= 0.91), and that conversion of Q → N may also be photosensitized: (a) G. S. Hammond, P. Wyatt, C. D. deBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964); (b) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

(5) We have found that cyclic five-membered azoalkanes appear to possess a $S_0 \rightarrow T_1$ absorption which maximize near 450 nm and possess ϵ_{max} $\sim 10^{-2}$. For other reports of $S_0 \rightarrow T_1$ absorption of azo compounds, see L. C. Robertson and J. A. Merritt, *J. Chem. Phys.*, **57**, 316 (1972); J. Metcalfe, S. Chervinsky, and I. Oref, *Chem. Phys. Lett.*, **42**, 190 (1976).

(6) It has been conventionally assumed that (independent of whether loss of N_2 takes place in one or two steps) cyclic azoalkanes produce spin correlated hydrocarbon diradicals upon thermal or photochemical decomposition: (a) B. S. Solomon, T. F. Thomas, and C. Steel, *J. Am. Chem. Soc.*, **90**, 2249 (1968); (b) W. D. K. Clark and C. Steel, *ibid.*, **93**, 6347 (1971); (c) P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968); (d) E. L. Allred and R. L. Smith, *ibid.*, **91**, 6766 (1969); (e) H. E. Zimmerman, N. E. Buehler, G. E. Keck, and M. G. Steinmetz, *ibid.*, **98**, 7680 (1976); (f) P. S. Engel, *ibid.*, **91**, 6903 (1969); (g) H. Dürr and B. Ruge, *Top. Curr. Chem.*, **66**, 55 (1976).

(7) In general, it appears that near room temperature the $S_1 \rightarrow T$ intersystem crossing in cyclic azoalkanes is inefficient.[5e,f,g] Recent evidence[8] indicates that this inefficiency may be strongly temperature dependent if chemical processes leading to deactivation of S_1 are thermally activated, since the rate of intersystem crossing is generally temperature insensitive. Such appears to be the case for **1** and **2** (see temperature effects in Table I).

(8) N. J. Turro, C. A. Renner, W. A. Waddell, and T. J. Katz, *J. Am. Chem. Soc.*, **98**, 4320 (1976).

(9) (a) Michl has suggested the term "funnel" to describe regions of an energy surface that correspond to an excited-state minimum which can undergo a facile radiationless transition to lower energy surface: J. Michl, *Mol. Photochem.*, **4**, 243, 257, 287 (1972); *Photochem. Photobiol.*, **25**, 141 (1977), and references therein. (b) H. E. Zimmerman, *Acc. Chem. Res.*, **4**, 272 (1971). (c) L. Salem, *J. Am. Chem. Soc.*, **96**, 3485 (1974). (d) R. C. Dougherty, *ibid.*, **93**, 7187 (1971).

(10) W. G. Dauben, L. Salem, and N. J. Turro, *Acc. Chem. Res.*, **8**, 41 (1975).

(11) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972). For a discussion of the stability of cyclic triplet diradicals, see S. Kita and K. Fukui, *Bull. Chem. Soc. Jpn.*, **42**, 66 (1969).

(12) N. Ivanoff, F. Lahman, J. F. DeLouis, and T. L. Le Gouill, *J. Photochem.*, **2**, 199 (1973).

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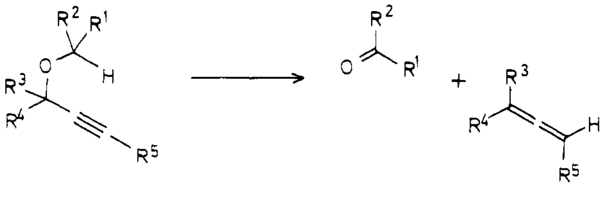
Intramolecular Pericyclic Reactions of Acetylenes. 7.[1] Concertedness of Acetylenic Retro-ene Reactions. Preparation of Optically Active Phenylallene-*3-d*

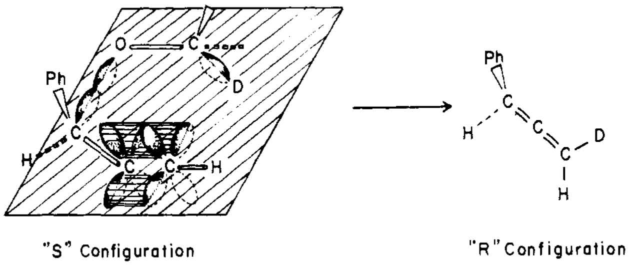
Sir:

