Intramolecular Rearrangements of Tertiary Amine Oxides

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Intramolecular acyl transfer to an *N*-oxide was examined as a route to a synthetically viable thermal ester cleavage. The pyrolysis of *N*-piperidylethyl *N*-oxides indicated that where structurally feasible, other thermal reactions (Cope elimination, Meisenheimer rearrangement, and deoxygenation) will dominate over the desired acyl transfer. However, where the ester cleavage was dictated by the use of 2-picolyl ester *N*-oxides, acceptable yields (50–84%) of isolated acids resulted from the thermolysis (ca. 140 °C) of 2-picolyl benzoate *N*-oxides in the presence of anhydrous ferric chloride.

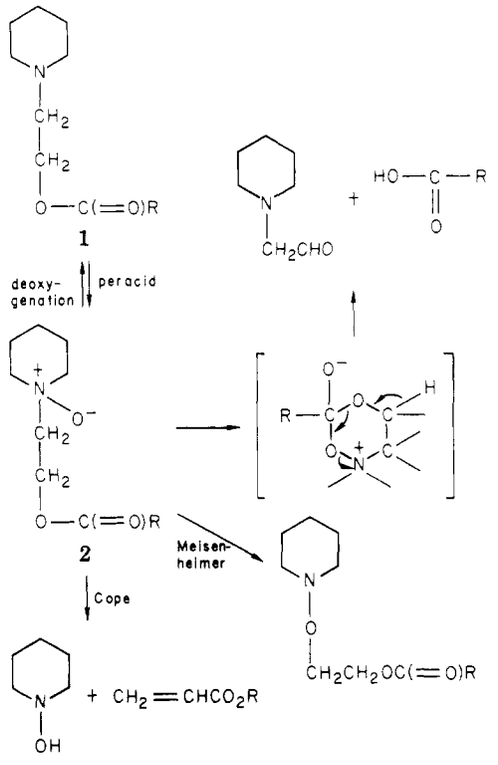
The rearrangement of aliphatic or aromatic tertiary amine oxides with acylating agents is a well-known phenomenon.[2-7] These interesting conversions have engendered considerable mechanistic investigation and have formed the basis for a number of useful synthetic applications.[2,8]

Two specific systems were designed to examine the scope and limitations of a proposed rearrangement where the acyl group could be transferred to the tertiary amine oxide from a proximate portion of the same molecule. In the first system, 2-(*N*-piperidyl)ethyl benzoate and palmitoate *N*-oxides [**2**, R = C_6H_5X and R = $(CH_2)_{14}CH_3$, Table II] would allow an examination of the competition of the desired rearrangement with the Cope elimination,[9-12] the Meisenheimer rearrangement,[13-17] and deoxygenation[2] (Scheme I). However, the alternative use of 2-picolyl benzoate or palmitoate *N*-oxides [**4**, R = C_6H_5X and R = $(CH_2)_{14}CH_3$, Table IV] would presumably force an acyl transfer to provide 2-pyridinecarboxaldehyde (**5**) and the corresponding carboxylic acid (Scheme II).

