termined with a Varian Associates H-100 spectrometer at 100 HMz with tetramethylsilane as the internal standard.

β-Nitroalkyl Nitrates. The compounds used in this study were prepared by the nitric oxide reduction of β-nitroalkyl peroxynitrates formed by the action of nitrogen dioxide and oxygen on the appropriate olefin according to the method of Lackowicz and Kreuz.[4]

1-Nitro 1-Olefins. A typical example for the preparation of 1-nitro 1-olefins is given below.[5] To 100 ml of octene was added 5.0 g of 1-nitro-2-decyl nitrate and this solution was heated at reflux for 12 hr. The solvent was removed under reduced pressure to give 4.7 g of a complex mixture. This mixture was transferred to a column containing 200 g of silica gel. Elution of the column with hexane gave in the initial fractions 3.4 g of 1-nitro-1-decene (90%). Subsequent elution with methanol gave 0.8 g of a solvent-derived nitrogen-containing mixture of compounds.

Kinetics. The appropriate amount of β-nitroalkyl nitrate was added to the olefin solution and the unstirred solutions were heated to the desired temperature. The decompositions of the β-nitroalkyl nitrates were followed by monitoring the disappearance of the 6.1-, 7.8-, and 11.6-μ infrared absorption bands. The solutions of β-nitroalkyl nitrates followed Beer's law in the concentration ranges studied (up to 0.22 *M*). The temperatures were maintained at ±0.5°. Aliquots were withdrawn at timed intervals and their spectra were recorded differentially in 0.1-mm sodium chloride cells *vs.* the appropriate solvent. A base-line, straddling the peak, technique was used to measure the absorbances of the band being monitored.[6] The rate constants were calculated from the slope of a log (β-nitroalkyl nitrate)/β-nitroalkyl nitrate *vs.* time plot and were reproducible within ±5%.

Inspection of all crude reaction mixtures was done by comparison of their infrared and nuclear magnetic resonance spectra with spectra of authentic samples of 1-nitro 1-olefins. The preparation and properties of the authentic 1-nitro 1-olefins is described by Cummings and Kreuz.[2]

Registry No.—2-Methyl-1,5-dinitro-2-pentanol, 49746-26-1.

References and Notes

(1) J. M. Larkin and K. L. Kreuz, *J. Org. Chem.*, **37**, 3079 (1972).
(2) W. M. Cummings and K. L. Kreuz, *J. Org. Chem.*, **37**, 3929 (1972).
(3) They are purified by column chromatography on silica gel and the purity is established by chemical analysis, nmr, and ir. Therefore, small amounts of impurity could easily go undetected.
(4) D. R. Lachowicz and K. L. Kreuz, *J. Org. Chem.*, **32**, 3885 (1967); U. S. Patent 3,282,983 (1966).
(5) U. S. Patent 3,510,531 (1900).
(6) H. Morgan, R. M. Sherwood, and T. A. Washall, *Anal. Chem.*, **38**, 1009 (1966).

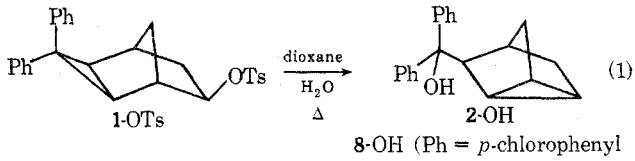
On the Solvolysis Pathway for *exo*-3,3-Diaryltricyclo[3.2.1.0^{2,4}]oct-*exo*-6-yl Tosylates[1,2]

James W. Wilt* and John R. Flanyak

Department of Chemistry, Loyola University of Chicago, Chicago, Illinois 60626

Received October 1, 1973

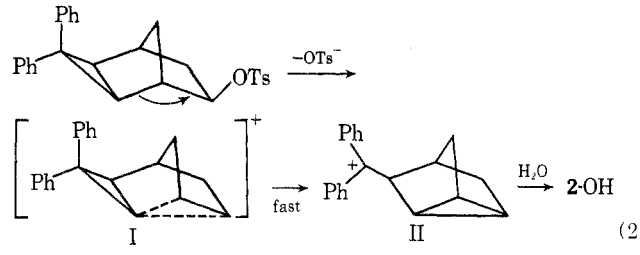
The solvolytic rearrangement of the parent title tosylate 1-OTs leads to a nortricyclyl product 2-OH (eq 1).[3] Two



