Acetolysis of Some Bicyclo[3.3.0]-2-octenyl Tosylates[1]

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The products of the acetolysis of the stereoisomeric 6-, 7-, and 8-bicyclo[3.3.0]-2-octenyl tosylates are reported. These tosylates were themselves stable to skeletal rearrangements but were found to undergo 1,2 hydride shifts and elimination solvolysis.

A wide variety of mono-, bi-, and tricyclooctane derivatives undergo solvolysis in polar solvents to form products with skeletal rearrangement.[2,3] Formation of bicyclo[3.3.0]octane derivatives is not uncommon in such rearrangements. In connection with the solution to a different problem relating to such ring systems, we have investigated the acetolysis of the stereoisomeric 6-, 7-, and 8-bicyclo[3.3.0]-2-octenyl derivatives with which, in addition to carbon and hydrogen migrations, there is also the possibility of double-bond participation.

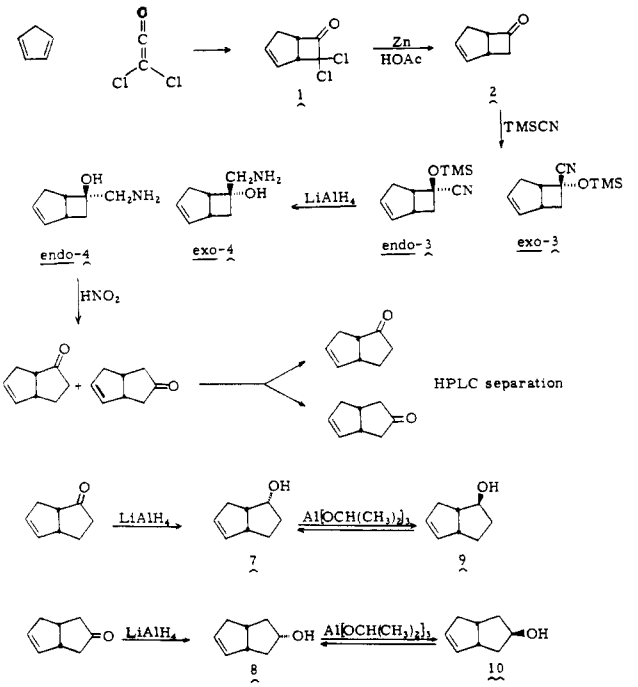
Results and Discussion

Acetolysis products of the saturated parent system 2-bicyclo[3.3.0]octanyl tosylate have previously been reported[4] and are given in Table I. A small amount of the carbon-migration product, *anti*-8-bicyclo[3.2.1]octanyl acetate, was obtained from the *exo*-2-bicyclo[3.3.0]octanyl tosylate, and some of the 1,2-hydride migration product, 1-bicyclo[3.3.0]octanyl acetate, was observed from both *endo*- and *exo*-2-bicyclo[3.3.0]octanyl tosylates, along with substantial amounts of the elimination product, bicyclo[3.3.0]-2-octene. The unrearranged acetates formed are the result of inversion with the *endo*-tosylate, and mixed inversion and retention with the *exo*-tosylate.

