coefficients) for both dyes are not known.[30,31]

In summary, the quenching of the fluorescence of coumarin laser dyes by a variety of electron donors and acceptors has been observed. Net electron transfer is not a dominant path for donor–acceptor quenching, although the photoreduction of methyl viologen on quenching of dye singlets or triplets is confirmed by flash photolysis results. The ranges of oxidation and reduction potential for additives which will diminish the fluorescence of several representative coumarin dyes have been established.

Experimental Section

Materials. Dyes 1–5 were laser grade materials obtained from Eastman Kodak Co. (coumarins 1, 35, 102, 153, and 6, respectively). The dyes were checked for purity by TLC (silica, ethyl acetate/hexane) and in most cases used as received. Several of the commercial samples were recrystallized from heptane or methanol/water. The amine quenchers and DMM were distilled prior to use; DMA was dried by addition of lithium aluminum hydride under nitrogen prior to distillation under reduced pressure (20 torr). FUM was recrystallized three times from hexane/chloroform and DCB and MV (chloride salt) were recrystallized twice from methanol. Solvents employed were spectroquality acetonitrile used as received and triply distilled water.

Fluorescence Quenching. Dye emission was recorded on a Perkin-Elmer MPF-44A fluorimeter equipped with a spectrum correction unit and quartz cells. Solutions of 10^{-5} M dye were excited at the absorption maximum and the fluorescence intensity (at λ_{max}) recorded as a function of added quencher (samples were air saturated). No changes were recorded in the emission maximum or in the dye absorption profile as the result of addition of quencher. Intensity changes were plotted vs. quencher concentration by using the Stern–Volmer equation, $I_0/I = 1 + k_q\tau$ [Q]. Linear regression analysis ($r = \geq 0.98$) provided slopes ($k_q\tau$ values) and intercepts (typically 1.00 ± 0.02).

Triplet Quenching. Flash Photolysis. Flash photolysis apparatus which consisted of a Xenon flash lamp with ca. 35 μs duration (fwhm) and a 22-cm Pyrex cell has been described previously.[31] Argon-purged solutions of ca. 10^{-5} M dye were employed. Photographs of oscilloscope traces were obtained to record percent transmission values which were converted to transient absorbance. For measurement of relative yield of transients, absorbance values were recorded at their maximum at the shortest practical times following lamp discharge (usually 100 μs following the flash).

Cyclic Voltammetry. Current–voltage curves were obtained for 10 mM dye in reagent grade (wet) acetonitrile with 0.1 M tetraethylammonium perchlorate (TEAP) or 0.1 M $LiClO_4$ supporting electrolyte with a Bioanalytical Systems potentiostat. Other conditions included working electrode (Au or Pt), reference electrode (Ag, $AgNO_3$ (0.01 M)), auxiliary electrode (Pt), and operating temperature (22 °C).

Acknowledgment. This work was supported by the Office of Naval Research. We thank also Drs. W. R. Jackson and S. Kanoktanaporn for technical assistance, and Professors M. Z. Hoffman and M. F. Delaney for the loan of equipment.

Registry No. 1, 91-44-1; 2, 41934-47-8; 3, 41267-76-9; 4, 53518-18-6; 5, 38215-36-0; DEA, 109-89-7; TEA, 121-44-8; DMA, 121-69-7; DMM, 624-48-6; DCB, 623-26-7; FUM, 764-42-1; MV, 1910-42-5.

(30) Dempster el al.[25] report $\epsilon = 19\,000 \pm 2000$ M^{-1} cm^{-1} for triplet 1 in ethanol, also to be compared with a value of 14 000 M^{-1} cm^{-1} for MV in water. A weak transient (λ_{max} ~500 nm) can be observed on quenching 5 with DMA in acetonitrile. This absorption is much like that of the DMA radical–cation.[22]

(31) Caspari, G.; Hughes, R. G.; Endicott, J. F.; Hoffman, M. Z. *J. Am. Chem. Soc.*, **1970**, *92*, 6801.