Although acetylenic bonds frequently participate in intramolecular reactions whose olefinic analogues are believed to proceed via cyclic six-membered transition states, the ground-state linearity of the acetylenic system raises doubts about the concert of such reactions. We wish to report that stereochemical integrity is preserved in an acetylenic retro-ene reaction as further evidence for concertedness in that reaction, and that we have used this process to generate the first reported allene which is optically active by virtue of isotopic substitution.[2]

As part of our continuing study of the thermal behavior of acetylenic compounds, we have examined the thermolyses of a number of propargylic ethers.[3] Normally the products are those to be expected from a retro-ene cleavage, and the kinetic parameters for about 25 compounds are those to be expected from a concerted process, with E_a ranging from 36 to 42 kcal/mol and $\Delta S^{\ddagger}$ from −6 to −13 eu.[4]



The stereospecificity of concerted, intramolecular rearrangements has been used previously to generate two allenic derivatives of predictable absolute configuration from optically active acetylenic precursors: an acetylenic Claisen rearrangement provided an allenic aldehyde[5] and the S_Ni' reaction of thionyl chloride on a propargylic alcohol gave a chloroallene.[6] It has been suggested that acetylenic retro-ene reactions proceed via a concerted planar transition state which maximizes orbital overlap of participating bonding systems.[7] If such be the case, then (*R*)-phenylallene-*3-d* (**1**) should be produced from the thermolysis of the trideuteriomethyl ether of (*S*)-1-phenylprop-2-yn-1-ol (**2**).