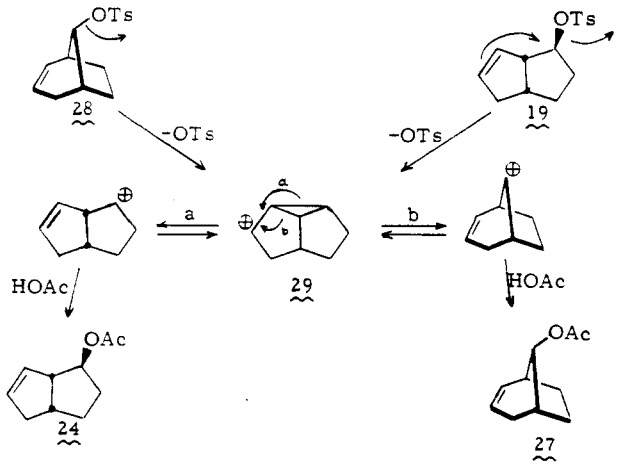
The acetolysis products of the stereoisomeric 6- and 7-bicyclo[3.3.0]-2-octenyl tosylates derived from the alcohols prepared by Scheme I as well as the corresponding 8-tosylates are given in Table II. The acetolysis of the *endo*-tosylates **11**, **13**, and **17** leads predominantly to the substitution products **20**, **22**, and **24**, respectively, resulting from an S_N2-type mechanism and the elimination products **25** and **26**. Some 1,2-hydride shift products were also observed, which included shifts from C6 to C7 and vice versa as well as shifts from C8 to C7. The 1,2-hydride shifts do not occur with equal facility in either direction. *exo*-6-Bicyclo[3.3.0]-2-octenyl tosylate (**12**) solvolyzes to yield a relatively large amount (~60% of the ester formed) of the 1,2-hydride shift products **22** and **23**. On the other hand, *exo*-7-bicyclo[3.3.0]-2-octenyl tosylate (**14**) yields only a small amount of hydride-shift product **20**. Inversion of stereochemistry is usual, except with 8-*exo*-bicyclo[3.3.0]-2-octenyl tosylate (**19**),[5] which yields mostly the retention product **24** and what appears to be *anti*-8-bicyclo[3.2.1]-2-octenyl acetate (**27**).[6]

Very few carbon skeletal rearrangements take place in the acetolysis of bicyclo[3.3.0]-2-octenyl tosylates, except with **19**. This indicates a greater degree of stability of bicyclo[3.3.0]octanes relative to the other ring systems which might be produced by rearrangement. This stability has a thermodynamic rationalization. Schleyer et al.[7] have calculated that the equilibrium between the bicyclo[3.2.1]octane system and the bicyclo[3.3.0] system should favor the [3.2.1] system at room temperature. However, at higher temperatures, >373 K, the equilibrium shifts in favor of the [3.3.0] system because of a more favorable entropy. Some formation of the [3.2.1] products might be

Scheme I



Scheme II



† Contribution no. 6259.

(1) Supported by the National Science Foundation.

(2) Cope, A. C.; Peterson, P. E. *J. Am. Chem. Soc.* **1959**, *81*, 1643-1650. Cope, A. C.; Grisar, J. M.; Peterson, P. E. *Ibid.* **1960**, *82*, 4299-4307. Cope, A, C.; Moon, S.; Park, C. H. *Ibid.* **1962**, *84*, 4850-4855. Foote, C. S.; Woodward, R. B. *Tetrahedron* **1964**, *20*, 687-715. Meinwald, J.; Kaplan, B. E. *J. Am. Chem. Soc.* **1967**, *89*, 2611-2618. Cope, A. C.; Gleason, R. W.; Moon, S.; Park, C. H. *J. Org. Chem.* **1967**, *32*, 942-946. Paquette, L. A.; Cox, O.; Oku, M.; Henzel, R. P. *J. Am. Chem. Soc.* **1974**, *96*, 4892-4901. Paquette, L. A.; Carmody, M. J. *J. Org. Chem.* **1978**, *43*, 1299-1304.

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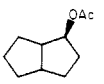
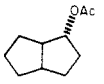
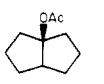
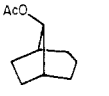
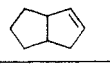
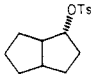
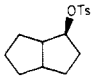
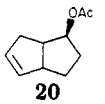
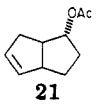
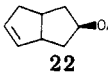
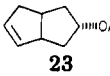
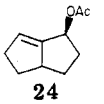
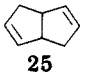
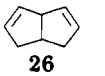
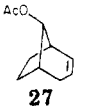
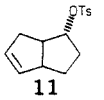
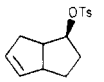
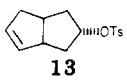
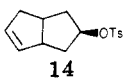
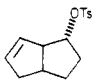
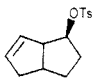
Table I. Acetolysis Products of *endo*- and *exo*-2-Bicyclo[3.3.0]octyl Tosylates

tosylate[a]	% product				
					
	51.3		1.7	0	47
	24.6	14.7	0.9	7.9	52

[a] Reference 4.