Rauwolfia Alkaloid Synthesis Approach Employing the Zwitterionic Amino-Claisen Rearrangement. Improvements in the Efficiency for Yohimbane Ring Construction and Unambiguous DE-Ring-Fusion Stereochemical Assignments

Shouchung Chao, Fen-Ann Kunng, Jia-Ming Gu, Herman L. Ammon, and Patrick S. Mariano*

Department of Chemistry, University of Maryland, College Park, Maryland 20742

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A high yielding method for inducing amino-Claisen rearrangement of the *tert*-butyl propiolate *N*-tryptophylisoquinuclidene 1 system to form the *N*-tryptophylisoquinoline 6 has been found. Accordingly, reaction of 1 with the acetylene ester in refluxing CH_3CN generates 6 in a 65% yield in contrast to earlier results which had suggested that the above reaction fails; causes for the variable success are proposed. Isoquinoline 6 is smoothly (75%) transformed to the C-3 epimeric yohimbanes 8 and 9. Spectroscopic and X-ray crystallographic data are presented to support the assignments of stereochemistry to 8 and 9 and conformational preferences as 8A and 9A.

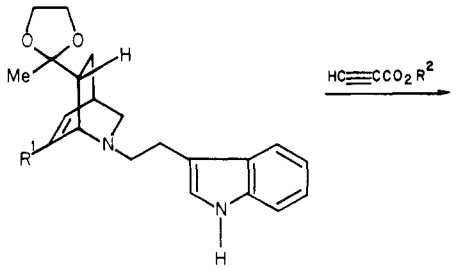
In a recent publication,[1] we have described the results of our investigations of a new version of the amino-Claisen rearrangement of *N*-vinylisoquinuclidene systems.[2] In particular, we have pointed out how reactions of *N*-tryptophylisoquinuclidenes 1 and 2 with propiolate esters proceed to generate the *N*-tryptophylhydroisoquinolines 4 and 5 via zwitterionic intermediates 3. Further studies with the hydroisoquinoline 4 have demonstrated that the base-induced, Wenkert[3] cyclization process, e.g., 4 → 7, can be used to generate substances (H-3 α and β) possessing pentacyclic yohimbane skeletons. Lastly, this exploration has provided results which authenticate the viability of

(1) Kunng, F. A.; Gu, J. M.; Chao, S.; Chen, Y.; Mariano, P. S. *J. Org. Chem.* **1983**, 48, 4262.

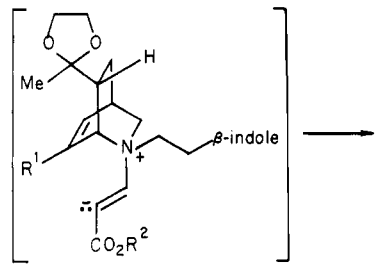
(2) For previous publications on studies in this area, see: Mariano, P. S.; Dunaway-Mariano, D.; Huesmann, P. L. *J. Org. Chem.* **1979**, *44*, 124. Chen, Y.; Mariano, P. S.; Little, G. M.; O'Brien, D.; Huesmann, P. L. *Ibid.* **1981**, *46*, 4643. Chen, Y.; Huesmann, P. L.; Mariano, P. S. *Tetrahedron Lett.* **1983**, *24*, 1021.

(3) Wenkert, E.; Dave, K. G.; Haglid, F. *J. Am. Chem. Soc.* **1965**, *87*, 5461.

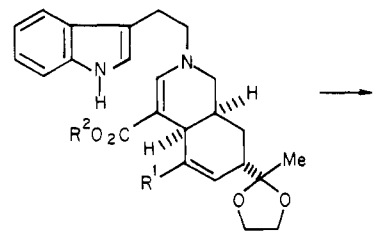
0022-3263/84/1949-2708$01.50/0



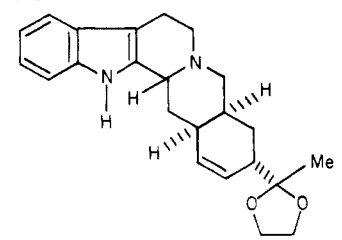
1, R^1 = H
2, R^1 = CO_2Me



3



4, R^1 = H; R^2 = Et
5, R^1 = CO_2Me; R^2 = Et
6, R^1 = H; R^2 = *t*-Bu

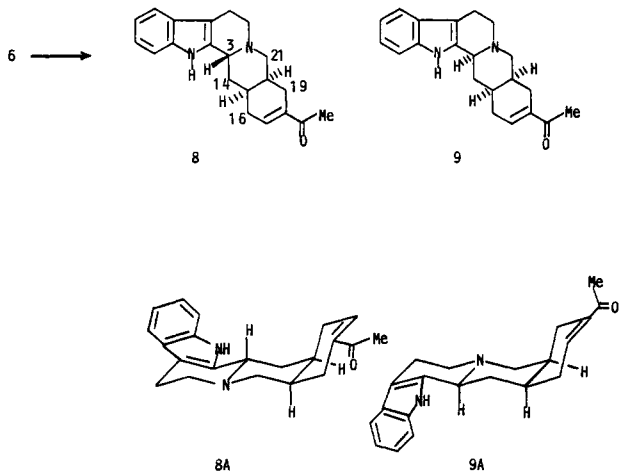


7

Rauwolfia alkaloid synthetic designs based upon the amino-Claisen rearrangement methodology.