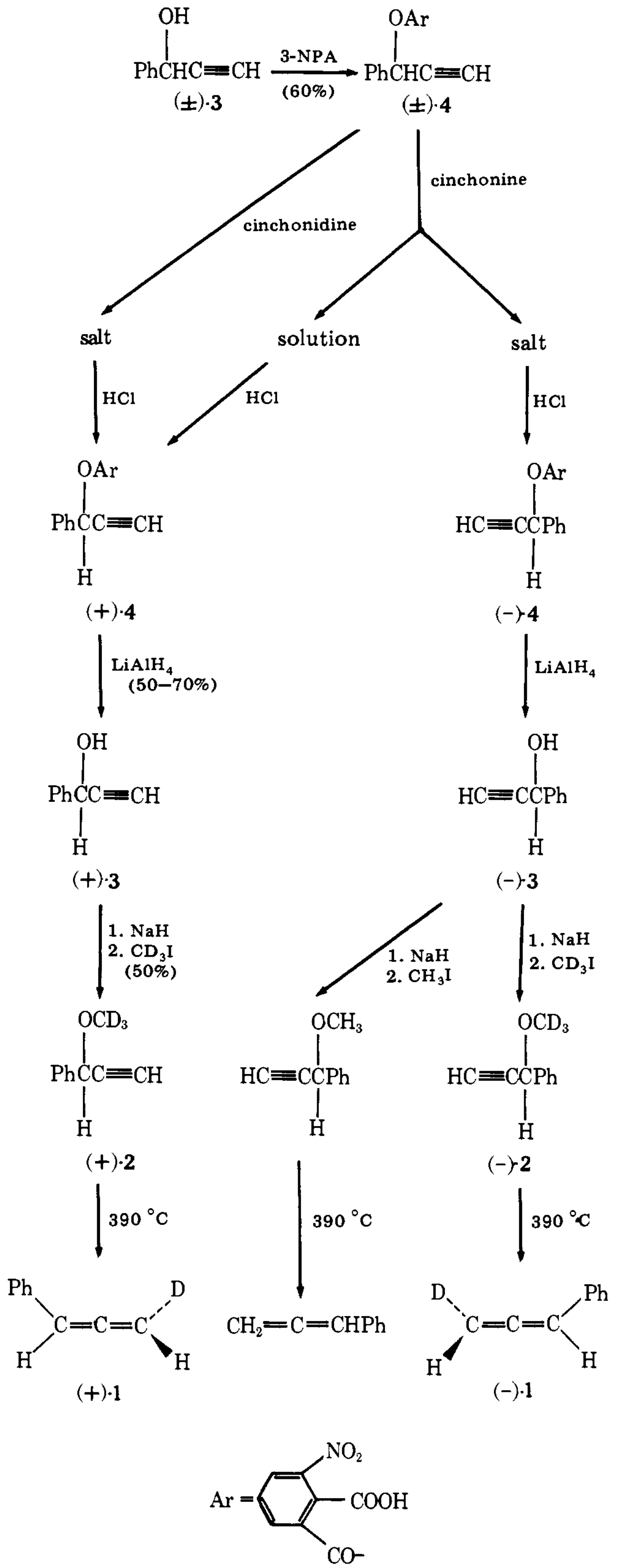


The choice of the phenyl group as a substituent is dictated by the following factors: 1-phenylprop-2-yn-1-ol (**3**) is commercially available (Farchan Division, Chemical Samples Co.), its resolution has been reported,[8] and the presence of the polarizable phenyl substituent provides enhanced optical rotation in the case of isotopic substitution at sp^3-hybridized carbon atoms.[9]

The resolution[10] of **3** is outlined in Scheme I. Reaction of racemic **3** with 3-nitrophthalic anhydride (3-NPA) provided the racemic half-acid-ester **4**. Treatment of (±)-**4** with cinchonine led to the precipitation of a crystalline salt, a sample of which was recrystallized from $CHCl_3/MeOH$ to constant melting point, 185–186 °C.[11] Hydrolysis with dilute aqueous HCl provided (−)-**4**, $[\alpha]^{25}{}_D$ −53.9° (*c* 2.17), mp 152–155 °C. Treatment of the active ester with $LiAlH_4$ gave (−)-**3**, $[\alpha]^{22}{}_D$ −27.1° (*c* 2.42). The optical purity of this sample was essentially 100% as determined by use of the chiral NMR shift reagent, $Eu(hfc)_3$,[12] which cleanly separated the resonance lines due to the benzylic protons of the two enantiomeric components in a sample of racemic **3**. Etherification of (−)-**3** with NaH and CD_3I provided the desired trideuteriomethyl ether,[13] (−)-**2**, $[\alpha]^{25}{}_D$ −42.8° (*c* 1.08). Since the chiral shift reagent did not separate the benzylic protons of **2**, a sample of the same batch of alcohol, (−)-**3**, used to prepare the deuterated either, was converted via the identical procedure, but using CH_3I, into the corresponding protio ether.[13] The application of $Eu(hfc)_3$ indicated less complexation with the ether, but the methyl signal in racemic protio-**2** was cleanly divided into two singlets. Since no trace of one of these singlets could be detected in the spectrum of the active protio ether, its optical purity is also essentially 100% and the Williamson etherification does not lead to any detectable racemization.

The positive antipode of **4** could be obtained from the mother liquor, after removal of the precipitated crystalline cinchonine salt, by treatment with dilute HCl. Reduction of the half-ester with $LiAlH_4$ gave (+)-**3**, but with an optical purity of only ~65% as determined with $Eu(hfc)_3$. Since cinchonidine is an epimer of cinchonine, it was hoped that use of the former as a resolving agent might lead to a higher optical purity of (+)-**3**. True to expectation, treatment of (±)-**4** with cinchonidine also produced a crystalline salt, which was recrystallized from $CHCl_3/MeOH$, mp 175–177 °C, and was then hydrolyzed with aqueous HCl to yield (+)-**4**, $[\alpha]^{25}{}_D$ +52.5° (*c* 0.83), mp 155–166 °C. Treatment of (+)-**4** with $LiAlH_4$ gave (+)-**3**, $[\alpha]^{25}{}_D$ +27.0° (*c* 1.35), which represents optically pure material based on the specific rotation of optically pure (−)-**3**.

Scheme I



For thermolysis purposes, samples of ethers with lower optical purity were used, since these were more readily available in larger quantity.[14] Thermolysis[15] of (−)-**2**, 73% optical purity, afforded[16] (−)-**1**, $[\alpha]^{25}{}_D$ −0.47° (*c* 11.1), which corresponds to a specific rotation −0.64° for optically pure starting material. Similarly, (+)-**2**, 93% optical purity, gave (+)-**1**, $[\alpha]^{25}{}_D$ +0.61° (*c* 1.96), which corresponds to a specific rotation of +0.65° for optically pure starting material.