Table II. Acetolysis Products of 2-Bicyclo[3.3.0]octenyl Tosylates

tosylate	% products								
	 20	 21	 22	 23	 24	 25	 26	 27	other
 11	50		5	2		41			2
 12	3	10	5	14		58	9		1
 13	2		45	10		30	10		3
 14	2		5	38		21	25		5
 17			7.5	1	63	4	21		3.5
 19					69	3	19	8[a]	1

[a] Tentative assignment.

Table III. Products of 6- and 7-Bicyclo[3.3.0]-2-octenyl Tosylates in 2,4,6-Trimethylpyridine

tosylate	concn, M	temp °C	time, h	% product						
				25	26	11	12	13	14	10
11	0.88	80	16.5			93	7			
		90	16.3			93	7			
		90–120	3.5			83	17			
		120	15	81			19			
11 + 0.093 M *p*-TsOH	0.91	95	24	20		36	36			
13 + 0.084 M *p*-TsOH·H_2O	0.86	95	25.5	31	22			12	19	16

expected at our solvolysis temperatures (368 K) as is seen in the solvolysis of *exo*-2-bicyclo[3.3.0]octanyl tosylate and *exo*-8-bicyclo[3.3.0]-2-octenyl tosylate (**19**). It is interesting that **19** yields a rearranged product; the very similar **12** yields none. The difference is between a vinyl and an allyl migration, as can also be seen in the acetolysis of *anti*-8-bicyclo[3.2.1]-2-octenyl tosylate (**28**),[3] where vinyl migration occurs when either vinyl or allyl migration is possible (Scheme II), as expected from formation of a tricyclic cation, **29**. One ring opening of **29** leads to 8-bicyclo-[3.3.0]-2-octenyl acetate (**24**), while the other leads to 8-bicyclo[3.2.1]-2-octenyl acetate (**27**).

1,2-Hydride shifts appear to occur somewhat more readily with unsaturated tosylates than with the corresponding saturated tosylates, while each series gives es-

(3) LeBel, N. A.; Spurlock, L. A. *Tetrahedron* **1964**, *20*, 215–229.
(4) Closson, W. D.; Kwiatkowski, G. T. *Tetrahedron Lett.* **1966**, 6435–6440.
(5) A previous solvolysis study done on *endo*- and *exo*-bicyclo-[3.3.0]-2-octen-8-yl brosylates in 70% aqueous dioxane found no rearrangement products. Chien, C.-C. Ph.D. Dissertation, University of Illinois, 1974.
(6) This product is tentatively identified; however, it was definitely a rearrangement product and not one of the bicyclo[3.3.0]-2-octenyl acetates.
(7) Schleyer, P. v. R.; Blanchard, K. R.; Woody, C. D. *J. Am. Chem. Soc.* **1963**, *85*, 1358–1359.

sentially the same amount of 1,2-elimination products. However, no consistent pattern is obvious to permit rationalization of the results.

In conjunction with another study to be described later, the elimination products and stabilities of some of the bicyclo[3.3.0] 2-enyl tosylates in collidine–2,4,6-trimethylpyridine were investigated, and the results are summarized in Table III. Some epimerization occurs faster than elimination when tosylate **11** is heated at 90 °C for 16 h in neat collidine. However, no 1,2-hydride shift was observed, and, at higher temperatures (125 °C), elimination appears to give only the diene, bicyclo[3.3.0]-2,6-octadiene (**25**). The *exo*-tosylate eliminates less readily, and some is still left after heating at 125 °C for 15 h. If 0.1 equiv of *p*-toluenesulfonic acid is added to the collidine to provide either an acid catalyst or a higher ionic strength, such as would be present after 10% elimination has taken place, then epimerization occurs quite easily in competition with elimination. Thus, after 24 h at 95 °C, the product mixture consists of 36% each of the *exo*- and *endo*-6-bicyclo-[3.3.0]-2-octenyl tosylates, **11** and **12**, in addition to diene **25**. Similar results were obtained with *endo*-7-bicyclo-[3.3.0]-2-octenyl tosylate (**13**). It is clear that when elimination is attempted in neat collidine, as soon as some *p*-toluenesulfonic acid is formed the ionic character of the solvent changes, and epimerization can occur at a significant rate. When the temperature is low, epimerization can be faster than elimination. The importance of *p*-toluenesulfonic acid in facilitation of epimerization suggests an internal-return-type mechanism.[8]