Two observations made in these earlier studies appeared troublesome. The first concerned the failure of the zwitterionic amino-Claisen rearrangement reaction when *tert*-butyl propiolate was used as the acetylenic addend. For example, while reaction of 1 with ethyl propiolate furnished the isoquinoline 4 in 60% yield, reaction of 1 with the *tert*-butyl ester generated none of the desired rearrangement product and gave only an "uncyclized" diene of undetermined regiochemistry.[1] The second problem was related to the low yield observed for the base-induced cyclization of the *N*-tryptophylisoquinoline 4. Thus, conversion of 4 to the yohimbanes 7 under the Wenkert conditions (25% KOH, 1:1 EtOH–H_2O, 85 °C) occurred in only a 40% optimized yield. This yield is nearly identical with those reported by Wenkert for cyclizations of more simple, model systems.[3]

These observations were frustrating since *N*-tryptophyltetrahydronicotinate cyclization processes usually occur in superior yields when *tert*-butyl rather than ethyl esters are used and when reactions are run under acidic rather than basic conditions.[3] This apparent dilemma encouraged us to explore more fully the reaction of isoquinuclidene 1 with *tert*-butyl propiolate. The results of investigations focused on this and related questions demonstrate that the zwitterionic amino-Claisen rearrangement of 1 initiated by reaction with *tert*-butyl propiolate when run under proper conditions is an efficient process and that cyclization of the derived isoquinoline 6 occurs smoothly under acidic conditions to generate the C-3 epimeric yohimbanes 8 and 9. Also, evidence is



provided from an X-ray crystallographic study to support the assignment of DE-ring fusion stereochemistry in 8 and 9.

Reaction of 1[1] with purified[4] *tert*-butyl propiolate in CH_3CN at 80 °C for 24 h provides the hydroisoquinoline 6 in a modest yield of 65% after silica gel chromatography. The spectroscopic properties of 6 are nearly identical with those observed for 4 and, thus, are useful in assigning the cis-ring fusion hydroisoquinoline stereochemistry (see below). A potential cause for the variable success of this process may be related to the purity of the *tert*-butyl propiolate used. When care is not taken to remove trace quantities of acid impurities,[4] substantial autocatalyzed decomposition of the acetylenic ester can occur to generate propiolic acid. As a result, the zwitterionic intermediate 3 can be protonated by propiolic acid, giving rise to an ammonium salt capable of ring opening by C–N bond cleavage and deprotonation[5] to yield the diene product observed earlier.[1] However, when the propiolate ester is free of acid impurities, amino-Claisen rearrangement of the zwitterion 3 proceeds smoothly to generate the isoquinoline 6.

The success of this rearrangement process has ramifications on the overall usefulness of this methodology for Rauwolfia alkaloid synthesis since it opens the way for use of the acid-induced, Wenkert[3] annulation procedure for construction of the pentacyclic ring system. We have found that treatment of isoquinoline 6 with 25% aqueous acetic acid at reflux for 12 h followed by flash chromatography on silica gel gives the crystalline yohimbanes 8 (45%) and 9 (30%). The overall efficiency for the cyclization process of 75% compares favorably to that recorded by Wenkert in studies of model systems[3] and is far superior to the analogous base-induced process on the ethyl ester

(4) *tert*-Butyl propiolate, formed by the sulfuric acid catalyzed esterification of the parent acid with isobutylene, is an exceptionally labile compound when heated in the presence of trace quantities of acid. We have only recently found that purification in base-washed glassware and following the addition of small quantities of $NaHCO_3$ can be smoothly accomplished by distillation.

(5) (a) A similar observation concerning protonation of a related zwitterionic intermediate by protic solvents has been made by Kanematsu.[5b] (b) Hayakawa, K.; Fujii, I.; Kanematsu, K. *J. org. Chem.* **1983**, *48*, 166.