(1)

8-OH (Ph = *p*-chlorophenyl

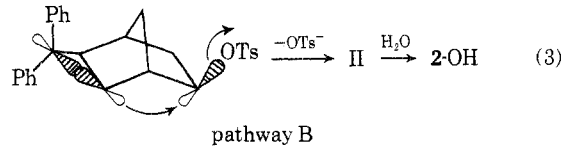
pathways were suggested[3] for this process. The first suggestion (pathway A) invoked a 1,2 σ-bond participation in the rate-determining step to produce ion I as an intermediate species (eq 2). It was further suggested that in a subsequent fast step, I was converted to the more stable benzhydrylic cation II, which then gave the alcohol product 2-OH. Such σ participation should be absent in the endo tosylate related to 1-OTs. Indeed, the exo/endo



(2)

pathway A

rate ratio for the epimeric tosylates was over 4000-fold at 25°.[3] A second suggested pathway (pathway B) invoked direct cyclopropyl ring participation *via* a "back-lobe" mechanism to produce ion II at once (eq 3). This idea would also accommodate a large exo/endo rate ratio. Moreover, such a notion has literature precedent,[4] as pathway A obviously has as well.

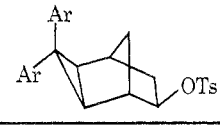


(3)

pathway B

It has now been found that pathway A seems to be in better accord with further results. Use of aryl groups in 1-OTs other than phenyl allowed a structure–reactivity study. Table I contains some of the results of that study.[5]

Table I
Kinetic Data on Tricyclic Tosylates, 64.5° [a]

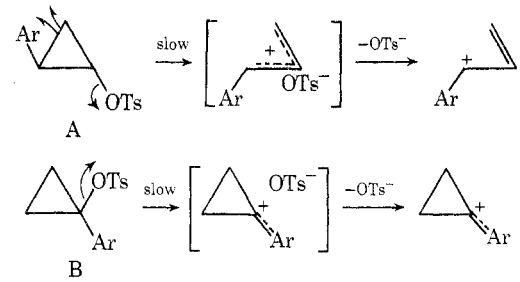


Compd	Ar	$10^5 k_1$, sec^{-1}	k_{rel}
3-OTs	*p*-Anisyl	28.85	27
4-OTs	*p*-Tolyl	15.97	15
5-OTs	*p*-Chlorophenyl	1.07	1

[a] In dioxane–water (80:20, v/v) containing 2,6-lutidine.

A plot of log k_1 *vs.* 2σ[6] gave a value of $\rho = -1.44 \pm 0.04$. Use of σ^+[7] values gave a poor correlation with pronounced curvature. Clearly, the rate correlation with σ instead of σ^+ and the small spread in k_{rel} are in better keeping with pathway A, wherein no appreciable cationic charge development on the aromatic ring; so the reaction wherein direct conjugation with the aryl groups exists in ion II.

A comparison might be made with the arylcyclopropyl systems shown in eq 4.[8] In A, solvolysis occurs with little

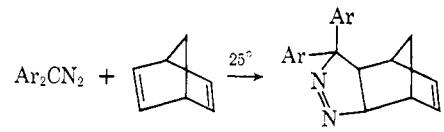


(4)

charge development on the aromatic ring, so the reaction follows σ and $\rho = -1.75$ (108°). In B, solvolysis occurs with extensive charge development on the aromatic ring; so the reaction follows σ^+ and $\rho = -4.31$ (108°). It is suggested that pathway A of the present study relates to A and pathway B relates to B.

