unidentified products. Product identification was established by comparing ir and nmr spectra with those of authentic samples. The quantum yield for disappearance of DPE in neat 2-propanol at 2800 Å was 0.16.

Xanthone (E_T = 74 kcal/mol) sensitized the photolysis at 3500 Å. DPE is transparent at this wavelength. The photolysis of DPE (0.01 *M*) at 2800 Å was completely quenched by piperylene (0.10 *M*). The reaction must therefore proceed *via* the excited triplet.[8] We propose the following mechanism.

$$\mathrm{DPE} \xrightarrow{h\nu} {}^1\mathrm{DPE}$$

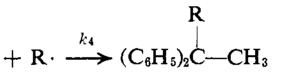
$${}^1\mathrm{DPE} \xrightarrow{k_d} \mathrm{DPE}$$

$${}^1\mathrm{DPE} \xrightarrow{k_{isc}} {}^3\mathrm{DPE}$$

$${}^3\mathrm{DPE} \xrightarrow{k_1} \mathrm{DPE}$$

$${}^3\mathrm{DPE} + \mathrm{RH} \xrightarrow{k_2} \mathrm{C_6H_5\dot{C}CH_3} + \mathrm{R}\cdot$$

$$2(\mathrm{C_6H_5})_2\mathrm{\dot{C}CH_3} \xrightarrow{k_3} (\mathrm{C_6H_5})_2(\mathrm{CCH_3})_2(\mathrm{C_6H_5})_2$$



$$(\mathrm{C_6H_5})_2\mathrm{\dot{C}CH_3} + \mathrm{R}\cdot \xrightarrow{k_4} (\mathrm{C_6H_5})_2\overset{\mathrm{R}}{\overset{|}{\mathrm{C}}}\mathrm{-CH_3}$$

$$2\mathrm{R}\cdot \xrightarrow{k_5} \mathrm{R{-}R}$$

$$\mathrm{R} = \mathrm{CH_3COHCH_3}$$

Stern–Volmer quenching studies of DPE were performed in degassed acetonitrile solutions containing varying concentrations of 2-propanol (1–5 × 10^{-2} *M*) and piperylene at 2900 Å and 25°. Relative quantum yields for DPE disappearance were determined by uv and glpc. Stern–Volmer plots (eq 1) were linear.

$$\Phi_0/\Phi = 1 + k_q\Upsilon[\mathrm{Q}] \qquad (1)$$

k_q and Υ represent quenching rate constant and triplet lifetime, respectively. Values for $k_q\Upsilon$ and Υ are given in Table I in which k_q is assumed to be 1.1 × 10^{10} M^{-1} sec^{-1}.[9] Rate constants for unimolecular triplet decay (k_1) and triplet hydrogen abstraction (k_2) were obtained from the plot of $1/\Upsilon$ *vs.* [2-propanol] according to eq 2 and were found to be 0.74 × 10^7

$$1/\Upsilon = k_1 + k_2\,[\text{propanol}] \qquad (2)$$

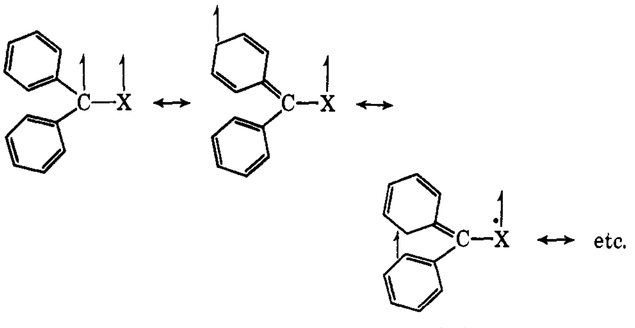
sec^{-1} and 1.4 × 10^9 M^{-1} sec^{-1}, respectively. The triplet decay rate constant is in agreement with the work of Ullman and Henderson,[10] who determined this value to be greater than 0.45 × 10^7 sec^{-1}.

Table I. Quenching of the Reaction of 1,1-Diphenylethylene with 2-Propanol by Piperylene in Acetonitrile

[2-Propanol], $10^{-2}M$	$k_q\Upsilon$, M^{-1}	Υ,[a] 10^{-8}sec
1.1	472	4.29
2.9	224	2.03
3.4	196	1.78
4.6	151	1.38

[a] Assuming k_q = 1.1 × 10^{10} M^{-1} sec^{-1}.

