 Hz, MeO_2CCH), 3.70 (3, s, CO_2CH_3); IR ($CHCl_3$) 1734 (CO_2Me), 1717 (C=O) cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.89; H, 9.50. Found: C, 67.50; H, 9.81.

4-Carbomethoxy-2-ethyl-6-methylcyclohexanone (5). (Allyl)Fp (412 mg, 1.89 mmol), 2,4-dibromohexan-3-one (258 mg, 1.00 mmol), and diiron nonacarbonyl (400 mg, 1.10 mmol) were combined to yield, upon demetalation and purification, 73 mg (37%) of **5** as a clear oil (R_f 0.51). The analytical sample was obtained as a clear, colorless oil by preparative GC at 180 °C: ^{1}H NMR (360 MHz) δ 0.90 (3, t, J = 7.5 Hz, CH_2CH_3), 1.04 (3, d, J = 6.5 Hz, $CHCH_3$), 1.16–1.31, 1.48–1.61, 1.77–1.91, 2.21–2.56 (8, m, CH, CH_2), 2.91 (1, t of t, J = 12.5, 3.6, 3.6 Hz, MeO_2CCH), 3.70 (3, s, CO_2CH_3); IR ($CHCl_3$) 1733 (CO_2CH_3), 1715 (C=O) cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 65.05; H, 9.27. (The sample appeared hydrated. Anal. Calcd for $C_{11}H_{18}O_3 \cdot {}^1/_4H_2O$: C, 65.16; H, 9.20).

4-Carbomethoxy-2,6-dimethylcyclohexanone (6). (Allyl)Fp (454 mg, 2.08 mmol), 2,4-dibromopentan-3-one (244 mg, 1.00 mmol), and diiron nonacarbonyl (400 mg, 1.10 mmol) were combined to yield, upon demetalation and purification, 55 mg (30%) of **6** as a clear oil (R_f 0.43). The analytical sample was obtained as a clear, colorless oil by preparative GC at 170 °C: ^{1}H NMR (360 MHz) δ 1.05 (6, d, J = 6.4 Hz, CH_3), 1.58 (2, q, J = 16.3 Hz, CH_3CH), 2.30–2.38 (2, m, *H*CH), 2.47 (2, m, HC*H*), 2.93 (1, t of t, J = 12.5, 3.6, 3.6 Hz, MeO_2CCH), 3.70 (3, s, CO_2CH_3); IR ($CHCl_3$) 1732 (CO_2Me), 1713 (C=O) cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 64.83; H, 8.94.

4-Carbomethoxy-2,2,6-trimethylcyclohexanone (7). (Allyl)Fp (473 mg, 2.17 mmol), 2,4-dibromo-2-methylpentan-3-one (258 mg, 1.00 mmol), and diiron nonacarbonyl (400 mg, 1.10 mmol) were combined to yield, upon demetalation and purification, 62 mg (31%) of **7** as a clear oil (R_f 0.49). The analytical sample was obtained as a low-melting, white solid by preparative GC at 180 °C: ^{1}H NMR (360 MHz) δ 1.03 (3, d, J = 6.5 Hz, $HCCH_3$), 1.08 (3, s, CH_3CCH_3), 1.21 (3, s, CH_3CCH_3), 1.55 (m), 1.76 (t, J = 13.3 Hz), 2.02 (d of t, J = 13.6, 3.5 Hz), 2.28 (m), 2.71 (m, 5, HCH, MeCH), 3.03 (1, t of t, J = 12.8, 3.6, 3.6 Hz), 3.70 (3, s, CO_2CH_3); IR ($CHCl_3$) 1732 (CO_2Me), 1708 (C=O) cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.85; H, 9.00.

