TABLE I

QUANTUM YIELD OF THE PHTHALIMIDO OXALATE REACTION[a]

Phthalimido oxalate, $M \times 10^2$	H_2O_2, $M \times 10^2$	I_{max}, ft lambert cm^{-1}	$t^1/_4$,[b] min	Quantum yield,[c] einstein mol^{-1} × 10^2
0.1	2.4	0.01	94.0	8.7
0.1[d]	3.4	0.04	6.7	2.6
1.0	2.4	0.01	307.0	2.3
1.0[d]	3.4	0.09	10.1	1.4
1.0	9.0	0.01	269.0	1.9
1.0[e]	9.0	0.03	169.0	2.7
1.0[f]	9.0	0.04	184.0	4.3

[a] In the presence of 6×10^{-4} *M* 9,10-diphenylanthracene in dimethyl phthalate solution at 25°. [b] The time of light decay from maximum to one-quarter intensity. [c] Based on phthalimido oxalate. [d] In 1,3-propylene carbonate. [e] 1×10^{-1} *M* H_2O added. [f] 8.3×10^{-6} *M* Et_3N added.

produced 0.165 einstein mol^{-1} under similar conditions, and 0.29 einstein mol^{-1} with rubrene].[3]

Increasing the concentration of VII decreased the quantum yield. The addition of triethylamine or water decreased the chemiluminescent lifetime and moderated the efficiency loss. The lifetime was shorter and the reaction was less efficient in propylene carbonate solution than in dimethyl phthalate.

The results are insufficient for a definite statement about the mechanism. However, it is likely that the phthalamido oxalate reaction proceeds through a 1,2-dioxetanedione V intermediate, first proposed in connection with the aryl oxalate reaction.[3] By analogy to the phthalamido oxalate reaction, reactive oxalates of other substituted hydroxylamines and oximes should also produce chemiluminescence. Carboxylic esters of N-hydroxypiperidine and other hydroxylamines have been prepared and used in peptide synthesis.[10] We found that the reaction of an admittedly atypical oxime ester bis(heptafluorobutyramideoxime) oxalate[11] $C_3F_7C(NH_2){=}NC(O)C(O)N{=}(NH_2)CC_3F_7$ with hydrogen peroxide and fluorescer produced only weak light emission.

Experimental Section

Materials.—Dimethyl phthalate and propylene carbonate were fractionally distilled. Oxalyl chloride and N-hydroxyphthalimide (Aldrich) were used without purification. 9,10-Diphenylanthracene (Aldrich) was recrystallized from a mixture of absolute ethanol and chloroform to obtain material, mp 250–251° (lit.[12] mp 250–251°). Hydrogen peroxide solutions were prepared from the 98% reagent (Becco Chemical Division, FMC Co.) and were analyzed iodometrically.[13]

Diphthalimido Oxalate.—To a rapidly stirred solution of 1.63 g (0.01 mol) N-hydroxyphthalimide in 100 ml of freshly distilled (from $LiAlH_4$) 1,2-dimethoxyethane, 0.43 ml (0.005 mol) of oxalyl chloride and 1.4 ml of triethylamine were added at 25°. After 1-hr stirring the mixture was evaporated to dryness under vacuum and the solid residue was digested with three 30-ml portions of chloroform to obtain a white crystalline product, mp 233–234° dec, in 42% yield which showed infrared absorption at 1817, 1795, 1758, and 1735 cm^{-1} in methylene chloride solution.

Anal. Calcd for $C_{18}H_8O_8$: C, 56.85; H, 2.12; N, 7.37. Found: C, 56.79; H, 2.08; N, 7.49.

Bis(heptafluorobutyramidoxime)oxalate was prepared by the method of H. C. Brown and C. R. Wetzel,[11] mp 180–181° (acetone–ether 1:1) [lit.[11] mp 195–196° (xylene)].

Anal. Calcd for $C_{10}H_4F_{14}N_4O_4$: C, 23.54; N, 10.98; F, 52.14. Found: C, 23.54; N, 11.0; F, 52.04.