As another point for investigation, one might note that a fundamental difference between the pathways lies in the

Table II
Diaryldiazomethane–Norbornadiene Adducts

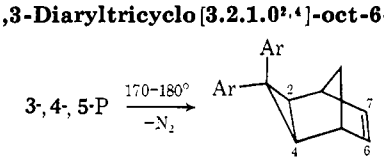


3-, 4-, 5-P

Ar	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H
p-Anisyl, **3**-P[a]		40				
p-Tolyl, **4**-P	121–122.5	44	84.05	7.05	84.08	7.19
p-Chlorophenyl, **5**-P	131–132	39.5	67.62	4.53	67.64	4.42

[a] Used crude in the subsequent steps.

Table III
***exo*-3,3-Diaryltricyclo[3.2.1.0^{2,4}]-oct-6-enes**

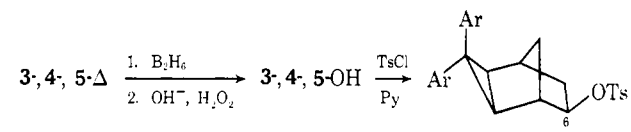


3-, 4-, 5-Δ

Ar	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H
p-Anisyl, **3**-Δ[a]	76–77.5	88	82.99	6.96	83.19	6.90
p-Tolyl, **4**-Δ[b]	110–112	92	92.25	7.74	92.07	7.96
p-Chlorophenyl, **5**-Δ[c]	134.5–136	97	73.41	4.92	73.35	4.84

[a] δ H-2,4, 1.63 (s); δ H-6,7, 6.53 (t). [b] δ H-2,4, 1.71 (s); δ H-6,7, 6.50 (t). [c] δ H-2,4, 1.53 (s); δ H-6,7, 6.51 (t).

Table IV
***exo*-3,3-Diaryltricyclo[3.2.1.0^{2,4}]-oct-*exo*-6-yl Tosylates**

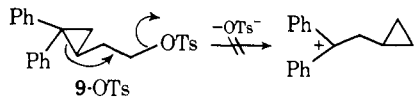


3-, 4-, 5-OTs

Ar	Mp, °C	Yield, %	Calcd, % C	Calcd, % H	Found, % C	Found, % H
p-Anisyl, **3**-OTs[a]	84–87 dec	74	71.00	6.16	70.93	6.37
p-Tolyl, **4**-OTs[b]	100.5–103 dec	84	75.95	6.58	76.20	6.62
p-Chlorophenyl, **5**-OTs[c]	116–118 dec	86	64.93	4.84	65.15	4.74

[a] δ H-6, 4.51 (br d). [b] δ H-6, 4.51 (br d). [c] δ H-6, 4.52 (br d). Note: the alcohols **3**- and **5**-OH were used in crude form to prepare these tosylates. Alcohol **4**-OH had mp 129–131° from hexane. *Anal.* Calcd for $C_{22}H_{24}O$: C, 86.80; H, 7.94. Found: C, 87.06; H, 8.06.

participation suggested: a norbornyl type in A but a cyclopropyl ring type in B. If pathway B operated in eq 1, then perhaps β-(*gem*-diphenylcyclopropyl)ethyl tosylate (**9**-OTs) would behave similarly, as in eq 5. This tosylate



9-OTs (5)

was prepared in a straightforward fashion which requires no discussion (see Experimental Section). In 80% dioxane, however, it was found that **9**-OTs solvolyzed without rearrangement; *i.e.*, only **9**-OH was obtained (k_1 = 2.5 × 10^{-6} sec^{-1} at 75°), presumably *via* SN solvolysis.[9,12] Likewise, acetolysis of **9**-OTs proceeded without rearrangement to the acetate **9**-OAc. While these negative results do not disprove the existence of pathway B in eq 1, the failure of **9**-OTs to rearrange *coupled with* the low ρ value found for eq 1 make this pathway definitely less likely. On the other hand, these same facts are accommodated by pathway A, which is therefore suggested as the operative route in eq 1.