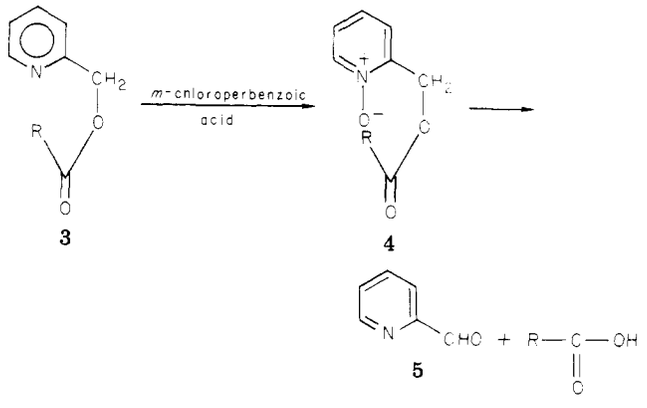
Results and Discussion

The thermal decomposition of 2-(*N*-piperidyl)ethyl benzoates or palmitoate in the heated inlet of a gas chromatograph (Table V) indicated no tendency toward the acyl transfer necessary for the ester cleavage (Scheme I). The lack of this type of rearrangement was confirmed by the absence of the parent carboxylic acids under "normal" pyrolysis conditions (see Experimental Section). The products were quantitated from spectra obtained from the output of a gas chromatograph and reflected the full range of *alternative* reaction pathways, including Cope elimination, Meisenheimer rearrangement, and deoxygenation (Table V). The results indicated that the Meisenheimer rearrangement dominated the Cope elimination only with the aliphatic ester and when there was an electron-withdrawing group (NO_2) present in the benzoate.

Scheme I



Scheme II



(1) Taken in part from the Master's thesis of L. J. Heinis, University of Minnesota, 1978.
(2) S. Oae and K. Ogino, *Heterocycles*, **6**, 583 (1977).
(3) E. Ochiai, "Aromatic Amine Oxides", Elsevier, Amsterdam, 1967.
(4) R. A. Abramovitch and J. G. Saha, *Adv. Heterocycl. Chem.*, **6**, 229 (1966).
(5) M. Polonovski and M. Polonovski, *Bull. Soc. Chim. Fr.*, **41**, 1190 (1927).
(6) R. N. Renaud and L. C. Leitch, *Can. J. Chem.*, **46**, 385 (1968).
(7) H. Volz and L. Ruchti, *Justus Liebigs Ann. Chem.*, **763**, 184 (1972).
(8) R. T. Lalonde, E. Auer, C. F. Wong, and V. P. Muralidharan, *J. Am. Chem. Soc.*, **93**, 2501 (1971).
(9) A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.*, **71**, 3929 (1949).
(10) C. H. DePuy and R. W. King, *Chem. Rev.*, **60**, 448 (1960).
(11) A. C. Cope and E. R. Trumbull, *Org. React.*, **11**, 361 (1960).
(12) M. R. V. Sahyun and D. J. Cram, *J. Am. Chem. Soc.*, **85**, 1263 (1963).
(13) J. Meisenheimer, *Chem. Ber.*, **52**, 1667 (1919).
(14) R. A. W. Johnstone in "Mechanisms of Molecular Migrations", Vol. II, Interscience, New York, 1969, p 249.
(15) N. Castagnoli, Jr., J. C. Craig, A. P. Milikan, and S. K. Roy, *Tetrahedron*, **26**, 4319 (1970).
(16) A. R. Lepley, *J. Am. Chem. Soc.*, **92**, 1101 (1970).
(17) D. J. Pokorny and W. W. Paudler, *J. Org. Chem.*, **37**, 3101 (1972).

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Table I. 2-(*N*-Piperidyl)ethyl Benzoates and 2-(*N*-Piperidyl)ethyl Palmitoate 1

R	% yield	bp, °C	*P*, mmHg	NMR ($CDCl_3$ 1% Me_4Si) δ
Ph	98	125	0.075	1.48 (s, 6), 2.48 (d, 4), 2.75 (t, 2), 4.58 (t, 2), 7.71 (m, 3), 8.35 (m, 2)
p-CH_3Ph	92	154	0.050	1.55 (s, 6), 2.44 (s, 3), 2.59 (d, 4), 2.80 (t, 2), 4.56 (t, 2), 7.42 (d, 2), 8.20 (d, 2)
p-CH_3OPh	92	155	0.050	1.59 (s, 6), 2.65 (m, 4), 2.87 (t, 2), 3.95 (s, 3), 4.60 (t, 2), 7.12 (d, 2), 8.25 (d, 2)
p-$(CH_3)_3$CPh	94	154	0.30	1.40 (s, 9), 1.59 (s, 6), 2.62 (m, 4), 2.85 (t, 2), 4.71 (t, 2), 7.72 (d, 2), 8.20 (d, 2)
p-NO_2Ph	69	168	0.30	1.56 (s, 6), 2.56 (d, 4), 2.86 (t, 2), 4.69 (t, 2), 8.57 (s, 4)
$(CH_2)_{14}CH_3$	97	178–180	0.50	1.00 (t, 3), 1.29 (s, 26), 1.58 (d, 6), 2.41 (m, 8), 4.25 (t, 2)