It is noteworthy that the bimolecular rate constant for triplet DPE hydrogen abstraction is considerably greater than the corresponding value reported for benzophenone triplet, 10^6 M^{-1} sec^{-1}.[11] We suggest that the electron repulsion between the unpaired electrons in triplet DPE and benzophenone strongly induces delocalization of one electron so that the reaction sites in these biradical species resemble free radicals. The relative reactivities of triplet DPE and benzophenone may therefore parallel those of alkyl and alkoxy radicals.[12]



X = O, CH$_2$

The ability of triplet olefins to abstract hydrogen is probably related to the rate of other processes such as triplet decay and competitive reactions.

---

[8] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966).

[9] P. J. Wagner and I. Kochvar, *ibid.*, **90**, 2232 (1968).

[10] E. F. Ullman and W. A. Henderson, *ibid.*, **89**, 4390 (1967).

[11] A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963); S. G. Cohen and W. V. Sherman, *J. Amer. Chem. Soc.*, **85**, 1642 (1963); J. A. Bell and H. Linschitz, *ibid.*, **85**, 528 (1963).

[12] We have been unable to find comparative data for rates of hydrogen abstraction by alkyl and alkoxy radicals in solution.

Herbert M. Rosenberg
Air Force Materials Laboratory
Wright-Patterson Air Force Base, Ohio 45433

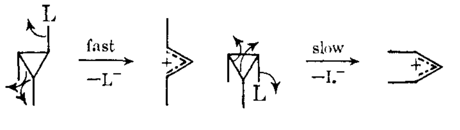
Paul Servé
The Department of Chemistry, Wright-State University
Dayton, Ohio 45433

Received May 12, 1970

Transannular Phenyl Participation and Electrocyclic Ring Opening in the Solvolysis of the Epimeric *exo*-3,3-Diphenyltricyclo[3.2.1.0^{2,4}]oct-8-yl Tosylates

Sir:

Stereospecific disrotatory opening of the ring has been used to rationalize the disparate solvolytic reactivities of cyclopropyl substrates.[1] We have sought to combine this effect with possible transannular phenyl participation in solvolysis. We here report an instance of such a combination, *viz.*, an unusual 1,4-phenyl migration in the solvolysis of a cyclopropyl compound which appears to involve transannular

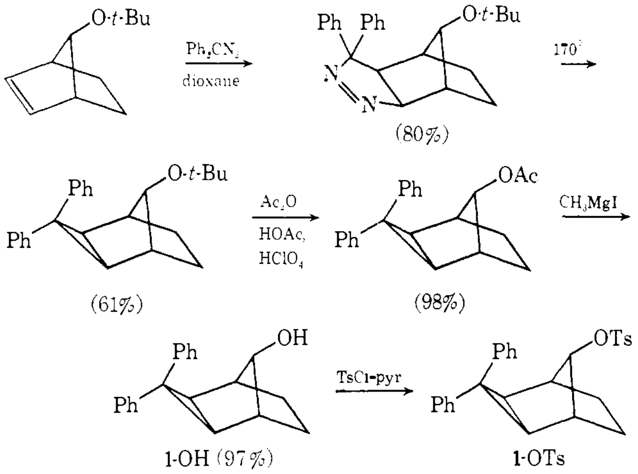


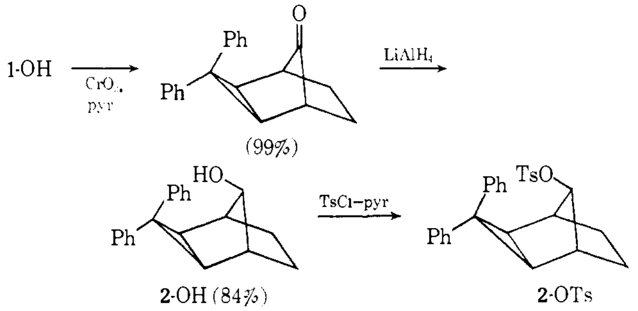
---

[1] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965); P. v. R. Schleyer, G. W. van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966); C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966); U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. Van Dine, *Tetrahedron Lett.*, 3639 (1967).

phenyl participation along with cyclopropyl ring opening.