Experimental Section

***endo*- and *exo*-bicyclo[3.3.0]-2-octen-6-ol and *endo*- and *exo*-bicyclo[3.3.0]-2-octen-7-ol** were prepared as summarized in Scheme I. The procedure was a modified version of that described by Roberts and Gorham.[9] The *endo*- and *exo*-bicyclo[3.3.0]-2-octen-8-ols were prepared by the procedure of Fujita.[10]

7,7-Dichlorobicyclo[3.2.0]-2-hepten-6-one (1) was prepared as described by Grieco.[11] From 143.5 g (0.97 mol) of dichloroacetyl chloride, 375 g (5.7 mol) of cyclopentadiene, and 100 g (0.99 mol) of triethylamine was obtained 124.3 g (72%) of **1**: bp 60–65 °C (2.5 mm) [lit.[11] bp 49–50 °C (0.3 mm)]; ^{1}H NMR ($CDCl_3$) δ 2.30–2.90 (m, 2 H), 3.90–4.35 (m, 2 H), 5.65–6.10 (m, 2 H).

Bicyclo[3.2.0]-2-hepten-6-one (2) was also prepared as described by Grieco,[11] and from 124.3 g (0.70 mol) of **1**, 261.7 g (4.00 mol) of zinc dust, and 400 mL of glacial acetic acid there was obtained 61.5 g (81%) of **2**: bp 25 °C (2.0 mm) [lit.[11] bp 60 °C (~15 mm)]; ^{1}H NMR ($CDCl_3$) δ 2.30–2.80 (m, 3 H), 3.10–3.55 (m, 2 H), 3.65–3.95 (m, 1 H), 5.60–5.85 (m, 2 H).

6-Cyano-6-[(trimethylsilyl)oxy]bicyclo[3.2.0]-2-heptene (3) was prepared by the method of Evans.[12] From 16.2 g (0.15 mol) of **2**, 16.5 g of trimethylsilyl cyanide (TMSCN, 0.17 mol) and a catalytic amount of zinc iodide was obtained 22.0 g (71%) of **3** (approximately a 50:50 mixture of the *endo*-**3** and *exo*-**3** isomers): bp 54–55 °C (0.6 mm); IR (neat) 1600, 1255 (Si–C), 1147, 882, 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.23 (split s, 9 H, $Si(CH_3)_3$), 1.85–3.50 (m, 6 H), 5.70 (br s, 2 H); mass spectrum, *m/e* 207 (molecular ion).

Anal. Calcd for $C_{11}H_{17}NOSi$: C, 63.72; H, 8.26; N, 6.76. Found: C, 63.55; H, 8.10; N, 6.49.

6-(Aminomethyl)bicyclo[3.2.0]-2-hepten-6-ol (4) was prepared by the method of Evans.[12] From 87.3 g (0.42 mol) of **3** and 26.0 g of lithium aluminum hydride (0.69 mol) was obtained 48.0 g (82%) of **4** (approximately a 50:50 mixture of *endo*-**4** and *exo*-**4** isomers): bp 67 °C (1 mm) [lit.[9] bp 83–84 °C (1.5 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.5–3.3 (m, 11 H), 5.65 and 5.75 (2 s, 2 H).

Bicyclo[3.3.0]-2-octen-6-one (5) and bicyclo[3.3.0]-2-octen-7-one (6) were prepared by a Tiffeneau–Demjanov ring expansion of **4**, as described previously.[9] From 10.8 g (~78 mmol) of crude **4**, 4.5 mL (78 mmol) of glacial acetic acid, and 5.35 g (78 mmol) of sodium nitrite was obtained 8.75 g (92%) of a 62:38 mixture of **5** and **6**. The isomeric ketones were separated on a Waters 500 Prep HPLC by using a 95:5 hexane–ethyl acetate solvent mixture and a flow rate of 0.4 L/min. Isomer **5** has a retention volume of about 2.2 L and **6** of about 2.7 L (column volume of 1 L). For bicyclo[3.3.0]-2-octen-6-one (**5**): ^{1}H NMR ($CDCl_3$) δ 1.40–2.33 (m, 4 H), 2.33–3.10 (m, 3 H), 3.30–3.63 (m, 1 H), 5.47–5.77 (m, 2 H). For bicyclo[3.3.0]-2-octen-7-one (**6**): ^{1}H NMR ($CDCl_3$) δ 1.70–3.17 (m, 7 H), 3.17–3.63 (m, 1 H), 5.50–5.80 (m, 2 H).