Qualitative Chemiluminescence Tests.—Approximately 3–5 mg of diphthalimido oxalate was added to a 5-ml solution of 1 mg of 9,10-diphenylanthracene and 0.2 ml of 1 *M* H_2O_2 (in DMe) in anhydrous 1,2-dimethoxyethane (DMe) at 25°. In other experiments the solution also contained 0.2 g of KOH, 0.2 g of KOH + 0.1 ml of water, and 0.2 ml of methanesulfonic acid and 0.2 ml of water. The chemiluminescent light was observed visually in a dark room, and the results are collected in Table II.

TABLE II

QUALITATIVE CHEMILUMINESCENCE TESTS[a]

H_2O_2	H_2O_2 + KOH	H_2O_2 + KOH + H_2O	CH_3SO_3H + H_2O
S (long)	S (short)	MS (long)	W (long)

[a] Qualitative intensities are based on the oxalyl dichloride–hydrogen peroxide reaction taken as strong (S). Other designations are M, medium; W, weak but clearly visible.

Chemiluminescence Emission Measurements.—Procedures and instrumentation for the determinations of absolute emission intensities, spectra, and quantum yields have been described previously.[6,14] Chemiluminescent reactions were initiated by injecting an aliquot of stock hydrogen peroxide solution from an all glass syringe into the combined aliquots of the other reactants in a stirred 3-ml cylindrical cuvette attached to a spectroradiometer. The raw intensity data from the radiometer was converted to einsteins sec^{-1} ml^{-1} by a Scientific Data 925 Computer programmed with the calibration data.

Registry No.—VII, 17447-57-3; hydrogen peroxide, 7722-84-1.

Acknowledgments.—Research reported in this publication was supported by the Advanced Research Project Agency under contract to the Office of Naval Research. The authors wish to thank Dr. M. M. Rauhut for discussions and encouragement. Elemental microanalysis was carried out under the direction of Mr. G. Clarke.

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[10] S. M. Beaumont, B. O. Handford, J. H. Jones, and G. T. Young, *Chem. Commun.*, 53 (1965).

[11] H. C. Brown and C. R. Wetzel, *J. Org. Chem.*, **30**, 3724, 3729, 3734 (1965).

[12] G. Wittig and R. W. Hoffmann, *Ber.*, **95**, 2718 (1962).

[13] I. W. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p 630.

[14] B. G. Roberts and R. C. Hirt, *Appl. Spectrosc.*, **21**, 250 (1967).

Alcohol Formation in the Aprotic Bamford–Stevens Reaction. III.[1] On the Nature of the Precursors

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Received May 8, 1968

The unusual formation of alcohols from certain aldehyde tosylhydrazones **1** in the aprotic Bamford–Stevens reaction has been explained according to the mechanism outlined in Scheme I.[2] N-Methyl-2-pyrrolidone (N-MP) is particularly effective in the last step though any solvent with >CH–CO–N<: present can be used.[3] Whereas the proton donation by **1**, the intermediacy of

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[1] References 2 and 3 should be considered papers I and II, respectively, of this series.

[2] J. W. Wilt, C. A. Schneider, H. F. Dabek, Jr., J. F. Kraemer, and W. J. Wagner, *J. Org. Chem.*, **31**, 1543 (1966).

[3] J. W. Wilt, R. G. Stein, and W. J. Wagner, *ibid.*, **32**, 2097 (1967).