Addition of diphenyldiazomethane to *anti*-7-*t*-butoxynorbornene,[2] followed by the reactions shown in the flowsheet afforded *exo*-3,3-diphenyltricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol (**1**-OH),[3] mp 154.5–155°, tosylate (**1**-OTs),[3] mp 140–141°, δ^{CDCl_3} 3.95 broad m (H-8), 1.58 s (H-2, H-4). Oxidation of **1**-OH produced its ketone.[3,4] Reduction of the ketone with lithium aluminum hydride yielded the epimeric *syn*-8-alcohol **2**-OH,[3] mp 132.5–134°, tosylate **2**-OTs,[3] mp 186–188°, δ^{CDCl_3} 4.20 sharp m (H-8), 1.70 s (H-2, H-4).



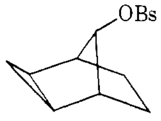


The solvolytic data for **1**-OTs and **2**-OTs are collected in Table I. As the data in the table show, **1**-OTs and **2**-OTs have comparable reactivity. Contrariwise, the reactivities of the nonphenyl brosylate analogs **3** and **4** are much different. The *syn*-epimer **4** is over 8000-fold faster in acetolysis than the *anti*-epimer **3**.[5] The dramatic increase in reactivity shown in our study by **1**-OTs may be rationalized as the result of transannular participation by the phenyl group as shown, followed by or coupled with disrotatory opening of the cyclopropyl ring. This mode of ring opening of the cyclopropyl ring is symmetry controlled.[1] This allows the phenyl migration to occur stereospecifically across the ring to displace the *anti*-tosylate function.[6] Such reasoning rationalizes the >10^3-fold increased reactivity of **1**-OTs compared to **3**. The *syn*-epimer **2**-OTs cannot use this path and in fact has a somewhat decreased reactivity compared to **4**.[7]

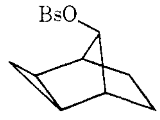
Table I

Tosylate^a	Temp,^{b} °C	10^5k_1, sec^{-1}
1-OTs^c	112.0	1.45 ± 0.02
	122.5	4.04 ± 0.08
	133.0	11.2 ± 0.2
2-OTs^d	112.0	2.09 ± 0.02
	122.5	5.57 ± 0.13
	133.0	15.2 ± 0.4

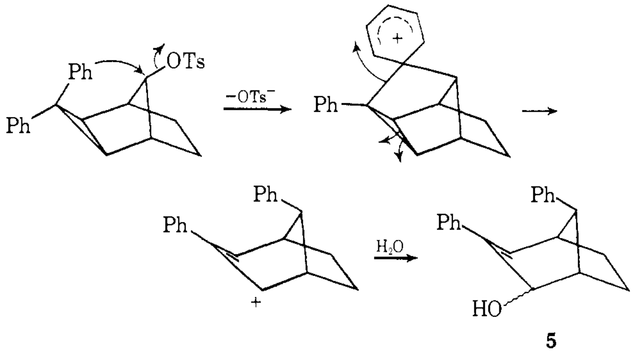
^{a} The tosylates were 0.030 *M* solutions in 80:20 dioxane–water (% v/v) containing 0.044 *M* 2,6-lutidine. ^{b} ±0.2°. ^{c} ΔH^* 29.4 ± 0.8 kcal mol^{-1}; ΔS^* −4.7 ± 2.1 eu. ^{d} ΔH^* 28.7 ± 1.0 kcal mol^{-1}; ΔS^* −6.0 ± 2.5 eu.



3



4



The solvolysis product **5**,[3] mp 102–109°, is an 85:15 mixture of epimeric alcohols. Present evidence favors the *endo* epimer as the major component. Presumably this is the result of steric hindrance by the *syn*-8 phenyl group in product formation from the intervening cation. The structure of **5** was established chemically as shown. The samples of all-*cis*-2-phenylcyclopentane-1,3-dicarboxylic acid,[3] mp 232.5–235.5° dec, from **5** and from *syn*-7-phenylnorbornene[3,8] were completely identical. They were also characterized as the dimethyl ester,[3] mp 66–67.5°, δ^{CDCl_3} 3.90 t (J = 7 Hz, H-2), 3.27 s ($-COOCH_3$). The pertinent spectral data that support the structure assigned to **5** include: δ^{CDCl_3} 6.58 and 6.30 d (J = 6 and 7 Hz, respectively, $-CH{=}C<$ of *endo* and *exo* epimers), 4.60 and 4.25 broad d (J = 5 and 10 Hz, respectively, $>CH-OH$ of *exo* and *endo*

---

[2] B. Franzus and E. I. Snyder, *J. Amer. Chem. Soc.*, **87**, 3423 (1965).