Table II. 2-(*N*-Piperidyl)ethyl Benzoate *N*-Oxides and 2-(*N*-Piperidyl)ethyl Palmitoate *N*-Oxide 2

R	% yield	mp, °C	NMR ($CDCl_3$ 1% Me_4Si) δ
Ph	84	132.5–133	1.74 (m, 6), 2.40 (m, 2), 3.41 (d, 4), 3.70 (t, 2), 5.20 (t, 2), 7.80 (m, 3), 8.30 (m, 2)
p-CH_3Ph	61	142–143	1.72 (m, 6), 2.35 (s, 3), 3.40 (m, 4), 3.76 (m, 2), 5.19 (m, 2), 7.48 (d, 2), 8.18 (d, 2)
p-CH_3OPh	87	147–148	1.89 (m, 4), 2.50 (m, 2), 3.55 (m, 4), 3.86 (m, 2), 4.14 (s, 3), 5.32 (m, 2), 7.35 (d, 2), 8.42 (d, 2)
p-NO_2Ph	86	157–159	1.81 (m, 4), 2.38 (m, 2), 3.56 (m, 4), 3.86 (t, 2), 5.36 (t, 2), 8.56 (s, 4)
p-$(CH_3)_3$CPh	86	124.5–125	1.34 (s, 9), 1.86 (m, 6), 3.70 (m, 4) 4.12 (m, 2), 5.05 (m, 2), 7 69 (d, 2), 3.22 (d, 2)
$(CH_2)_{14}CH_3$	97	101–102	1.10 (s, 31), 2.04 (m, 6), 3.05 (m, 4), 3.36 (t, 2), 4.54 (m, 2)

Table III. 2-Picolyl Benzoates and 2-Picolyl Palmitoate 3

R	% yield	mp, °C	bp, °C (mmHg)	NMR ($CDCl_3$ 1% Me_4Si) δ
Ph	96		150 (0.09)	5.70 (s, 2), 7.80 (m, 6), 8.48 (d, 2), 8.95 (d, 1)
p-CH_3Ph	76	49–52		2.42 (s, 3), 5.64 (s, 2), 7.41 (d, 2), 7.81 (m, 3), 8.22 (d, 2), 8.85 (d, 1)
p-NO_2Ph	87	73–80		5.72 (s, 2), 7.68 (m, 3), 8.69 (s, 4), 8.95 (d, 1)
p-CH_3OPh	83		154 (0.02)	3.90 (s, 3), 5.62 (s, 2), 7.12 (d, 2), 7.66 (m, 3), 8.88 (d, 1)
p-$(CH_3)_3$CPh	84		175 (0.02)	1.30 (s, 9), 5.62 (s, 2), 7.60 (m, 3), 7.62 (d, 2), 8.80 (d, 1)
$(CH_2)_{14}CH_3$	86	35–37		1.31 (m, 29), 2.35 (t, 2), 5.34 (s, 2), 7.53 (m, 3), 8.82 (d, 1)

The desired thermolysis reaction was effected by heating, without solvent, a sample of 2-picolyl ester *N*-oxide at temperatures near 180 °C (Table VI). This aromatic *N*-oxide system in which the Cope and Meisenheimer pathways cannot occur was not deoxygenated. It was also observed that the reaction could be carried out at lower temperatures (140 °C) in the presence of anhydrous ferric chloride. This enhancement of the thermolysis was not observed for other anhydrous metal chlorides ($ZnCl_2$, $MgCl_2$, $CuCl_2$). The nonhydrolytic character of the reaction was confirmed by the observed stability of benzyl benzoate under the optimized reaction conditions (1 equiv of $FeCl_3$, 140 °C). Moreover, the generation of 2-pyridinecarboxaldehyde (**5**) was confirmed by isolation and comparison with an authentic sample.