Since all active compounds in each enantiomeric series shared the same sign of rotation, it appeared necessary to eliminate the possibility that a small impurity of any of the precursors, carried through the isolation process, may be responsible for the observed activity of the allene. Consequently, thermolysis of a sample of the protio analogue of (−)-**2**, $[\alpha]^{25}{}_D$ −27.6° (*c* 2.0), followed by the identical isolation procedure[16] used for the preparation of (−)-**1**, provided phenylallene devoid of any detectable optical rotation.

Phenylallene-*3-d* gave ^{1}H NMR[17] and mass[18] spectra commensurate only with 100% monodeuterium incorporation in the 3 position.

There remains only the question of configurational relationships between the ether and the allene produced therefrom. The "*S*" configuration has been assigned to the (+) enantiomer of **3** via its relationship to D-(−)-mandelic acid[8] and the chiral center is not involved in the subsequent etherification to produce **2**. The concerted reaction, proceding via the postulated transition state illustrated above, must then produce the "*R*" configuration in the allenic product. The "*R*" configuration can be assigned[19] to the (+)-allene based upon Brewster's rule[20] as adapted for allenes by Lowe.[21] Polarizabilities of the three different substituents about the allene framework are in the order Ph > H > D,[20] such that the "*R*" configuration is the one which provides the dextrorotatory "screw pattern of polarizability".

It may therefore be concluded that the concerted retro-ene reaction of propargylic ethers can be used to generate optically active allenes of predictable configuration.

Acknowledgments. We thank Dr. Paul Vouros for the mass spectral determination and Professor G. Lyle for the attempted ORD determination. We thank Dr. John J. Collins and Professors P. D. Bartlett, E. L. Eliel, K. Gollnick, and R. Huisgen for helpful discussions and Professor R. Huisgen for providing the facilities, at the Institut für Organische Chemie der Universität München, where this manuscript was prepared during a sabbatical leave.

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(1) Part 6: N. Filipp, J. J. Collins, and A. Viola, submitted for publication.

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(4) For the specific substrate reported herein, 1-methoxy-1-phenyl-2-propyne, $E_a = 37.3$ kcal/mol and $\Delta S^{\ddagger} = -12.5$ eu.[3]

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(7) A. Viola, J. H. MacMillan, R. J. Proverb, and B. L. Yates, *J. Am. Chem. Soc.*, **93**, 6967 (1971); A. Viola, R. J. Proverb, B. L. Yates, and J. Larrahondo, *Ibid.*, **95**, 3609 (1973).

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(10) All optical rotations were determined with a PE 141 polarimeter in a 1-dm path cell of 1-mL capacity and in $CHCl_3$ solution, except for the phenylallenes where CCl_4 was used. Concentrations are expressed in grams/100 mL of solution.

(11) The melting points of partially resolved derivatives vary considerably. The previously reported[8] specific rotations, and melting points where appropriate, for both enantiomeric series as resolved by means of cinchonine,

follow: racemic **4**, mp 164–165 °C; cinchonine salt, mp 184–185 °C; (−)-**4**, mp 152–153 °C, $[\alpha]^{25}{}_D$ −56.8°; (+)-**4**, mp 152–153 °C, $[\alpha]^{25}{}_D$ +55.7°; (−)-**3**, $[\alpha]^{27}{}_D$ −23.9°; (+)-**3**, $[\alpha]^{28}{}_D$ +22.6°.

(12) Tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III), available from Aldrich Chemical Co.

(13) Both (+)- and (−)-deuteriomethyl ethers as well as the protio ether provided ^{1}H NMR and IR spectra in accord with the assigned structures.

(14) The $LiAlH_4$ reduction did not produce consistently good yields, nor did the etherification, where the lability of the benzylic proton aids the base-catalyzed acetylene–allene isomerization to produce phenyl vinyl ketone as a substantial by-product.

(15) Thermolyses were carried out in the previously described flow system: A, Viola, E. J. Iorio, K. K. Chen, G. M. Glover, N. Nayak, and P. J. Kocienski, *J. Am. Chem. Soc.*, **89**, 3462 (1967).