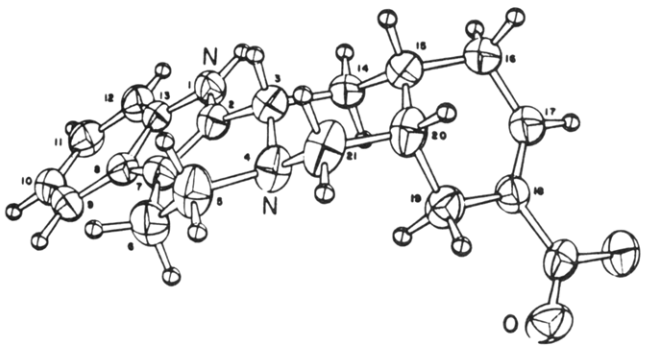


Figure 1. ORTEP drawing of X-ray crystallographically determined structure of **9**. The carbon, nitrogen, and oxygen atoms are drawn as 50% ellipsoids. The hydrogen atoms are drawn as 0.1-Å diameter spheres.

(**4** → **7**, 40%). The presence of the acetylcyclohexene E ring in these substances and the observation that both C-3 epimers are formed in nearly equal quantities—note the base cyclization stereochemical result[1]—is understandable, since the aqueous acid conditions should lead to ketal hydrolysis, π-bond isomerization, and C-3 epimerization.[6] Indeed, treatment of **7** (C-3 β-isomer only) with aqueous acetic acid at elevated temperatures leads to formation of a mixture of the yohimbanes **8** and **9**.

The assignments of stereochemistry to **8** and **9** and conformational preferences as **8A** and **9A** rest on firm spectroscopic grounds. In particular, the ^{13}C NMR chemical shifts for C-14, -16, -19, and -21 resonances reflect their axial vs. equatorial disposition relative to the D and E six-membered rings (e.g., the respective values for **8** are 33.8, 27.0, 26.5, and 55.3 ppm and for **9**, 32.4, 32.1, 23.2, and 60.1 ppm). Similarly, the H-3 proton resonances for **8** and **9** display coupling to H-14 (dd, J = 10, 1 HZ and J = 9, 2 Hz), suggesting an axial orientation. More importantly, X-ray crystallographic analysis of **9** (see Figure 1) provides unambiguous evidence to support the stereochemical designations suggested above, and the key hypothesis proposed earlier[1] that the zwitterionic amino-Claisen rearrangement leads to production of cis-fused hydroisoquinolines.

When taken together, the observations presented above show that the approach to Rauwolfia alkaloid synthesis which takes advantage of sequential amino-Claisen rearrangement and Wenkert-cyclization processes is a highly efficient route. The stage is now set for its application to the preparation of selected natural product systems.

Experimental Section

General Methods. Flash column chromatography was performed by using silica gel (E. Merck 60, 230–400 mesh). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WP-200 spectrometer with $(CH_3)_4Si$ as an internal standard. Chemical shifts are recorded in ppm relative to $(CH_3)_4Si$. The numbering patterns for carbon and proton identification in all compounds are based upon yohimbane numbering (see Discussion section).