The study has demonstrated the potential for *intra*molecular acyl transfer to tertiary amine oxides, as well as providing a new thermal ester cleavage as shown by isolating yields of acids that are moderate to good (50–84%) (Table VI). Moreover, the thermolysis occurs at temperatures far lower than those of pyrolytic conditions (500–600 °C) normally considered typical for thermal ester cleavage.[18]

Experimental Section

General Procedures. Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (NMR) spectra were recorded on a Varian Associates Model EM-360. Chemical shifts are reported as δ (ppm). Elemental analyses were obtained at Robertson Laboratories. Gas chromatographic (GC) analysis was made by using a Tracor MT-160 gas chromatograph equipped with a flame ionization detector (FID), a Hewlett Packard HP 3380S recording integrator, and a 6 ft × 4 mm (i.d.) glass column packed with 1.5% SP-2250/1.95% SP-2401 (methyl phenyl silicone and fluoropropyl silicone) on 100/120 Supelcoport (Supelco catalog number 1-1947; maximum temperature rated at 250 °C) with Anakrom fluxcalcined diatomaceous earth in the column ends (110/120 mesh; Analabs, Inc.) to allow a 325 °C inlet temperature with minimum column bleed.

The organic reactants and the 2-pyridinecarboxaldehyde were obtained from Aldrich Chemical Co. The solvents were of the best commercial grade available and were used without further purification unless noted. Anhydrous ferric chloride was obtained by drying Eastman practical grade anhydrous ferric chloride in an Abderhalden apparatus at 110 °C over phosphorus pentoxide at 0.05 mm for 60 h. Aluminum oxide (activated basic CAMAG 95+%, 60 mesh) and silica gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM) were used for column chromatography.

2-(*N*-Piperidyl)ethyl and 2-Picolyl Carboxylates (Tables I and III). The following example illustrates the procedure used to prepare all of the 2-(*N*-piperidyl)ethyl and 2-picolyl carboxylates. A 250-mL round-bottom flask was charged with 175 mL of anhydrous diethyl ether and fitted with a rubber septum. After the flask was flushed with dry N_2 for 5 min, 2.00 mL (0.0207 mol) of 2-pyridylcarbinol was added dropwise via syringe. To the stirred solution was added very slowly dropwise via syringe 2.41 mL (0.0207 mol) of benzoyl chloride. After 3 h, 25 mL of saturated aqueous sodium bicarbonate was added with vigorous stirring. The ether was extracted with two 10-mL portions of sodium bicarbonate solution, washed with 5 mL of water, dried over anhydrous magnesium sulfate, filtered, and concentrated on a rotary evaporator to a clear yellow oil. The oil was fractionated through a 40-cm distillation head to give 4.23 g (96%) of 2-picolyl benzoate. For a summary of the experimental results, see Tables I and III.

2-(*N*-Piperidyl)ethyl and 2-Picolyl Carboxylate *N*-Oxides (Tables II and IV). The procedure of Craig and Parushothamen,[19] as described in the example below, was used to prepare

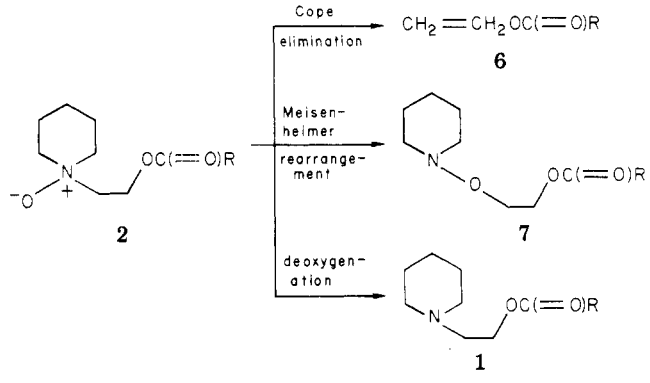
(18) E. Haslam in "Protective Groups in Organic Chemistry", J. F. W. McOmie, Ed., Plenum Press, New York, 1973, pp 183–215.