1,3,3a,4,4a,5,6,7,7a,7b-Decahydro-1,3-diethyl-2-keto-3a-methyl-4-[(4-methylphenyl)sulfonyl]dicyclopenta[*b*,*d*]pyrrole (11). A solution of benzene (7 mL), *cis*-*N*-tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (100 mg, 0.36 mmol), 3,5-

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dibromoheptan-4-one (98 mg, 0.36 mmol), and $Fe_2(CO)_9$ (146 mg, 0.40 mmol) was heated at reflux under argon for 24 h. After the mixture was cooled, 15 mL of EtOAc was added, the solution washed with 10 mL of saturated $NaHCO_3$ and then 10 mL of saturated brine and dried ($MgSO_4$), and the solvent removed in vacuo. Preparative TLC (3:1 hexane/EtOAc: R_f 0.52) yielded 78 mg (68%) of the product as a gummy semisolid: ^{1}H NMR (360 MHz) δ 0.55, 0.74, 0.76, 0.86, 0.92, 0.94, 1.00, 1.07 (6, multiple t, CH_2CH_3), 1.3–2.3 (15, m, CH_2, CH), 1.56, 1.58 (3, 2 s, $NCCH_3$), 2.41, 2.43 (3, 2 s, $PhCH_3$), 2.96 (1, m, CH), 4.15–4.30 (1, m, CH), 7.3 (2, m, Ar H), 7.7 (2, m, Ar H); IR ($CHCl_3$) 1734 (C=O), 1600, 1495, 1450, 1344, 1153 cm^{-1}. Anal. Calcd for $C_{22}H_{31}NO_3S$: C, 67.83; H, 8.02; N, 3.60. Found: C, 67.79; H, 8.05; N, 3.54.

1,3,3a,4,4a,5,6,7,7a,7b-Decahydro-2-keto-1,3,3a-trimethyl-4-[(4-methylphenyl)sulfonyl]dicyclopenta[*b*,*d*]pyrrole (12). Under argon, a solution of benzene (7 mL), *cis*-*N*-tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (100 mg, 0.36 mmol), 2,4-dibromopentan-3-one (88 mg, 0.36 mmol), and $Fe_2(CO)_9$ (146 mg, 0.40 mmol) was heated at reflux for 24 h. After the mixture was cooled, 15 mL of EtOAc was added, the solution washed with 10 mL of saturated $NaHCO_3$ and then 10 mL of saturated brine and then dried ($MgSO_4$), and the solvent removed in vacuo. Preparative TLC (3:1 hexane/EtOAc, R_f 0.35) yielded the product as a clear, colorless oil that solidified upon standing (79 mg, 61%). The analytical sample was obtained by recrystallization from hexanes: mp 144–147 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 1.40–1.61 (m, 3, *H*CH), 1.63–1.77 (m, 3, HC*H*), 1.11 (d, *J* = 6.9 Hz, 3, $CHCH_3$) 1.29 (d, *J* = 6.9 Hz, 3 $CHCH_3$), 1.53 (s, 3, CCH_3), 2.22–2.24 (m, 2, COCH), 2.39–2.44 (m, 2, CH), 2.43 (s, 3, $PhCH_3$), 4.14–4.19 (m, 1, NCH), 7.29 (d, 2, *J* = 8.1 Hz, Ar H), 7.76 (d, 2, *J* = 8.1 Hz, Ar H); IR (KBr) 1736 (C=O), 1600, 1457 (Ar), 1307, 1152 cm^{-1}. Anal. Calcd for $C_{20}H_{27}NO_3S$: C, 66.45; H, 7.53; N, 3.87. Found: C, 66.58; H, 7.70; N, 3.64.

1,3,3a,4,4a,5,6,7,7a,7b-Decahydro-2-keto-3a-methyl-4-[(4-methylphenyl)sulfonyl]-1,3-diphenyldicylopenta[*b*,*d*]pyrrole (13). Under argon, a solution of benzene (7 mL), *cis*-*N*-tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (100 mg, 0.36 mmol), 1,3-dibromo-1,3-diphenylacetone (1.33 mg, 0.36 mmol), and $Fe_2(CO)_9$ (146 mg, 0.40 mmol) was heated at reflux for 22 h. After the mixture was cooled, 15 mL of EtOAc was added, the solution washed with 10 mL of saturated $NaHCO_3$ and 10 mL of saturated brine and then dried ($MgSO_4$), and the solvent removed in vacuo. Preparative TLC (3:1 hexane/EtOAc, R_f 0.31) gave 73 mg (42%) of the product as a white solid: mp 94–97 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.8–2.0 (m, 9, CH_2, $NCCH_3$), 2.3–2.6 (m, 2 CH), 2.39 (s, 3 $PhCH_3$), 4.0–4.4 (m, 3 PhCH, NCH), 7.1–7.4 (m, 12, Ar H), 7.6–7.9 (m, 2, Ar H); IR (KBr) 1742 (C=O), 1598, 1494, 1450, 1332, 1151 cm^{-1}. Anal. Calcd for $C_{30}H_{31}NO_3S$: C, 74.20; H, 6.43; N, 2.88. Found: C, 74.07; H, 6.63; N, 2.75.