Experimental Section

Melting points, spectra, and analyses were obtained as previously described.[3] Boiling points are uncorrected. See Tables II-IV for selected characterization data. For complete nmr and ir spectral data, consult the dissertation of J. R. F.

Tosylates **3**-, **4**-, and **5**-OTs were prepared from the corresponding alcohols in pyridine with *p*-toluenesulfonyl chloride. The alcohols **3**-, **4**-, and **5**-OH, their alkene precursors **3**-, **4**-, and **5**-Δ, and the pyrazoline adducts **3**-, **4**-, and **5**-P, obtained from norbornadiene and the appropriate diaryldiazomethane that served as starting points for these syntheses, were all prepared as described for the diphenyl analog.[3] Analytical samples of the pyrazolines and alkenes were recrystallized from methanol. The tosylates were recrystallized from petroleum ether (bp 30–60°)–benzene mixtures.

β-(*gem*-Diphenylcyclopropyl)acetonitrile. Into a stirred solution of sodium cyanide (0.13 g, 2.6 mmol) in dimethyl sulfoxide (10 ml) at 60° was added dropwise a solution of (*gem*-diphenylcyclopropyl)carbinyl tosylate [mp 67–68° (lit.[14] mp 58–80°), 1.0 g, 2.6 mmol] in dimethyl sulfoxide (5 ml). The reaction material was held at 60° for 32 hr and then poured into water and extracted with ether. Distillation of the dried ether extracts gave the nitrile as an oil (0.58 g, 92%): bp 148–152° (0.35 mm); $n^{28}D$ 1.5772; d_4^{26} 1.112; ir (neat) λ 4.54 μ (CN).

Anal. Calcd for $C_{17}H_{15}N$: C, 87.51; H, 6.48. Found: C, 87.61; H, 6.63.

Methyl β-(*gem*-Diphenylcyclopropyl)acetate. The nitrile above (2.0 g, 8.5 mmol) in alcohol (15 ml) was added in portions over 15 min to a solution of potassium hydroxide (7.0 g, 0.125 mol) in water (10 ml). After an overnight reflux period, the solution was cooled and acidified. The crude acid so precipitated (1.75 g, 88%) was used directly in the next step. The acid (1.51 g, 6 mmol) in ether was esterified with excess diazomethane. Distillation afforded the ester as an oil (1.20 g, 76%): bp 151–155° (0.4 mm); $n^{28}D$ 1.5602; d_4^{26} 1.242; nmr ($CDCl_3$) δ 3.62 (s, OCH_3); ir (neat) λ 5.84 μ (C=O).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.11; H, 6.83.

β-(*gem*-Diphenylcyclopropyl)ethyl Alcohol (9-OH). The acetate ester above (1.2 g, 4.5 mmol) in ether (25 ml) was added dropwise over a 15-min period to lithium aluminum hydride (0.17 g, 4.5 mmol) in ether (25 ml). The solution was stirred under reflux for 3 hr and processed in the usual way. Distillation yielded the alcohol as an oil (1.05 g, 77%): bp 153–158° (0.25 mm); $n^{28}D$ 1.5913; d_4^{26} 1.210; nmr ($CDCl_3$) δ 3.68 (t, $-CH_2OH$); ir (neat) λ 3.02, 9.43–9.69 μ (primary alcohol).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.68; H, 7.61. Found: C, 85.62; H, 7.50.

β-(*gem*-Diphenylcyclopropyl)ethyl Tosylate (9-OTs). Reaction of the alcohol above in pyridine with *p*-toluenesulfonyl chloride in the standard manner[15] gave tosylate **9-OTs** as a colorless solid; mp 95–97° from absolute alcohol; nmr ($CDCl_3$) δ 4.10 (t, $-CH_2OTs$); ir (KBr) λ 8.38, 8.47 μ ($-SO_2-$).

Anal. Calcd for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16. Found: C, 73.29; H, 6.27.