(19) J. C. Craig and K. K. Parushothamen, *J. Org. Chem.*, **35**, 1721 (1970).

Table IV. 2-Picolyl Benzoate 1-Oxides and 2-Picolyl Palmitoate 1-Oxide 4

R	% yield	mp, °C	NMR ($CDCl_3$ 1% Me_4Si) δ
Ph	94	124-125	5.82 (s, 2), 7.52 (m, 6), 8.50 (m, 3)
p-CH_3Ph	91	123-123.5	2.52 (s, 3), 5.89 (s, 2), 7.42 (m, 5), 8.39 (d, 2), 8.62 (t, 1)
p-NO_2Ph	74	164-165	5.86 (s, 2), 7.56 (m, 3), 8.56 (s, 5)
p-CH_3OPh	83	132-133	4.00 (s, 3), 5.80 (s, 2), 7.16 (d, 2), 7.56 (m, 3), 8.32 (d, 2), 8.50 (m, 1)
p-$(CH_3)_3$CPh	90	115-115.5	1.90 (s, 9), 5.89 (s, 2), 7.63 (m, 3), 7.79 (d, 2), 8.40 (d, 2), 8.60 (m, 1)
$(CH_2)_{14}CH_3$	94	66-68	0.92 (t, 3), 1.32 (s, 26), 2.46 (t, 2), 5.49 (d, 2), 7.52 (m, 2), 8.50 (t, 1), 8.84 (t, 1)

Table V. Thermal Reactions of 2-(*N*-Piperidyl)ethyl Benzoate *N*-Oxides and 2-(*N*-Piperidyl)ethyl Palmitoate *N*-Oxide[a]



R	inlet temp, °C	products, % 6	1	7	6/7
$(CH_2)_{14}CH_3$	225		44.1	55.9	
p-NO_2Ph		1.4	76.6	22.0	0.06
Ph		33.7	30.0	35.3	0.95
p-CH_3Ph		26.4	56.3	15.9	1.66
p-CH_3OPh		25.7	55.9	16.5	1.55
p-$(CH_3)_3$CPh		42.6	33.4	23.0	1.85
$(CH_2)_{14}CH_3$	275	trace	2.9	97.1	
p-NO_2Ph		5.7	69.8	24.5	.23
Ph		26.8	59.3	11.6	2.31
p-CH_3Ph		28.7	54.1	15.7	1.82
p-CH_3OPh		21.5	73.2	4.7	4.57
p-$(CH_3)_3$CPh		34.9	58.2	5.7	6.12
$(CH_2)_{14}CH_3$	325	trace	2.9	97.1	
p-NO_2Ph		13.0	62.1	24.8	0.52
Ph		29.9	59.1	10.2	2.93
p-CH_3Ph		32.0	56.8	10.0	3.2
p-CH_3OPh		34.7	59.1	5.5	6.3
p-$(CH_3)_3$CPh		34.6	60.9	3.0	11.53

[a] All analyses were performed by using a 130-180 °C oven temperature program.

all of the carboxylate *N*-oxides. A 500-mL round-bottom flask was charged with 150 mL of methylene chloride and 10.00 g (0.047 mol) of 2-picolyl benzoate **10**, fitted with a pressure-equalizing addition funnel with a drying tube, and cooled to 0–5 °C in an ice–water bath. A solution of 9.52 g (0.047 mol) of *m*-chloroperbenzoic acid in 150 mL of methylene chloride was cooled to 0–5 °C and added dropwise via a pressure-equalized addition funnel to the magnetically stirred solution of the amine. The resulting solution was allowed to come to room temperature over a period of 3 h from the time the addition was complete. The solution was poured onto a column of basic alumina (20 times the combined weight of starting materials), washed with methylene chloride (2 bed volumes), and eluted with methylene chloride/methanol (3:1) (2 bed volumes). The solvent was removed in vacuo and the residue was recrystallized from diethyl ether and dried in vacuo 8 h to give 10.16 g (94%) of 2-picolyl benzoate *N*-oxide as a white solid. For a summary of experimental results, see Tables II and IV.