***endo*-Bicyclo[3.3.0]-2-octen-6-ol (7)** was prepared by lithium aluminum hydride reduction of **5** at 0 °C: bp 46–47 °C (0.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.07–1.83 (m 4 H), 1.83–2.87 (m, 3 H), 2.90–3.43 (m, 2 H), 3.77–4.30 (m, 1 H), 5.40–5.73 (m, 2 H).

***endo*-Bicyclo[3.3.0]-2-octen-7-ol (8)** was prepared by lithium aluminum hydride reduction of **6** at 0 °C: bp 94–95 °C (1.5 mm); ^{1}H NMR ($CDCl_3$) δ 1.10–2.88 (m, 8 H), 2.88–3.38 (m, 1 H), 4.11 (p, $J \approx 6$ Hz, 1 H), 5.47–5.89 (m, 2 H).

***exo*-Bicyclo[3.3.0]-2-octen-6-ol (9)** was obtained by equilibration of the endo isomer, **7**, with aluminum isopropoxide by using the Cope[13] procedure. The exo isomer, **9**, was separated from the endo isomer by preparative high-performance LC under the same conditions as those for the separation of **5** and **6**: ^{1}H NMR ($CDCl_3$) δ 1.1–3.0 (m, 9 H), 3.8–4.0 (m, 1 H), 5.4–5.8 (m, 2 H).

***exo*-Bicyclo[3.3.0]-2-octen-7-ol (10)** was also obtained by equilibration of the endo isomer, **8**, with aluminum isopropoxide.[13] The exo isomer, **10**, was separated from the endo isomer by preparative high-performance LC: ^{1}H NMR ($CDCl_3$) δ 1.21–2.18 (m, 6 H), 2.40–3.06 (m, 2 H), 3.23 (m, 1 H), 4.24 (p, $J \approx 5.5$ Hz, 1 H), 5.52 (c, 2 H).

***endo*-6-Bicyclo[3.3.0]-2-octenyl tosylate (11)** was obtained from treatment of the alcohol **7** with 1.1 equiv of *p*-toluenesulfonyl chloride in the presence of excess pyridine at 0 °C for 1 h and stirring of the mixture at room temperature for 15 h. The mixture was diluted with ether and then washed with 1 N hydrochloric acid, 5% sodium bicarbonate solution, and water. The ethereal layer was dried over potassium carbonate. The crude tosylate obtained by evaporation of the ether was not further purified: ^{1}H NMR ($CDCl_3$) δ 1.05–1.85 (m, 4 H), 1.85–2.92 (m, 3 H), 2.42 (s, 3 H), 2.92–3.36 (m, 1 H), 4.52–4.92 (m, 1 H), 5.32–5.66 (m, 2 H), 7.54 (dd, 4 H).

***exo*-6-Bicyclo[3.3.0]-2-octenyl tosylate** was prepared as described for **11** by starting from **9**: ^{1}H NMR ($CDCl_3$) δ 1.65–3.50 (m, 8 H), 2.40 (s, 3 H), 4.53–4.68 (m, 1 H), 5.43 (br s, 2 H), 7.55 (dd, 4 H).

***endo*-7-Bicyclo[3.3.0]-2-octenyl tosylate (13)** was prepared from **8** in the same manner as described for **11**: ^{1}H NMR ($CDCl_3$) δ 1.34–1.77 (m, 3 H), 1.77–2.82 (m, 4 H), 2.40 (s, 3 H), 2.82–3.21 (m, 1 H), 4.77 (p, $J \approx 6.4$, 1 H), 5.50 (br s, 2 H), 7.52 (dd, 4 H).