2-Tryptophyl-4-carbo-*tert*-butoxy-7-[1,1-(ethylenedioxy)eth-1-yl]-1,2,7,8,9,10-hexahydroisoquinoline (6). A solution of 3.00 g (8.87 mmol) of isoquinuclidene **1** and 4.47 g (0.035 mol) of *tert*-butyl propiolate in 60 mL of CH_3CN was stirred at 80 °C for 24 h under N_2. The mixture was cooled to 25 °C and concentrated in vacuo, giving a residue which was purified by flash column chromatography (0.7% MeOH–$CHCl_3$) to yield 2.67 g (65%) of the hydroisoquinoline **6**: ^1H NMR ($CDCl_3$) 8.2 (br s, 1 H, indole NH), 7.0–7.6 (m, 5 H, H-3, H-9, H-10, H-11, H-12), 6.9 (d, H-2, J = 2 Hz), 5.8 (d, H-16, J = 10 Hz), 5.5 (ddd, H-17, J = 10, 2, 2 Hz), 3.9 (m, 4 H, OCH_2CH_2O), 3.4 (m, 2 H, H-5), 3.2 (br s, 1 H, H-15), 3.1 (t, 1 H, J = 12 Hz, H-21$_a$), 3.0 (m, 2 H, H-6), 2.8 (dd, 1 H, J = 12.4 Hz, H-21$_e$), 2.2 (m, 2 H, H-18, H-20), 1.8 (m, 2 H, H-19), 1.4 (s, 9 H, t-Bu CH_3), 1.2 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) 168.7 (CO_2-*t*-Bu), 145.8 (C-3), 136.9 (C-13), 133.7 (C-17), 127.7 (C-8), 122.7 (C-16), 122.5 (C-11, C-12), 122.6 (C-2), 119.8 (C-10), 118.9 (C-9), 112.9 (C-7), 112.2 (*t*-Bu quat), 111.8 (ketal quat), 99.5 (C-14), 65.3, 65.1 (OCH_2CH_2O), 56.7 (C-5), 47.1 (C-21), 40.8 (C-15), 32.7 (C-20), 30.7 (C-18), 29.1 (*t*-Bu CH_3) 27.4 (C-6), 25.4 (C-19), 21.3 (CH_3); IR ($CHCl_3$) 3495 (NH), 1660 (NC=CCO), 1600 cm^{-1}; UV (EtOH) max 290 nm (ϵ 17 600); mass spectrum, m/e (relative intensity) 464 (M^+, 12), 419 (4), 407 (10), 391 (5) 363 (11), 334 (1), 278 (47), 144 (23), 130 (7), 87 (100); high-resolution mass spectrum, m/e 464.2655 ($C_{28}H_{36}N_2O_4$ requires 464.2611).

18-Acetyl-$\Delta^{17,18}$-dehydroalloyohimbane (9) and -epialloyohimbane (8). A solution of 1.00 g (2.14 mmol) of the hydroisoquinoline **6** in 15 mL of THF was added to 25% aqueous AcOH (30 mL). The mixed solution was stirred at reflux under N_2 for 12 h, cooled to 25 °C, neutralized with $NaHCO_3$ (aq), and extracted with $CHCl_3$ layer was dried and concentrated in vacuo, giving a residue which was subjected to flash column chromatography (1% MeOH–$CHCl_3$ to 2% MeOH–$CHCl_3$) to yield 0.20 g (30%) of the alloyohimbane **9** (mp 207 °C) and 0. 31 g (45%) of the epialloyohimbane **8** (mp 210 °C).

Spectroscopic data for 9: ^1H NMR ($CDCl_3$) 7.7 (br s, 1 H, NH), 7.0–7.5 (m, 4 H, H-9, H-10, H-11, H-12), 6.8 (dd, 1 H, H-17, J = 2, 3 Hz), 3.3 (dd, H-3, J = 9, 2 Hz), 2.9 (m, 4 H, H-5, H-21), 2.6 (m, 5 H, H-6, H-16), 2.2 (S, 3 H, CH_3), 2.1 (m, 2 H, H-19), 1.6 (m, 4 H, H-14, H-15, H-20); ^{13}C NMR ($CDCl_3$) 198.8 (CO), 138.6 (C-18), 136.7 (C-17), 136.2 (C-13), 135.0 (C-2), 127.6 (C-8), 121.3 (C-11), 119.5 (C-10), 118.0 (C-9), 110.6 (C-12), 108.6 (C-7), 60.1 (C-21), 60.0 (C-3), 53.0 (C-5), 32.4 (C-14), 32.1 (C-16), 31.9 (C-20), 31.8 (C-15), 25.2 (CH_3), 23.2 (C-19), 21.8 (C-6); IR ($CHCl_3$) 3490 (NH) 2840, 2800, 2740, 1660 cm^{-1}; UV (EtOH) max 290 nm (ϵ 4608), 283 nm (ϵ 5325); mass spectrum, m/e (relative intensity) 320 (M^+, 82), 319 (100), 277 (52), 235 (12), 221 (77), 197 (18), 184 (34), 169 (51), 156 (44), 143 (46), 130 (16): high-resolution mass spectrum, m/e 320.1895 ($C_{21}H_{24}N_2O$ requires 320.1916).