Pyrolysis of 2-(*N*-Piperidyl)ethyl Benzoate *N*-Oxides and 2-(*N*-Piperidyl)ethyl Palmitoate *N*-Oxide (Table V). The pyrolysis reactions of *N*-piperidylethyl benzoate *N*-oxides and of *N*-piperidylethyl palmitoate *N*-oxide were carried out by the injection of 1 μL of an acetonitrile solution (9.9–21.1 mg/mL) of the appropriate amine oxide into the gas chromatograph inlet at 225, 275, and 325 °C in three separate trials (Table V). A 130–180 °C temperature program with a 3–4.5 min initial hold allowed detection of the compounds of interest. The peaks were identified by the comparison of retention times of pure compounds (NMR) prepared by the low-pressure fractionation of the products of an amine oxide pyrolysis reaction in which no acid was observed.

Rearrangements of 2-Picolyl Benzoate 1-Oxides and 2-Picolyl Palmitoate 1-Oxide. Method 1. 2-Picolyl Benzoate 1-Oxide. To a 25-mL round-bottom flask equipped with a magnetic stirrer were added 0.2379 g (0.00104 mol) of 2-picolyl benzoate 1-oxide and 0.3469 g (0.00214 mol) of dried ferric chloride. The flask was one-third filled with dried purified sand, fitted with a rubber septum, and flushed with dry N_2. After 18 h of stirring at 120 °C (sand bath) under a continuous purge of N_2, the mixture was cooled in an ice–water bath. The entire dark reaction mixture was transferred to a separatory funnel. Any residue was triturated with two 10-mL portions of anhydrous diethyl ether and transferred to the separatory funnel. Following extraction with three 25-mL portions of saturated aqueous sodium bicarbonate solution, the combined ethereal extract was dried over anhydrous magnesium sulfate and filtered, and the ether was removed by rotary evaporation to give 0.106 g (83%) of benzoic acid. The results are summarized in Table VI.

Method 2. 2-Picolyl Benzoate 1-Oxide. In a manner similar to method 1, a 25-mL round-bottom flask was charged with ferric chloride and one-third filled with sand. The flask was then sealed with a rubber septum, flushed with N_2, and heated to 140 °C with stirring to impregnate the sand with a fine layer of ferric chloride. After the flask was cooled to room temperature, the rearrangement procedure followed method 1. For the results, see Table VI.

Method 3. 2-Picolyl Benzoate 1-Oxide. The reaction sequence was identical with that of method 1. The workup was accomplished by dissolving the reaction mixture in anhydrous diethyl ether. The sand and residue were triturated with diethyl

Table VI. Thermal Reactions of 2-Picolyl Benzoate 1-Oxides and 2-Picolyl Palmitoate 1-Oxide 4

R	time, h	temp, °C	molar equiv of $FeCl_3$	exptl method[a]	% yield of acid	method[a]
Ph	5.0	142	1.0	2	82	3
	3.0	158	1.0	1	73	1
	3.5	140	1.0	1	65	2
p-CH_3Ph	12.0	142	1.0	1	84	1
p-$(CH_3)_3$CPh	13.0	145	1.0	1	50	1
p-CH_3OPh	15.5	180	1.0	1	81	1
p-NO_2Ph	12.0	148	1.0	1	50	1
$(CH_2)_{14}CH_3$	5.0	180	1.0	2	56	3

[a] See Experimental Section.

ether and then the ethereal solution was poured onto a column of silica gel (50 times the amount of starting amine oxide). The ethereal solution of the product was then poured onto the column. Elution with diethyl ether (2 bed volumes) was followed by rotary evaporation of the solvent to give the carboxylic acid. The results are summarized in Table VI.