Solvolysis Studies. A. In Dioxane–Water (80:20 v/v). The kinetic and preparative solvolyses were performed as described earlier.[3] From 4-OTs at 110° for 24 hr there was obtained **bis(*p,p'*-dimethyl)benzhydrylidenenortricyclene (6, 99%)**: mp 103–105° from aqueous methanol; nmr ($CDCl_3$) δ 7.07 (narrow m, ArH), 2.56 (broad s, H-4), 2.33 (s, $ArCH_3$), 1.85–1.26 (m, remaining H's); ir (KBr, prominent absorptions only) λ 6.12, 6.68, 7.32, 7.90, 8.62, 9.25, 9.80, 10.01, 10.69, 11.45, 12.62, 13.10–13.41, 14.25 μ. The spectra were closely analogous to those reported[3] for benzhydrylidenenortricyclene (7).

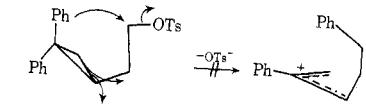
From 5-OTs at 75° for 14 hr there was obtained 8-OH (88%): mp 98–100° from aqueous methanol; nmr ($CDCl_3$) δ 7.65–7.03 (m, ArH), 2.55 (broad s, OH), 2.38 (broad s, H-4), 2.07 (d, exo H-5, $J_{exo-endo}$ = 11 Hz), 1.47 (broad s, H-1), 1.38–0.82 (m, remaining H's); ir (KBr, prominent absorptions only) λ 2.85, 6.81, 7.24, 7.70, 7.81, 8.12, 8.76, 9.35, 10.20, 10.41, 11.25, 12.43–12.72, 14.10–14.55 μ. The spectra were in close analogy to those reported for 2-OH.[3] From tosylate 9-OTs at 130° for 16 hr there was obtained only 9-OH (77%).

B. In Acetic Acid. Tosylate 9-OTs (0.19 g, 0.8 mmol) was heated in dry acetic acid (20 ml) containing sodium acetate (0.04 *M*) at 120° for 46 hr. Reaction work-up yielded only 9-OAc (0.17 g, 87%): nmr ($CDCl_3$) δ 4.05 (t, $-CH_2OAc$, J = 7.5 Hz), 1.91 (s, -OAc); ir neat) λ 5.90 μ (C=O). The nmr total spectrum was in close correspondence to 9-OH and 9-OTs and left no doubt that all three possessed the same parent structure.

Registry No.—3-OTs, 50323-69-8; 3-P, 50323-89-2; 3-OH, 50323-71-2; 3-Δ, 50323-72-3; 4-OTs, 50323-73-4; 4-P, 50323-90-5; 4-OH, 50323-74-5; 4-Δ, 50323-75-6; 5-OTs, 50323-76-7; 5-P, 50323-91-6; 5-OH, 50323-77-8; 5-Δ, 50323-78-9; 6, 50323-92-7; 8-OH, 50323-93-8; 9-OH, 38674-45-2; 9-OTs, 50323-95-0; 9-OAc, 50323-96-1; di-*p*-anisyldiazomethane, 1221-72-3; di-*p*-tolyldiazomethane, 1143-91-5; di-*p*-chlorophenyldiazomethane, 1143-92-6; norbornadiene, 121-46-0; β-(*gem*-diphenylcyclopropyl)acetonitrile, 50323-99-4; β-(*gem*-diphenylcyclopropyl)carbinyl tosylate, 50324-00-0; methyl β-(*gem*-diphenylcyclopropyl)acetate, 38674-44-1.