SCHEME I

$$\underset{\mathbf{1}}{\mathrm{RCH{=}NNHSO_2\text{-}}p\text{-}\mathrm{Tol}} \xrightarrow[-\mathrm{H}^+]{\text{base}} {}^{-}\mathrm{O_2S\text{-}}p\text{-}\mathrm{Tol} + \mathrm{RCHN_2} \xrightarrow[\Delta]{} \mathrm{RCH\colon} + \mathrm{N_2}$$

$$\mathrm{RCH\colon}\ \text{or}\ \mathrm{RCHN_2} + \mathbf{1} \xrightarrow[-\mathbf{1}^-]{} \mathrm{RCH_2}^+\ \text{or}\ \mathrm{RCH_2N_2}^+ \xrightarrow{{}^{-}\mathrm{O_2S\text{-}}p\text{-}\mathrm{Tol}} \mathrm{RCH_2OSO\text{-}}p\text{-}\mathrm{Tol}$$

$$\mathrm{RCH_2OSO\text{-}}p\text{-}\mathrm{Tol} \xrightarrow{\text{solvent}} \mathrm{RCH_2OH}$$

sulfinic esters, and the mechanism of their cleavage to the alcohol product seem well established by earlier work,[2,3] the evidence for a diazoalkane precursor to the sulfinic ester has been indirect. Others had observed diazoalkane formation from tosylhydrazones under other conditions[4] and even had isolated them in some cases, but it was felt that a direct study of them under these alcohol-forming conditions was needed to complete the above studies.

Because the diazoalkanes from the earlier studied systems would be anticipated to be rather unstable, we chose diphenyldiazomethane (**2**) as the test substance. This choice seemed acceptable for two reasons. First, it is stable enough to be weighed into the reaction stoichiometrically. Second, **2** cannot give rise to products by hydride shifts or insertion. This is crucial because alcohol formation demands the absence of such intramolecular processes. The cases reported earlier met this requirement and **2** serves nicely as perhaps a simpler example.[5]

Results

Diphenyldiazomethane (**2**) was treated with *p*-toluenesulfinic acid in hot NMP, and the products were compared with those obtained by heating benzhydryl *p*-toluenesulfinate (**6**) alone in NMP. The results are gathered in Table I.

TABLE I

REACTIONS IN NMP AT 160–180°

Reaction[a]	Products, %[b] $\mathrm{Ph_2CHOH}$ (**3**)	$\mathrm{(Ph_2CH)_2O}$ (**4**)	$\mathrm{Ph_2CHSO_2\text{-}}p\text{-}\mathrm{Tol}$ (**5**)
$\mathrm{Ph_2CN_2}$ (**2**) + *p*-$\mathrm{TolSO_2H}$	75.5	10.4	14.1
$\mathrm{Ph_2CHOSO\text{-}}p\text{-}\mathrm{Tol}$ (**6**) + Δ	72.2	11.5	16.3

[a] The reaction of **2** was commenced at 115° and brought slowly to 160° as nitrogen evolved. [b] Composition values. The isolated yields were 60–70%.

Discussion

It seems inescapable that the sulfinic ester **6** is formed from **2** and gives rise to the products shown in Table I because the product spectrum is essentially the same regardless of starting material. Such identity in both the nature and percentage of the several products is a compelling argument for the intermediacy of both diazoalkanes and sulfinic esters in the formation of the alcohol product under these conditions.

As for the products themselves, the cleavage of **6** to **3** is another case of aprotic solvolysis by NMP, as reported.[3] The ether **4** and the sulfone **5** each represent the product of an alternative process from **6**. Benzhydryl *p*-toluenesulfinate (**6**) is known to rearrange thermally to the sulfone **5** by a dissociation–recombination mechanism.[6] Because **6** concomitantly forms the alcohol **3** in NMP, some benzhydryl cation is trapped by **3** to form **4**. The two processes removing the cation are roughly comparable in rate as evidenced by the yields of **4** and **5**, but neither compares to the cleavage affording **3**—a result in accord with the extreme rapidity of this cleavage.[3] The entire process can be seen in Scheme II. With these results we feel the reaction sequence given in Scheme I is finally secure.