[3] The compound gave an acceptable combustion analysis and its spectra were in agreement with the structure proposed.

[4] This ketone has its carbonyl stretching frequency at 1769 cm^{-1} (2% in CCl_4). By the correlation due to C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964), unassisted acetolysis of an arenesulfonate at C-8 in this system should be quite slow at 25° relative to cyclohexyl-OTs (log k_{rel} = −6.3) and comparable to 7-norbornyl-OTs itself (log k_{rel} = −7.0). As both **1**- and **2**-OTs are much faster than 7-norbornyl-OTs, they are by this criterion considerably assisted in their solvolysis.

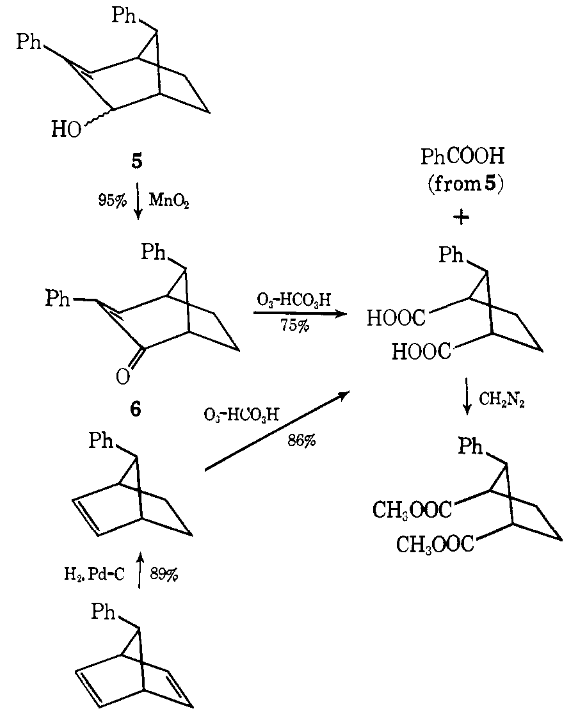
[5] J. S. Haywood-Farmer and R. E. Pincock, *J. Amer. Chem. Soc.*, **91**, 3020 (1969).

[6] Work in progress is aimed at the causality involved in this reaction. Specifically, is indeed the phenyl group pushed off or does it rather initiate transannular participation and thereby force the electrocyclic ring opening?

[7] The rate constant for **4** is 7.0 × 10^{-5} sec^{-1} at 100° in 0.1 *N* NaOAc–HOAc.[5] If this rate is increased twofold (0.33 for the leaving group change × 6 for the solvent change), then **4**-OTs is calculated to be 23-fold faster than **2**-OTs (k_1 = 0.6 × 10^{-5} sec^{-1}) in 80% dioxane at 100°. With regard to **3** and **4**, the point we wish to make in this report is the large gain shown in the reactivity of **1**-OTs. The more detailed studies under way will hopefully give more information on the slight decrease in the reactivity of **2**-OTs.

[8] This olefin was prepared by catalytic hydrogenation of 7-phenylnorbornadiene.[9] Only the *syn* epimer was obtained, bp 95–96° at 0.75 mm, δ^{CCl_4} 5.77 t (HC=CH), 2.85 sharp m (H-7).

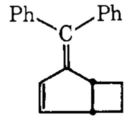
[9] P. R. Story and S. R. Fahrenholtz, *J. Org. Chem.*, **28**, 1716 (1963).



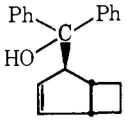
epimers); *m/e* fragments of 276 (parent), the *separated* phenyl fragments 159 (base peak, CH_2=CH—C$^+$-(OH)—C(Ph)=CH_2) and 117 (PhCH=CH—CH_2^+).[10]

The important intermediate ketone **6**[3] was the *only* product of oxidation of **5** with manganese dioxide, a fact which supports the epimeric constitution of **5**. As evidence for its structure aside from the ozonolysis shown, ketone **6**, mp 107–108°, *m/e* 274 (parent), exhibited λ_{KBr} 6.03 μ and λ_{max} (EtOH) 265 mμ (ϵ 4460), indicative of an α,β-unsaturated ketone. Also, upon reduction with lithium aluminum hydride **6** re-formed **5**, although as a different mixture of epimers now richer in the *exo*.