Spectroscopic data for 8: ^1H (C-19), ($CDCl_3$) 7.7 (br s, 1 H, NH), 7.0–7.5 (m, 4 H, H-9, H-10, H-11, H-12), 6.9 (d, J = 4 Hz, H-17), 3.6 (dd, J = 10, 1 Hz, H-3), 3.0 (m, 2 H, H-5), 2.7 (m, 4 H, H-6, H-21), 2.3 (m, 4 H, H-16, H-19), 2.2 (s, 3 H, CH_3), 1.7–2.0 (m, 4 H, H-14, H-15, H-20); ^{13}C NMR ($CDCl_3$) 198.6 (CO), 137.8 (C-18), 137.5 (C-17), 136.3 (C-13), 134.7 (C-2), 127.7 (C-8), 121.4 (C-11), 119.5 (C-10), 118.1 (C-9), 110.8 (C-12), 108.8 (C-7), 55.3 (C-21), 54.2 (C-3), 53.1 (C-5), 33.8 (C-14), 32.6 (C-20), 29.0 (C-15), 27.0 (C-16), 26.5 (C-19), 21.4 (C-6); IR ($CHCl_3$) 3490 (NH), 2840, 2800, 2760, 1660 cm^{-1}; mass spectrum, m/e (relative intensity) 320 (M^+, 96), 319 (100), 297 (92), 235 (21), 221 (39), 197 (7), 184 (17), 169 (37), 156 (18), 143 (13), 130 (8); high-resolution mass spectrum, m/e 320.1870 ($C_{21}H_{24}N_2O$ requires 320.1813); UV (EtOH) max 290 nm (ϵ 4800), 280 nm (ϵ 5653).

Crystallographic Study of the Alloyohimbane 9. Crystals were obtained by the slow evaporation of a CH_2ClCH_2Cl solution of the alloyohimbane **9**. A 0.07 × 0.3 × 0.7 mm specimen was used for all X-ray measurements. Data were collected on a Picker FACS-I diffractometer with graphite monochromated Cu radiation (Cu Kα = 1.5418 Å). Lattice parameters were obtained by least squares from the data of 11 reflections centered automatically at ±2θ. Crystal data: $C_{21}H_{24}N_2O$, M_r 320.4; orthorhombic, *Pbca*, a = 10.648 (9) Å, b = 12.840 (9) Å, c = 25.29 (1) Å; D_{calcd} = 1.231 g cm^{-3} for Z = 8.

Intensity data were collected to a 2θ maximum of 127 °C with the 2θ–θ scan geometry at 2° min^{-1} and with 10-s backgrounds. Four standards were measured at 200 reflection intervals. The average intensity decline was 3%. 3310 total data were measured with 2836 unique data (excluding systematically absent reflections) with 2836 unique data (excluding systematically absent reflections) and 1938 data with $I_0 \geq 3\ \sigma(I_0)$. The structure was solved with the MULTAN-80 system of programs.[7] The other crystallographic

(6) See: Woodward, R. B.; Bader, F. E.; Bickel, H.; Frey, A. J.; Kierstead, R. W. *Tetrahedron* **1958**, *2*, 1 and references therein.

(7) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, F. P.; Woolfson, M. M. "MULTAN 80, A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", University of York: England, and Louvain, England, 1980.

calculations were carried out with the X-ray 76 system[8] on a UNIVAC 1100/82 computer. The least-squares structure refinement minimized $\sum w(F_o - F_c)^2$, $w = 1/\sigma^2(F_o)$. Anisotropic temperature factors were used for carbon, nitrogen, and oxygen. The framework hydrogen atoms were placed in calculated positions at distances of C–H = 1.03 Å and N–H = 1.00 Å. Only the hydrogen temperature factors were refined. The methyl group hydrogen were not included in the calculations. The final R $(\sum[F_o - F_c]/\sum F_o$ and weighted R $(\sum(F_oL - F_c)^2/\sum(F_o)^2]^{1/2}$ are 0.074 and 0.087. Tables of atomic coordinates and temperature factors are included with the supplementary material.

(8) Stewart, J. M.; Machin, P. A.; Dickinson, C.; Ammon, H. L. "The XRAY System–Version of 1976", Tech. Rep. 446, Computer Science Center; University of Maryland, 1976.

Acknowledgment. Support for these studies by grants from NIH (GM-29016) and the University of Maryland Computer Science Center is acknowledged. The 200-MHz NMR spectrometer used in this research was purchased in part by funds derived in part from an NSF grant. The kind assistance provided by Dr. Kenneth B. Seaman in recording 400-MHz NMR spectra is gratefully appreciated.

Registry No. 1, 90693-43-9; 6, 90623-26-0; 8, 90693-44-0; 9, 90605-67-7; *tert*-butyl propiolate, 13831-03-3.