1,3,3a,4,4a,5,6,7,7a,7b-Decahydro-2-keto-1,1,3,3,3a-pentamethyl-4-[(4-methylphenyl)sulfonyl]dicyclopenta[*b*,*d*]pyrrole (14). Under argon, a solution of benzene (7 mL), *cis*-*N*-tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (100 mg, 0.36 mmol), 2,4-dibromo-2,4-dimethylpentan-3-one (98 mg, 0.36 mmol), and $Fe_2(CO)_9$ (146 mg, 0.40 mmol) was heated at reflux for 60 h. After the mixture was cooled, 15 mL of EtOAc was added, the solution washed with 10 mL of saturated $NaHCO_3$ and 10 mL of saturated brine and then dried ($MgSO_4$), and the solvent removed in vacuo. Purification by chromatotron (7:2 hexane/EtOAc, second UV visible band) gave 62 mg (44%) of the product as a white solid. The analytical sample was obtained by recrystallization from hexanes: mp 135–137 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 0.67, 0.69, 0.95, 0.98, 1.15, 1.17, 1.21, 1.23, 1.25, 1.29 (multiple s, 12, $O=CCCH_3$), 1.68, 1.74 (2 s, 3, $NCCH_3$), 1.4–1.7 (m, 3, CH_2), 2.0–2.15 (m, 3, CH_2, CH), 2.41, 2.43 (2 s, 3, $PhCH_3$), 2.63 (m), 3.23 (br s, 1, CH), 4.26, 4.42 (2 m, 1, CH), 7.28 (d, 2, *J* = 8.3 Hz, Ar H), 7.69 (d, 1, *J* = 8.3 Hz, Ar H), 7.81 (d, 1, *J* = 8.3 Hz, Ar H); IR (KBr) 1734 (C=O), 1599, 1494, 1468, 1342, 1151 cm^{-1}. Anal. Calcd for $C_{22}H_{31}NO_3S$: C, 67.83; H, 8.02; N, 3.60. Found: C, 67.88; H, 8.07; N, 3.78.

1,2,3,3a,4,5,6,6a-Octahydro-5-keto-4,6,6a-trimethyl-1-[(4-methylphenyl)sulfonyl]cyclopenta[*b*]pyrrole-3-spirocyclohexane (18). A solution of benzene (7 mL), *N*-tosyl-3-methyl-2-azaspiro[5,6]undec-3-ene (90 mg, 0.29 mmol), 2,4-dibromopentan-3-one (72 mg, 0.29 mmol), and $Fe_2(CO)_9$ (118 mg, 0.32 mmol) was heated at reflux under argon for 23 h. After the mixture was cooled, 15 mL of EtOAc was added, the solution washed with 2 × 10 mL of saturated aqueous $NaHCO_3$ and then 10 mL of saturated brine and dried ($MgSO_4$), and the solvent removed in vacuo. Purification by chromatotron (4:1 hexane/EtOAc, second UV visible band) gave 67 mg (58%) of the product as a white solid. The analytical sample was obtained by recrystallization from hexanes: mp 154–156 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.81 (d, 3, *J* = 6.8 Hz, $CHCH_3$), 1.19 (d, 3, *J* = 6.8 Hz, $CHCH_3$), 1.0–1.7 (m, 13, CH_2, $NCCH_3$), 2.15–2.30 (m, 1, O=CCH), 2.44 (s, 3, $PhCH_3$), 2.50–2.65 (m, 1, O=CCH), 2.95–3.05 (m, 1, CH), 3.30–3.50 (m, 2, NCH_2), 7.31 (d, 2, *J* = 8.1 Hz, Ar H), 7.73 (d, 2, *J* = 8.1 Hz, Ar H); IR (KBr) 1741 (C=O), 1598, 1494, 1451, 1342, 1153 cm^{-1}. Anal. Calcd for $C_{22}H_{31}NO_3S$: C, 67.83; H, 8.02; N, 3.60. Found: C, 67.99; H, 8.01; N, 3.64.