SCHEME II

$$\begin{tikzcd}
\mathbf{2} \arrow[r, "p\text{-Tol-SO}_2\text{H}", "-\mathrm{N_2}"'] & \mathbf{6} \arrow[r, shift left, "\text{slow}"] \arrow[d, "\text{fast}", "\mathrm{NMP},\,\Delta"'] & \mathrm{Ph_2CH^+} \arrow[l, shift left] \arrow[d, "\mathbf{3}\ (-\mathrm{H}^+)"] & + & {}^{-}\mathrm{O_2S\text{-}}p\text{-}\mathrm{Tol} \arrow[r] & \mathbf{5} \\
 & \mathbf{3} & \mathbf{4} & & &
\end{tikzcd}$$

Experimental Section

Melting points were taken on a calibrated Fisher-Johns block and are uncorrected for stem exposure. Infrared spectra were determined on a Perkin-Elmer Model 21 instrument. Only characteristic functional absorption is given, in microns. Nuclear magnetic resonance spectra were taken on a Varian A-60A spectrometer using tetramethylsilane as an internal standard. The chemical shifts are given in parts per million (δ) units.

Preparations. Diphenyldiazomethane (**2**) was prepared as described[7] by oxidation of benzophenone hydrazone with mercuric oxide. **Benzhydrol** (**3**) was obtained as reported[8] by reduction of benzophenone with zinc dust [mp 66–67°; $\delta^{\mathrm{CCl_4}}$ 7.17 s ($\mathrm{C_6H_5}$–) 5.42 d (–CHOH–, J = 4 cps), 3.70 d (–OH); λ^{Nujol} 3.00 (–OH), 9.68, 9.8 (C–O) (lit.[8] mp 69°)]. **Benzhydryl ether** (**4**) was made from **3** and hydrochloric acid as described[9] [mp 106–107°; $\delta^{\mathrm{CDCl_3}}$ 7.37 m ($\mathrm{C_6H_5}$–), 5.45 s (–CHO–); λ^{Nujol} 8.49, 9.3, 9.55, 9.75, 9.94 (C–O) (lit.[9] mp 109–110°)]. **Benzhydryl *p*-tolyl sulfone** (**5**) resulted from the displacement reaction of sodium *p*-toluenesulfinate upon benzhydryl hydrogen phthalate as reported[10] [mp 188–189°; $\delta^{\mathrm{CDCl_3}}$ 7.72–7.10 m (Ar–H), 5.33 s (–CH–$\mathrm{SO_2}$–), 2.37 s (Ar–$\mathrm{CH_3}$); λ^{Nujol} 7.63, 7.70, 7.79, 8.80 (–$\mathrm{SO_2}$–) (lit.[6] mp 188–189°)]. **Benzhydryl *p*-toluenesulfinate** (**6**) was synthesized from **3** and *p*-toluenesulfinyl chloride by the literature method,[6] mp 83.5–84° (lit.[6] mp 84°). The compound is not too stable on standing (it forms **5**); so it was used immediately upon its preparation. ***p*-Toluenesulfinic acid** was dried under vacuum and used quickly after its preparation by acidification of its sodium salt, prepared as reported.[11] N-Methyl-2-pyrrolidone (NMP) was purified as described.[3]

Reaction of 2 with *p*-Toluenesulfinic Acid.—The acid (7.8 g, 50 mmol) in NMP (100 ml) was held at 115° while **2** (9.7 g, 50 mmol) was added over a 30-min period, then raised to 160° until no further nitrogen evolved. The cooled solution was diluted with water (300 ml) and extracted with ether (three 100-ml portions). The combined ether extracts were washed with base, then water, dried, and freed of solvent. Column chromatography on alumina (100 g) followed. Ether **4** (0.5 g, 6.4%) was eluted with benzene–hexane; sulfone **5** (1.4 g, 8.7%), with benzene–ether; and the alcohol **3** (4.3 g, 46.5%), with ether–acetone. Identification was made by mixture melting point and comparison of spectra with those of authentic materials, giving

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(4) *Cf.* W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, p 48.

(5) We have earlier[2] suggested the term "constrained carbenes" for those divalent carbon species incapable of intramolecular stabilization.

(6) A. H. Wragg, J. S. McMadyen, and T. S. Stevens, *J. Chem. Soc.*, 3603 (1958).