***exo*-7-Bicyclo[3.3.0]-2-octenyl tosylate (14)** was prepared from **10** in the same manner as described for **11**: ^{1}H NMR ($CDCl_3$) δ 1.13–3.32 (m, 8 H), 2.44 (s, 3 H), 4.91 (p, $J \approx 4.8$ Hz, 1 H), 5.50 (br s, 2 H), 7.56 (dd, 4 H).

3,4-Epoxycyclooctene (15) was prepared by oxidation of 1,3-cyclooctadiene with *m*-chloroperbenzoic acid in dichloromethane. From 6.1 g (56 mmol) of 1,3-cyclooctadiene and 12.0 g of *m*-chloroperbenzoic acid (80–90%) was obtained 5.5 g (79%) of **15**: bp 46–50 °C (3.5 mm) [lit.[14] bp 94–97 °C (41 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.10–2.53 (m, 8 H), 2.93–3.20 (m, 1 H), 3.35–3.49 (br d, 1 H), 5.45–5.91 (m, 2 H).

***endo*-Bicyclo[3.3.0]-2-octen-8-ol (16)** was prepared as described by Crandall.[14] From 5.6 g (45 mmol) of **15** and 2.5 equiv of lithium diethylamide was obtained 4.0 g (71%) of **16**: bp 69–70

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°C (5.5 mm) [lit.[14] bp 93–96 °C (20 mm)]; ^{1}H NMR ($CDCl_3$) δ 0.67–2.88 (m, 7 H), 3.00–3.37 (m, 1 H), 4.04–4.31 (m, 1 H), 5.50–5.94 (m, 2 H).

***endo*-8-Bicyclo[3.3.0]-2-octenyl tosylate (17)** was prepared from **16** in the same manner as described for **11**: ^{1}H NMR ($CDCl_3$) δ 1.29–2.89 (m, 7 H, s, 3 H), 3.04–3.36 (m, 1 H), 4.69–5.00 (m, 1 H), 5.36–5.83 (m, 2 H), 7.55 (dd, 4 H).

***exo*-Bicyclo[3.3.0]-2-octen-8-ol (18)** was prepared as described by Fujita,[10] except that the acetate was not isolated. The tosylate **17** was allowed to react with tetraethylammonium acetate tetrahydrate in acetone for 24 h to yield *exo*-bicyclo[3.3.0]-2-octen-8-yl acetate. The acetate was then saponified in a solution of potassium hydroxide and methanol to yield **17**. From 3.7 g of **16** was obtained 1.6 g (43%) of **18**: bp 66–70 °C (3 mm); ^{1}H NMR ($CDCl_3$) δ 1.03–3.00 (m, 10 H), 3.89–3.97 (m, 1 H), 5.30–5.60 (m, 2 H).

***exo*-8-Bicyclo[3.3.0]-2-octenyl tosylate (19)** was prepared from **18** in the same manner as described for **11**: ^{1}H NMR ($CDCl_3$) δ 1.17–2.98 (m, 7 H), 2.41 (s, 3 H), 3.07–3.33 (m, 1 H), 4.57–4.92 (m, 1 H), 5.25–5.72 (m, 2 H), 7.52 (dd, 4 H).

General Procedure for Acetolysis Reactions. The tosylate and 2 equiv of anhydrous sodium acetate were dissolved in anhydrous glacial acetic acid, and nitrogen was bubbled through the solution for 5 min. The container was sealed, immersed in a thermostated oil bath at 95 ± 0.5 °C for 18 h, and then cooled in an ice bath. Ether and water were added to the solution, and the excess acetic acid was removed by washing with saturated sodium carbonate solution. The ethereal layer was washed with water and then dried over potassium carbonate. The products were analyzed by gas chromatography. Samples for structural analysis were obtained by preparative gas chromatography. The stereoisomeric 7-substituted acetates had identical reaction times. The acetate mixtures were then reduced to the alcohols with lithium aluminum hydride and the alcohols analyzed. Proton NMR spectroscopy was used to identify the acetolysis products.

Stability of Tosylates in Collidine. In a round-bottomed flask equipped with a reflux condenser, drying tube, and magnetic stirrer was placed a solution of the tosylate in collidine. The flask was immersed in a preheated oil bath at the prescribed temperature for 15–24 h, at which time either the reaction mixture was worked up or a 1-mL aliquot was removed for analysis and the remainder heated further at a higher temperature. The product isolations involved taking up the cooled mixture in ether, washing the ethereal solution with iced 10% sulfuric acid and water, and drying over magnesium sulfate. The products were analyzed by proton NMR spectroscopy.