(16) Phenylallene was initially concentrated by fractional distillation of the crude thermolysate, bp 65 °C (10 Torr), and was then further purified by preparative VPC (2-ft 10% Triton-X 305). In the case of (+)-**1** a further purification step, consisting of column chromatography on silica gel with CCl_4 as eluent, did not alter the rotation.

(17) The vinyl region of phenylallene-*3-d* consists of a one-proton doublet, slightly broadened, centered at δ 6.1, and a one-proton doublet further split into deuterium triplets ($J \sim 1$ Hz) centered at 5.05. The splitting constant are such that even small amounts of phenylallene, not deuterated in the 3 position, can be detected by its triplet centered at δ 6.1.

(18) Since phenylallene has a substantial $(M - 1)^+$ peak, the ratio of $M^+/(M - 1)^+$ for phenylallene-*3-d* was compared with that of the nondeuterated species and indicated essentially 100% monodeuteration.

(19) The attempt to determine the configuration of the optically active allenes directly by means of their ORD spectra failed owing to the large extinction coefficient of phenylallene.

(20) J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959).

(21) G. Lowe, *Chem. Commun.*, 411 (1965).

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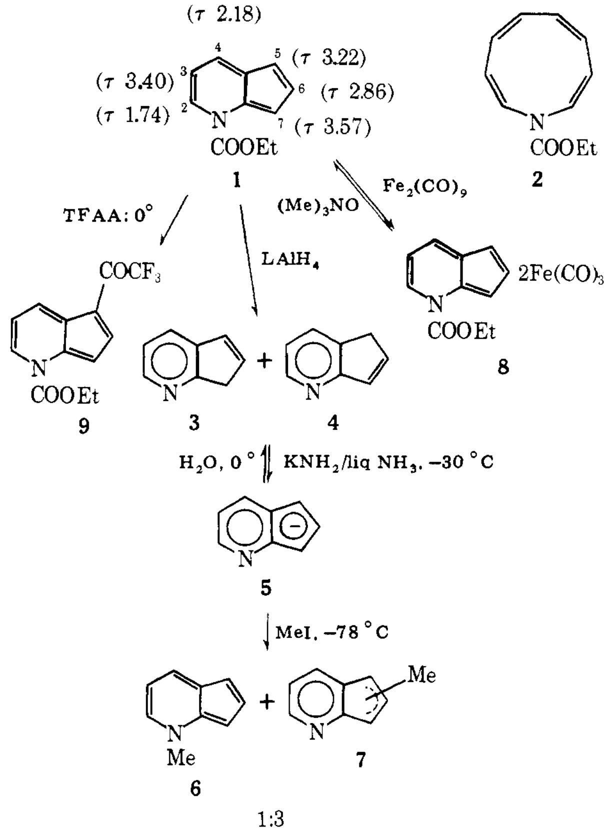
Development of Aromaticity in the 1-Pyrindine System. A Surprising Insensitivity to N-Substitution

Sir:

Attachment of an alkoxycarbonyl appendage to the π-excessive nitrogen centers of such Hückeloid heteromonocycles as the aza[9]-^{1,2} and aza[13]annulenes^{3,4} is known to deplete the system of its "aromatic" character. Surprisingly, this does not appear to happen with the 1-pyrindine system whose recently synthesized deep purple urethane **1** has properties characteristic of a well-delocalized periphery.^{5} Since **1** is basically a bicyclic π isomer of *N*-ethoxycarbonylazonine (**2**),^{6} a heteronin with well-recognized polyenic character, we resolved to compare this substance (**1**) directly with certain properly designed structural relatives and thus possibly gain some insight into this interesting anomally.