1,2,3,3a,4,5,6,6a-Octahydro-5-keto-4,6,6a-trimethyl-3-phenyl-1-[(4-methylphenyl)sulfonyl]cyclopenta[*b*]pyrrole (19). A solution of benzene (7 mL), *N*-tosyl-2-methyl-4-phenyl-Δ^2-pyrroline (90 mg, 0.29 mmol), 2,4-dibromopentan-3-one (70 mg, 0.29 mmol), and $Fe_2(CO)_9$ (115 mg, 0.32 mmol) was heated at reflux for 24 h under an argon atmosphere. Upon cooling, 15 mL of EtOAc was added, the solution washed with 2 × 10 mL of saturated aqueous $NaHCO_3$ and then 10 mL of saturated brine and dried ($MgSO_4$), and the solvent removed in vacuo. Preparative TLC (3:1 hexane/EtOAc, R_f 0.28) gave 58 mg (51%) of the product as a clear, colorless oil, which solidified on standing: mp 48–51 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.8–1.6 (m, 9, $CHCH_3$, $NCCH_3$), 2.1–2.6 (m, 2, O=CCH), 2.43 (s, 3, $PhCH_3$), 3.2–4.2 (m, 4, PhCH, NCH_2, CH), 7.1–7.4 (m, 2, Ar H), 7.31 (s, 5, Ar H), 7.6–7.8 (m, 2, Ar H); IR (KBr) 1739 (C=O), 1598, 1491, 1450, 1340, 1152 cm^{-1}. Anal. Calcd for $C_{23}H_{26}NO_3S$: C, 69.67; H, 6.61; N, 3.53. Found: C, 69.69; H, 6.76; N, 3.61.

Registry No. **1**, 97486-45-8; **2**, 97486-46-9; **3**, 97486-47-0; **4**, 97486-48-1; **5**, 97486-49-2; **6**, 97486-50-5; **7**, 97486-51-6; **11**, 97486-52-7; **12**, 97486-53-8; **13**, 97486-54-9; **14**, 97486-55-0; **18**, 97486-56-1; **19**, 97486-57-2; (allyl)Fp, 38960-10-0; 1,3-dibromo-1,3-diphenylpropan-2-one, 958-79-2; diiron nonacarbonyl, 15321-51-4; 2,4-dibromo-2,4-dimethylpentan-3-one, 17346-16-6; 3,5-dibromo-2,6-dimethylheptan-4-one, 30957-25-6; 3,5-dibromoheptan-4-one, 36461-40-2; 2,4-dibromohexan-3-one, 97486-44-7; 2,4-dibromopentan-3-one, 815-60-1; 2,4-dibromo-2-methylpentan-3-one, 37010-00-7; *cis*-*N*-tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene, 81097-07-6; *N*-tosyl-3-methyl-2-azaspiro[4.5]undec-3-ene, 81097-23-6; *N*-tosyl-2-methyl-4-phenyl-Δ^2-pyrroline, 81120-69-6.

The Regioselectivity of Epoxide-Opening Reactions Using Alkynylaluminum Reagents

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Received December 14, 1984

The reaction of dialkylalkynylalanes with epoxides is a general route to β-hydroxyacetylenes that has found important application in organic synthesis.[1,2] This epoxide-opening reaction is particularly useful in constructing intermediates to prostaglandins and prostaglandin analogues,[3,4] as illustrated in the two examples in Scheme I. The opening of diol epoxide **4** is a key reaction in Fried's general approach to prostanoids,[5] and the opening of ketal epoxide **7** has been reported by several groups[6,7] as an

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