Registry No. **1**, 5307-99-3; **2**, 13173-09-6; **3** (isomer 1), 75548-82-2; **3** (isomer 2), 75598-13-9; **4** (isomer 1), 75548-83-3; **4** (isomer 2), 75598-14-0; **5**, 32405-38-2; **6**, 53648-63-8; **7**, 53648-80-9; **8**, 75548-84-4; **9**, 53648-79-6; **10**, 75598-15-1; **11**, 75548-85-5; **12**, 75548-86-6; **13**, 75548-87-7; **14**, 75598-16-2; **15**, 6690-12-6; **16**, 41164-15-2; **17**, 40132-78-3; **18**, 10095-77-9; **19**, 40132-79-4; **20**, 17119-05-0; **21**, 32405-36-0; **22**, 75548-88-8; **23**, 75598-17-3; **24**, 40132-75-0; **25**, 41527-66-6; **26**, 41164-14-1; **27**, 75548-89-9; dichloroacetyl chloride, 79-36-7; cyclopentadiene, 542-92-7; trimethylsilyl cyanide, 7677-24-9; 1,3-cyclooctadiene, 1700-10-3.

Acylation of Monosubstituted Ferrocenes. Unusual Directive Effect of the Cyanomethyl Group

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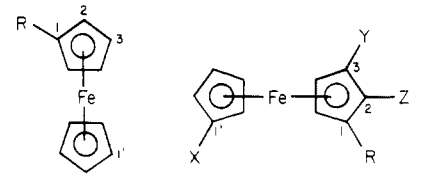
Ferrocenylacetonitrile (1) reacts with toluoyl chloride or acetic anhydride, under Friedel–Crafts conditions, to give largely heteroannular substitution (90% and 80%, respectively). By contrast, acylation reactions of methyl ferrocenylacetate (2) and methylferrocene (3) give mixtures of all three possible isomers with diminished regioselectivity and ca. 50% heteroannular substitution. ^{1}H and ^{13}C NMR data for ferrocene derivatives, which were used to characterize and/or quantitate the disubstituted ferrocenes in the isomeric mixtures, are reported.

Acyl ferrocenes, central intermediates for the preparation of ferrocene derivatives,[1,2] are generally available via the Friedel–Crafts ketone synthesis.[2] Acylation studies on substituted ferrocenes have defined some substituent directive effects.[2,3] Acyl, cyano, carbalkoxy, halo, and amido groups give almost exclusively heteroannular acylation, whereas alkyl and aryl groups give all possible isomers with a homoannular to heteroannular ratio around 1:1. Although the directive influence of simple alkyl groups on ferrocene acylation is known,[2,3] the influence of alkyl groups bearing polar residues has never been examined. This paper reports the unusually high regiochemical control of acylation caused by a cyanomethyl group.

Results and Discussion

Chemistry. In the course of synthetic work we found that acylation of ferrocenylacetonitrile (1) with *p*-toluoyl chloride and $AlCl_3$ affords an ca. 10:1 mixture of **6a** and **6b** (36–47% yield). Since this high regiocontrol of acylation by an alkyl group, giving almost exclusively heteroannular (i.e., 1,1′) product (**6a**), is unusual, we explored the toluoylation of methyl ferrocenylacetate (**2**) and methylferrocene (**3**). By contrast, **2** and **3** each gave a mixture of isomers corresponding to equal amounts of homoannular and heteroannular substitution.



1, R = CH_2CN
2, R = $CH_2CO_2CH_3$
3, R = CH_3
4, R = C_6H_5
5, R = $C(O)CH_3$
9, R = $C(O)C_6H_5$

6, R = CH_2CN
7, R = $CH_2CO_2CH_3$
8, R = CH_3
a, X = *p*-TolC(O), Y = Z = H
b, X = Z = H, Y = *p*-TolC(O)
c, X = Y = H, Z = *p*-TolC(O)

Our results for the toluoylation of **1–3** and acetylation of **3** are presented in Table I, along with selected reactions

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