Anion **5** (^{1}H NMR (100 MHz, NH_3, −30 °C) τ 2.22 (1 H, d, H^2 or H^4, J = 8.0 Hz), 2.41 (1 H, d, H^2 or H^4, J = 4.5 Hz), 3.17 (1 H, pseudo t (pt), H^6, J = 3.5, 3.5 Hz), 3.63 (1 H, dd, H^3, J = 8.0, 4.5 Hz), 4.02 (1 H, dt, H^5, J = 3.5, 1.5, 1.5 Hz), 4.13 (1 H, dd, H^7, J = 3.5, 1.5 Hz)) was prepared cleanly upon exposure of annulated pyridines **3** and **4** to potassium amide in liquid ammonia at ca. −30 °C. *N*-methylpyrindine (**6**)^{7,8a} (air-sensitive dark red liquid; ^{1}H NMR (100 MHz, acetone-d_6) τ 2.06 (1 H, d, H^2, J = 8.0 Hz), 2.32 (1 H, d, H^4, J = 6.5 Hz), 2.80 (1 H, pt, H^6, J = 4.5, 4.5 Hz), 3.40 (1 H, dd, H^3, J = 8.0, 6.5 Hz), 3.64 (1 H, dd, H^5, J = 1.5, 4.5 Hz), 3.94 (1 H, ddd, H^7, J = 4.5, 1.5 Hz, 1.0 Hz), 5.96 (3 H, s, methyl); S'^9 = 1.7; λ_{max} (C_6H_{14}) 255 nm (sh) (ϵ 20 400), 258 (22 500), 260 (sh) (21 300), 265 (sh) (17 000), 314 (sh) (5600), 319 (6800), 326 (6300), 333 (6400), 442 (sh) (630), 458 (sh) (740), 468 (800), 484 (810), 502 (710), 520 (560), 539 (sh) (340), 568 (196)) was obtained, together with what is tentatively formulated (^{1}H NMR, mass spectrum) as a mixture of the two *C*-methyl variants shown in **7**, upon quenching a solution of **5** in THF with methyl iodide at −78 °C. The heavily complexed urethane depicted in **8**^{8b,10,11} (reddish brown crystals; mp 118–120 °C; ^{1}H NMR (100 MHz, $CDCl_3$) τ 4.44 (1 H, br s), 4.72 (1 H, dd, J = 5.0, 3.0 Hz), 4.8–5.0 (2 H, m) 5.18 (1 H, pt, J = 3.0, 3.0 Hz), 5.81 (2 H, q), 6.21 (1 H, dd, J = 3.0, 1.5 Hz), 8.71 (3 H, t); λ_{max} (CH_3CN) ~210 nm (ϵ 23 500), 325 (sh) (3220), 385 (sh) (1450), 490 (580); ν_{CO} (KBr) 2020, 1965, 1940, 1915 (CO), 1705 cm^{-1} (COOEt)) was formed on treatment of **1** with diiron enneacarbonyl in benzene.



Brief examination of the ^{1}H NMR information described here reveals that urethane **1** (^{1}H NMR shifts given in scheme), amide **5**, and methylamine **6** all display basically the same, strongly diatropic, proton shifts.^{12} This obviously means that the system's lone pair heavily contributes to the development of "aromatic" delocalization and, surprisingly, that the magnitude of such contribution is insensitive to variations of heteroatom electronegativity. Metal complexation, on the other hand, does appear to drain the system of its "aromatic" character as judged by the considerable shielding each ring proton experiences on passing from **1** to **8**.

The ineffectiveness of the *N*-ethoxycarbonyl function in depleting the 1-pyrindine system of its "aromaticity" receives added confirmation from a comparison of solvent shift constants (S').^{9} One notes, for example, that under this criterion pseudoazulene **6** (S' = 1.7) emerges as strongly diatropic as either naphthalene or azulene (both with S' = 1.8) while the *N*-ethoxycarbonyl variant **1** with S' = 1.3 is only slightly less so. Also notable in this connection is that azonine **2**, i.e., the monocyclic π isomer of **1**, where the ethoxycarbonyl appendage is known^{1,2} to operate in its "normal" capacity of aromaticity quencher, emerges as paratropic (S' = −0.3) under the solvent shift criterion.

Chemically, the aromatic character of **1** was established by its ability to undergo ready aromatic substitution upon exposure to trifluoroacetic anhydride (TFAA) at 0 °C to yield the derivative shown in **9**^{8a,11} (dark orange liquid: ^{1}H NMR (100 MHz, $CDCl_3$) τ 1.81 (1 H, d, H^2 or H^4, $J \sim 7$ Hz), 1.89 (1 H, d, H^2 or H^4, $J \sim 7$ Hz), 2.33 (1 H, dq, H^6, J = 5.5, $J_{H\text{-}F} \sim 2$ Hz), 2.84 (1 H, dd, H^3, J = 6.5, 7.3 Hz), 3.38 (1 H, d, H^7, J