Registry No. 1 (R = Ph), 19069-56-8; 1 (R = p-CH_3Ph), 70415-62-2; 1 (R = p-CH_3OPh), 62557-46-4; 1 (R = p-$(CH_3)_3$CPh), 14377-42-5; 1 (R = p-NO_2Ph), 30727-41-4; 1 (R = $(CH_2)_{14}CH_3$), 70415-63-3; 2 (R = Ph), 70415-64-4; 2 (R = p-CH_3Ph), 70415-65-5; 2 (R = p-CH_3OPh), 70415-66-6; 2 (R = p-NO_2Ph), 70415-67-7; 2 (R = p-$(CH_3)_3$CPh), 70415-68-8; 2 (R = $(CH_2)_{14}CH_3$), 70415-69-9; 3 (R = Ph), 66310-15-4; 3 (R = p-CH_3Ph), 70415-70-2; 3 (R = p-NO_2Ph), 70415-71-3; 3 (R = p-CH_3OPh), 70415-72-4; 3 (R = p-$(CH_3)_3$CPh), 70415-73-5; 3 (R = $(CH_2)_{14}CH_3$), 70415-74-6; 4 (R = Ph), 50908-25-3; 4 (R = p-CH_3Ph), 70415-75-7; 4 (R = p-NO_2Ph), 50908-24-2; 4 (R = p-CH_3OPh), 70415-76-8; 4 (R = p-$(CH_3)_3$CPh), 70415-77-9; 4 (R = $(CH_2)_{14}CH_3$), 70415-78-0; 6 (R = p-NO_2Ph), 831-69-6; 6 (R = Ph), 769-78-8; 6 (R = p-CH_3Ph), 2653-44-3; 6 (R = p-CH_3OPh), 13351-86-5; 6 (R = p-$(CH_3)_3$CPh), 15484-80-7; 7 (R = $(CH_2)_{14}CH_3$), 70415-79-1; 7 (R = p-NO_2Ph), 70415-80-4; 7 (R = Ph), 70415-81-5; 7 (R = p-CH_3Ph), 70415-82-6; 7 (R = p-CH_3OPh), 70415-83-7; 7 (R = p-$(CH_3)_3$CPh), 70415-84-8; 2-pyridylcarbinol, 586-98-1; benzoyl chloride, 98-88-4; benzoic acid, 65-85-0; *p-tert*-butylbenzoic acid, 98-73-7; *p*-methylbenzoic acid, 99-94-5; *p*-methoxybenzoic acid, 100-09-4; *p*-nitrobenzoic acid, 62-23-7; palmitic acid, 57-10-3; 2-(*N*-piperidyl)ethanol, 3040-44-6; *p*-methylbenzoyl chloride, 874-60-2; *p*-methoxybenzoyl chloride, 100-07-2; *p-tert*-butylbenzoyl chloride, 1710-98-1; *p*-nitrobenzoyl chloride, 122-04-3; palmitoyl chloride, 112-67-4.

Synthesis and Solvolysis of β,β-Divinyl-β-phenethyl Tosylate[1,2]

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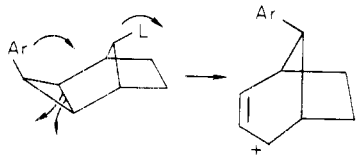
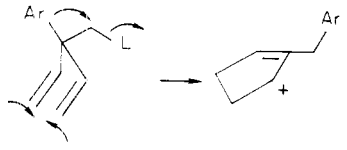
To seek aryl migration coupled with electrocyclic ring closure during solvolysis, we prepared and solvolyzed the title tosylate in aqueous dioxane and in acetic acid. The products were completely rearranged, both by vinyl (major) and phenyl (minor) migration. No cyclization via the sought electrocyclic closure was detected. The rate of acetolysis of the title tosylate was comparable to that of neophyl tosylate, indicating a balance of the opposing factors of inductive retardation and anchimeric acceleration centered in the vinyl groups.