From **2**-OTs at least four products are formed, among them the epimeric alcohols **5** (29.5%). The other products have tentatively been assigned structures **7** (22.5%) and **8** (43%) from their spectra. Thus, **7**

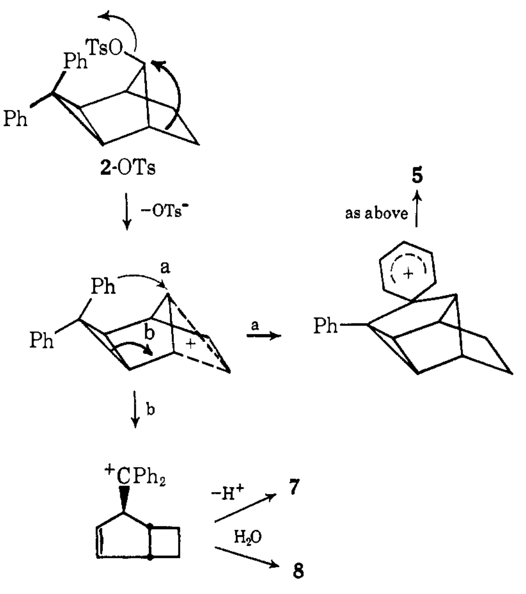


7



8

possessed λ_{max} (EtOH) 242 (ϵ 9650) and 294 mμ (ϵ 21,800)[11] as well as two vinyl protons at δ 6.36 d and 6.06 m (AB portion of an ABX pattern). Compound **8** was apparently a tertiary alcohol, ir (neat) 2.83 and 8.6 μ with two vinyl protons at δ 5.85 m and 5.37 m (AB portion of an ABX pattern) and an OH at δ 1.95 s. Such products may be rationalized as shown. This scheme combines σ participation by a ring bond (*à la syn*-7-norbornenyl tosylate[13]) and a facile cyclopropylcarbinyl rearrangement (b)[14] in competition with the transannular phenyl migration (a) observed with **1**-OTs.



Work continues on the present system as well as on additional systems potentially susceptible to solvolytic participation combined with electrocyclic ring reactions. To our knowledge, this work is the first to describe such combined orbital symmetry and participation effects.

Acknowledgment. We thank Dr. Henry F. Dabek, Jr., for the mass spectral determinations.

---

[10] The parent **1**-OTs has for its base peaks the *geminal* phenyl fragments *m/e* 191, 192 (Ph_2C^+—C≡CH, Ph_2C^+—CH=CH·).

[11] *Cf.* 1,1-diphenyl-1,3-butadiene: λ_{max} (EtOH) 236 and 287 mμ.[12]

[12] T. Holm, *Acta Chem. Scand.*, **17**, 1441 (1963).

[13] S. Winstein and E. T. Stafford, *J. Amer. Chem. Soc.*, **79**, 505 (1957).

[14] R. Breslow in "Molecular Rearrangements," P. de Mayo, Ed., Interscience, New York, N. Y., 1963, pp 259–276.

[15] National Science Foundation Trainee, 1968–1970.

James W. Wilt, Thomas P. Malloy[15]
Department of Chemistry, Loyola University of Chicago
Chicago, Illinois 60626

Received March 30, 1970

The Reaction of 1,3-Bisdiazopropane with Cyclohexane. The Possible Intermediacy of Diazocyclopropane

Sir:

We have reinvestigated the reaction of 1,3-bisdiazopropane (**1**) with cyclohexanone (**2**)[1] and have reassigned the structures of the two ketones which were formerly believed to arise by double expansion of the six-membered ring. Further, we have found a previously undetected product with a new ring system which rearranges to give one of the ketonic products. Diazocyclopropane is a possible intermediate in the reaction.

Gutsche and Smith reported that **1**, generated *in situ* from the bisnitroso urethane **3**, reacts with cyclohexanone (**2**) to give two isomeric ketones A and B along with the by-products **4** and **5**. Ketones A and B were isolated from the reaction mixture by column chromatography followed by distillation and a final purification by preparative vpc. The structures of A and B were assigned as **6** and **7** on the basis of analytical and spectral data.[1] In particular, A showed a carbonyl (1695 cm^{-1}) and cyclopropane hydrogens (τ 8.91 and 9.42) while **B** showed a four-membered ring ketone (1769 cm^{-1}) and low-field resonances in the nmr spec-

---

[1] C. D. Gutsche and T. D. Smith, *J. Amer. Chem. Soc.*, **82**, 4067 (1960).