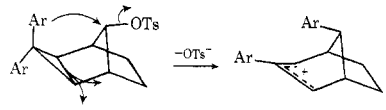
References and Notes

(1) (a) Studies on 3,3-Diaryltricyclo[3.2.1.^{2,4}]octanes. III. (b) Paper II: J. W. Wilt, T. P. Malloy, P. K. Mookerjee, and D. Sullivan, *J. Org. Chem.*, in press.
(2) Taken from portions of the dissertation of J. R. F., 1973.
(3) J. W. Wilt and T. P. Malloy, *J. Org. Chem.*, **38**, 277 (1973).
(4) P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).
(5) The extensive kinetic data for other temperatures and the activation parameters calculated therefrom have been omitted from Table I for the sake of brevity. The interested reader should inquire or consult the dissertation of J. R. F.
(6) The presence of two identical aryl groups in such studies has normally been handled in this fashion. *Cf.* H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
(7) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).
(8) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schollkopf, J. Paust, and K. Fellenberger, *J. Amer. Chem. Soc.*, **94**, 133 (1972).
(9) β-(Cyclopropyl)ethyl brosylate itself gave no rearrangement during acetolysis.[10] The same is true for 9-OTs, either in aqueous dioxane or in dry acetic acid. Formolysis of 9-OTs was not investigated, but rearrangement would not be unexpected here. Various substituted β-(cyclopropyl)ethyl brosylates (as well as the parent) do rearrange during solvolysis in this medium.[10,11]
(10) R. R. Sauers and R. W. Ubersax, *J. Org. Chem.*, **31**, 495 (1966).
(11) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **92**, 6557 (1970).
(12) It might be noted that this solvolysis of 9-OTs involved no proximate aryl migration coupled with cyclopropyl ring opening, as in eq i.



(i)

Such behavior characterizes the solvolysis of the more rigid *exo*-3,3-diaryltricyclo[3.2.1.$0^{2,4}$]oct-*anti*-8-yl tosylates (eq ii).[1b,13]



(ii)

(13) J. W. Wilt and T. P. Malloy, *J. Amer. Chem. Soc.*, **92**, 4747 (1970).
(14) H. M. Walborsky, L. Barasch, A. E. Young, and F. J. Impastato, *J. Amer. Chem. Soc.*, **83**, 2517 (1961).
(15) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

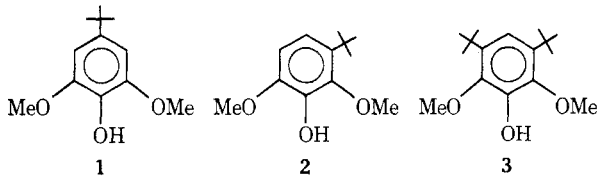
Novel Products from Oxidation of Hindered Phenols with One-Electron-Transfer Oxidants

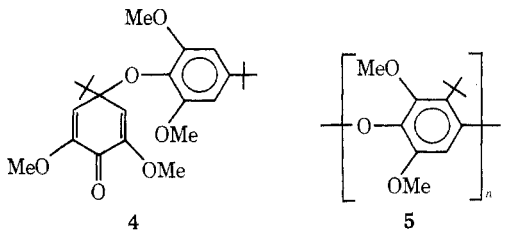
R. C. Eckert,[1a] Hou-min Chang,*[1b] and W. P. Tucker[1c]

School of Forest Resources, North Carolina State University, Raleigh, North Carolina 27607

Received September 25, 1973

As part of a study of the alkaline oxidation of lignin[2] it was of interest to determine the nature of the products resulting from the oxidation of model phenols **1**, **2**, and **3** by one-electron-transfer reagents such as potassium ferricyanide, lead dioxide, silver oxide, etc. The products of such oxidations are usually dimers and oligomers formed by the coupling of intermediate phenoxy radicals[3] and, indeed, phenol **1** is known to give the quinol ether **4** on treatment with potassium ferricyanide or silver oxide.[4] We found compound **2** to behave in a similar manner, giving, on oxidation by ferricyanide in a benzene–aqueous potassium hydroxide system, an 85% yield of the polyphenylene ether **5** (mol wt *ca.* 2900). The polymer **5**, like **4**, was formed by coupling of the initially produced phenoxy radicals.





Phenol **3** reacted sluggishly under the same conditions and, although the benzene layer showed the intense emer-