(7) L. I. Smith and K. L. Howard, "Organic Syntheses," Coll. Vol. III, John Wiley & Sons, Inc., New York, N. Y., 1955, p 351.

(8) F. Y. Miselogle and H. Sonnenborn, III, ref 7, Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 90.

(9) A. M. Ward, *J. Chem. Soc.*, 2285 (1927).

(10) M. P. Balfe, M. A. Doughty, J. Kenyon, and R. Poplett, *ibid.*, 605 (1942).

(11) F. C. Whitmore and F. H. Hamilton, ref 7, Coll.Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p 492.

the percentage composition listed in Table I. Small amounts of *p*-tolyl disulfide and benzophenone ketazine were also formed.

Reaction of 6.—A similar decomposition of 6 (50 mmol) in NMP (100 ml) at 160–180° for 1 hr gave a combined yield of 70% of product, isolated exactly as above and with the composition given in Table I.

Registry No.—**2**, 883-40-9; *p*-toluenesulfinic acid, 536-57-2; **6**, 17447-59-5; NMP, 872-50-4.

Transannular Nitrogen–Carbonyl Interaction. Generation of an α-Acetoxy Quaternary Ammonium Salt

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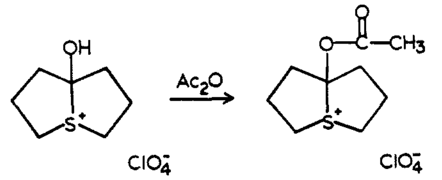
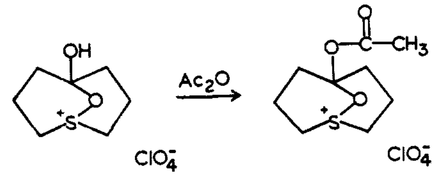
Received June 28, 1968

Earlier work on transannular interactions and reactions in this laboratory provided examples of α-acetoxysulfonium salts[1] and -oxosulfonium salts.[2,3]

For example, it was found that the perchlorate salt of 1-thiacyclooctan-5-one, which is in the transannular form 5-hydroxy-1-thioniabicyclo[3.3.0]octane perchlorate (**1**),[4] was converted with acetic anhydride into 5-acetoxy-1-thioniabicyclo[3.3.0]octane perchlorate (**2**).[1] The salt of 1-thiacyclooctan-5-one 1-oxide, also in the transannular form 5-hydroxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate (**3**), gave 5-acetoxy-9-oxa-1-thioniabicyclo[3.3.1]nonane perchlorate (**4**) with acetic anhydride at room temperature.[2]

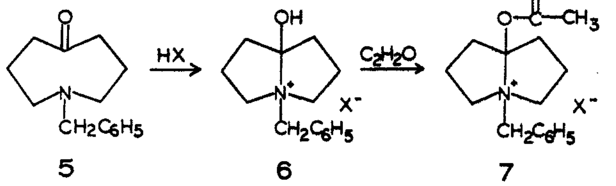


1 2



3 4

The salts of 1-alkyl-1-azacyclooctan-5-ones generally exist in the transannular form,[5,6] and we have now been able to acetylate the α-*t*-hydroxyl group of the transannular salt of an eight-membered-ring amino ketone by means of ketene.[7] Specifically the perchlorate and picrate salts of 1-benzyl-1-azacyclooctan-5-one (**5**)[8] are in the transannular form (**6a**, **b**), as evidenced by their infrared and nmr spectra. Neither salt exhibits ir absorption in the region 1620–1800 cm^{-1}, and both show hydroxyl absorption. The nmr spectrum of the perchlorate shows a singlet for the benzyl CH_2 protons in both acetonitrile-d_3 and trifluoroacetic acid. Splitting of these protons would be expected if the salt were in the alternative N-protonated form. The hydroxy proton of **6a** is observed in acetonitrile-d_3 as a broad singlet, δ 5.1–5.7, which disappears upon the addition of deuterium oxide.