Supplementary Material Available: Tables of atomic coordinates and temperature factors (2 pages). Ordering information is given on any current masthead page.

1,1-Dichloroethyl Hydroperoxide and 1,1-Dichloroethyl Peroxide Ion as Intermediates in the Ozonolysis of 2,3-Dichloro-2-butene†

Siegmar Gäb* and Walter V. Turner

Institut für Ökologische Chemie der Gesellschaft für Strahlen- und Umweltforschung mbH München, D-8050 Freising-Weihenstephan, Federal Republic of Germany

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On the basis of its spectroscopic and chemical properties, an unstable intermediate previously detected in the ozonolysis of *trans*-2,3-dichloro-2-butene (1) in inert solvents is reformulated as 1,1-dichloroethyl hydroperoxide (5). Ozonolysis of 1 in ethyl formate saturated with anhydrous HCl leads to high yields of this intermediate. 1,1-Dichloroethyl peroxide ion (10), rather than 5, is believed to be the precursor of acetyl 1,1-dichloroethyl peroxide (8), which is produced in higher yield on ozonolysis of 1 in the presence of tetraalkylammonium chloride.

Introduction

In a very thorough study of the ozonolysis of *trans*-2,3-dichloro-2-butene (1) in nonparticipating solvents, Griesbaum and Hofmann[1] have identified most of the products of the reaction, examined the influence of various solvents, and proposed a reaction scheme. An unstable species was observed in the ^{1}H NMR spectra of the fresh ozonolysis mixture as a singlet at δ 2.33; 3,5-dichloro-3,5-dimethyl-1,2,4-trioxolane (4), considered to arise by addition of the carbonyl oxide 2 to acetyl chloride (3) in analogy with the Criegee mechanism,[2] was suggested as a likely structure for this intermediate.

We have found that a number of 3,5-dichlorinated 1,2,4-trioxolanes derived from bi- or tricyclic olefins are stable enough to be isolated by column chromatography and be characterized by the usual analytical methods (NMR, IR, elemental analyses).[3] Although the trioxolane from 1,2-dichloroacenaphthylene decomposes at temperatures as low as 0 °C with loss of chlorine to naphthalic anhydride, the decomposition of the other trioxolanes, which also yield the corresponding anhydrides, begins only in the region of their melting points ($T > 100$ °C). Decomposition of the unstable species with δ 2.33 from 1 to acetic anhydride is not observed.

The species at δ 2.33 is reported to react with 3 and trideuterioacetyl chloride to produce 1,1-dichloroethyl peresters.[1] Although such a reaction of trioxolanes would be unprecedented, it is typical of the reaction of acid chlorides with hydroperoxides. On the basis of these observations, we have re-examined the ozonolysis of 1, with emphasis on the properties of the unstable intermediate. Considerable evidence has been adduced that this intermediate is not the trioxolane 4, but 1,1-dichloroethyl hydroperoxide (5).

Results and Discussion

The unstable species was found in very low yield, except in methyl formate, where it amounted to 18–20% of the total ^{1}H NMR signal intensity.[1] We found similar yields in ethyl formate. Because the formation of 5 requires the addition of HCl to the carbonyl oxide 2 (eq 3), we ozonized 1 in ethyl formate saturated with anhydrous HCl and obtained a 1:1 ratio of 3 and the unstable species with δ 2.33.[4] No other products were detected by NMR. This fact in itself speaks strongly for structure 5, since it is difficult to understand how the presence of HCl could lead to increased yields of 4. Careful removal of the solvent and

† Dedicated to Professor F. Korte on the occasion of his sixtieth birthday.

(1) Griesbaum, K.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 2877–2881.

(2) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745–752.

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(4) Identical results were obtained with the cis isomer of 1. The ^{1}H resonance of the unstable intermediate appears at δ 2.32–2.33 in mixtures of ethyl formate and $CDCl_3$, but at δ 2.34–2.35 in $CDCl_3$ alone. One of the referees questioned whether we could distinguish between direct attack by HCl on either a primary or a normal ozonide and attack on the carbonyl oxide to yield 5. We have not been able to detect any reaction of HCl with several chlorinated normal ozonides. Reaction of HCl with the primary ozonide cannot be excluded, but it should be pointed out that Bailey and Carter were able to show that in at least one case the reaction to form a methoxy hydroperoxide does not involve direct attack of methanol on the primary ozonide. (Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1982; Vol. I, p 111.)

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