In principle, the known process of aryl migration coupled with electrocyclic ring *opening*[1] found in eq 1 should have a converse process, viz., that of aryl migration coupled with electrocyclic ring *closure* as in eq 2. The two processes



(1)



(2)

can be viewed, as the aryl group migrates, in terms of a disrotatory cyclopropyl cation ring opening (eq 1) and a conrotatory pentadienyl cation ring closure (eq 2)—reactions with considerable literature precedent.[4] As an initial investigation of this latter possibility, the synthesis and solvolytic rearrangement of β,β-divinyl-β-phenethyl tosylate (**9**) has been studied. Although the desired result of eq 2 was *not* observed, certain synthetic and solvolytic items of interest were obtained, as well as a hindsight rationalization for the absence of the closure process.

Scheme I

$$PhCH_2CN \xrightarrow{1} PhCM_2G\ (1) \xrightarrow{2} 2 \xrightarrow{3} 3 \xrightarrow{4} 4 \xrightarrow{5} 5 \xrightarrow{6} 6 \xrightarrow{7} 7 \xrightarrow{8} 8 \xrightarrow{9} 9$$

	M	G	conditions (yield, %)
1	$CH_2CH_2OCH{=}CH_2$	CN	1. $ClCH_2CH_2$-$OCH{=}CH_2$, NaH, Me_2SO (80)
2	CH_2CH_2OH	CN	2. dilute HCl (75)
3	CH_2CH_2OTs	CN	3. TsCl, pyridine (72)
4	$CH{=}CH_2$	CN	4. KO-*t*-Bu, Me_2SO (85)
5	$CH{=}CH_2$	CONH-*t*-Bu	5. *t*-BuOH, HOAc, H_2SO_4 (40)
6	$CH{=}CH_2$	$CONH_2$	6. $BF_3 \cdot Et_2O$, $Cl_2C{=}CCl_2$ (91)
7	$CH{=}CH_2$	COOH	7. *i*-AmONO, HCl (87)
8	$CH{=}CH_2$	CH_2OH	8. $LiAlH_4$, Et_2O (60)
9	$CH{=}CH_2$	CH_2OTs	9. TsCl, pyridine (70)

Results and Discussion

After a number of unsuccessful attempts with other reagents, dialkylation of phenylacetonitrile was accomplished, using vinyl β-chloroethyl ether. The bis vinyl ether **1** so obtained was then eventually transformed to the desired tosylate **9** as shown in Scheme I.

A number of misadventures attended Scheme I, as might be expected for such hindered substances. Conversion of **1** to diol **2** was sensitive to the residence time with the dilute acid used in the hydrolysis. Longer contact times led to removal of **2** through the formation of lactone **10**,

(1) Electrocyclic Effects in Solvolysis. 2. Part 1: J. W. Wilt, T. P. Malloy, P. K. Mookerjee, and D. R. Sullivan, *J. Org. Chem.*, **39**, 1327 (1974).
(2) Taken in part from the dissertation of R.N., Loyola University of Chicago, 1977.
(3) University Fellow, 1975–1976.
(4) The disrotatory cyclopropyl cation opening has many examples and is discussed in a number of texts: e.g. T. H. Lowry and K. S. Richardson, "Mechanism and Theory in Organic Chemistry", Harper and Row, New York, N.Y., 1976, pp 647–50. The conrotatory pentadienyl cation closure is less referenced. A few recent studies are Y. Gaoni, *Tetrahedron Lett.*, 371 (1977), N. W. K. Chiu and T. S. Sorensen, *Can. J. Chem.*, **51**, 2776 (1973), and C. W. Shoppee and B. J. A. Cooke, *J. Chem. Soc., Perkin Trans. 1*, 1026 (1973).

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