5 6 7

a, X = ClO_4 ; b, X = $C_6H_2N_3O_7$

The reaction of 1-benzyl-5-hydroxy-1-azoniabicyclo[3.3.0]octane perchlorate (**6a**) and of the picrate (**6b**) in acetonitrile with ketene led to 5-acetoxy-1-benzyl-1-azoniabicyclo[3.3.0]octane perchlorate and picrate (**7a**, **b**). The structure proof was based on elemental analyses and on ir and nmr spectral evidence. Each compound exhibits only one ir absorption maximum in the carbonyl region ($\nu_{\max}^{\mathrm{KBr}}$ 1746 cm^{-1} for **7a**, 1750 cm^{-1} for **7b**) corresponding to an ester function. The nmr spectrum of the perchlorate **7a** is much like that of its precursor **6a** with the exception of a new sharp singlet at δ 2.20 (CD_3CN) and loss of the signal for the hydroxyl proton. For comparison, the corresponding 1-thionia analog **2** had $\nu_{\max}^{\mathrm{Nujol}}$ 1737 cm^{-1} (C=O)[1] and δ 2.33 in CF_3COOH (CH_3CO).[2]

The prediction that 5-acetoxy-1-benzyl-1-azoniabicyclo[3.3.0]octane perchlorate (**7a**) would behave as a powerful acetylating agent was verified qualitatively in two rather extreme examples. Acetylation of piperidine with **7a** at −20° in methylene chloride solution was complete in less than 2 min. Acetylation of potassium acetate to give acetic anhydride was accomplished in a melt of the two solids within a total manipulation time of less than 5 min.

Experimental Section

1-Benzyl-5-hydroxy-1-azoniabicyclo[3.3.0]octane Perchlorate (6a).—This salt was obtained quantitatively from 1-benzyl-1-azacyclooctan-5-one[8] and was recrystallized as colorless needles from acetone–ether: mp 144–145.5°; $\nu_{\max}^{\mathrm{Fluorolube}}$ 3260 cm^{-1}; $\nu_{\max}^{\mathrm{KBr}}$ 3290 cm^{-1}; $\nu_{\max}^{\mathrm{Nujol}}$ 3280 (OH), no absorption 1620–2000 cm^{-1}; nmr (CD_3CN) δ from TMS 2.0–2.6 (8 H), 2.85–3.4 (2 H), 3.5–4.0 (2 H) (all series of multiplets, ring protons), 4.25 (2 H, s, benzyl CH_2), 5.1–5.7 (1 H, br s, OH, disappears with D_2O), 7.74 (5 H, s, C_6H_5). In trifluoroacetic acid the nmr spectrum was similar except that no signal for the OH proton was observable.

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[1] N. J. Leonard, T. W. Milligan, and T. L. Brown, *J. Amer. Chem. Soc.*, **82**, 4075 (1960).

[2] N. J. Leonard and C. R. Johnson, *ibid.*, **84**, 3701 (1962).

[3] N. J. Leonard and W. L. Rippie, *J. Org. Chem.*, **28**, 1957 (1963).

[4] For current nomenclature, see IUPAC 1957 Rules, *J. Amer. Chem. Soc.*, **82**, 5545 (1960), especially p 5572.

[5] (a) N. J. Leonard, J. A. Adamcik, C. Djerassi, and O. Halpern, *ibid.*, **80**, 4858 (1958); (b) N. J. Leonard, D. F. Morrow, and M. T. Rogers, *ibid.*, **79**, 5476 (1957), and earlier papers in the series.

[6] (a) N. J. Leonard, *Rec. Chem. Progr.*, **17**, 243 (1956); (b) N. J. Leonard and M. Ōki, *J. Jap. Chem.*, **10**, 1003 (1956).

[7] Note Added in Proof.—R. A. Johnson, M. E. Herr, H. C. Murray, and G. S. Fonken [*J. Org. Chem.*, **33**, 3187 (1968)] have converted **6** into **7** by warming with acetic anhydride on the steam bath.

[8] N. J. Leonard and T. Sato, *ibid.*, in press.