heated in an oil bath at 160 °C in a 150-mL two-necked flask equipped with an addition funnel and a short condenser set for distillation. After 0.5 h 1,2-dibromocyclohexane (157 g) was added dropwise, which resulted in an immediate distillation of 1,3-cyclohexadiene. After all the dibromocyclohexane had been added (~1 h), a gentle stream of nitrogen was passed through the system which resulted in an additional small amount of distillate. The resulting 1,3-cyclohexadiene (42.6 g, 82%) was used for Diels–Alder additions and for a reaction with iron tricarbonyl without further purification. In some experiments at higher temperatures small amounts (<5%) of HMPTA could be detected by NMR spectroscopy.

1,3-Cyclohexadiene-*1,3-d*$_2$ (11) and 1,3-Cyclohexadiene-*2,6,6-d*$_3$ (12). A solution of bromine (9.63 g) in CCl_4 (6 mL) was added to cyclohexene-*1,3,3-d*$_3$ (5.07 g) in CCl_4 (12 mL) and absolute alcohol (0.6 mL) at −5 °C.[6] The solvent was evaporated off on a steam bath, and the resulting crude dibromide (12.46 g) was dehydrobrominated by the above procedure with lithium carbonate (9.5 g) and lithium chloride (6 g) in HMPTA (30 mL). The distillate was a 1:1 mixture of 1,3-cyclohexadiene-*1,3-d*$_2$ and 1,3-cyclohexadiene-*2,6,6-d*$_3$ (by mass spectrometry of the adduct with maleic anhydride, 3.15 g, 75%).

1,6-Dihydrophthalic Acid, Dimethyl Ester (16). Dehydrobromination of 4,5-dibromo-*trans*-cyclohexane-1,2-dicarboxylic acid, dimethyl ester[7] (**15**-*trans*, 17.1 g) by the procedure reported for 5,6-diacetoxy-1,3-cyclohexadiene[5] gave rise to **16** (bp 126–130 °C/(5–10 torr), 3.5 g). This compound was also obtained by the same procedure from 4,5-dibromo-*cis*-cyclohexane-1,2-dicarboxylic acid, dimethyl ester (**15**-*cis*). NMR: δ 2.38–3.25 (m, 3 H), 4.7 (s, 3 H), 4.8 (s, 3 H), 5.8–6.3 (m, 2 H), 7.1–7.3 (m, 1 H).

1,7-Bis(methoxycarbonyl)bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic Anhydride (17). A mixture of **16** (3 g), maleic anhydride (4.52 g), and 4-*tert*-butylcatechol (0.05 g) in 1,2-dichlorobenzene (25 ml) was refluxed (oil bath at 175 °C) for 4.5 h. After removal of the solvent (74 °C (30 torr)), the residue crystallized on the addition of ether: white crystals, 2.75 g; mp 114–116 °C. Recrystallization from petroleum ether (100–120 °C) raised the mp to 128–129 °C; NMR δ 1.9–2.2 (m, 2 H), 3.1–3.6 (m, 3 H), 3.7 (s, 3 H), 3.95 (s, 3 H), 6.3–6.8 (m, 2 H); mass spectrum, *m/z* (relative intensity) 294 ($M^{+\cdot}$, 44), 263 ($[M - CH_3O]^+$, 18), 262 ($[M - CH_3OH]^{+\cdot}$, 2), 208 (4), 190 (4), 181 (3), 180 (4), 163 (21), 137 (27), 136 (45), 131 (9), 105 (100), 103 (16), 91 (12), 78 (12), 77 (43), 59 (21), 55 (20); M_r found (high-resolution mass spectrometry) 294.0741, calculated for $C_{14}H_{14}O_7$ 294.0740. Anal. C, 57.24; H, 4.92. Calcd for $C_{14}H_{14}O_7$: C, 57.14; H, 4.80.

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Registry No. 1, 592-57-4; 2, 7429-37-0; 3, 89780-18-7; 4, 83992-79-4; 5, 90295-59-3; 6, 85015-25-4; 7, 85015-24-3; 10, 89831-48-1; 11, 17647-16-4; 12, 90295-60-6; 13, 85015-26-5; 14, 85015-27-6; 15-*cis*, 26595-97-1; 15-*trans*, 90409-98-6; 16, 90295-61-7; 17, 90295-62-8; lithium carbonate, 554-13-2; lithium chloride, 7447-41-8; hexamethylphosphoric triamide, 680-31-9; cyclohexene-*1,3,3-d*$_3$, 27926-35-8; maleic anhydride, 108-31-6.

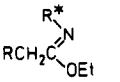
(6) Snyder, H. R.; Brooks, L. A. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. 2, p 171.
(7) Klein, J.; Dunkelblum, E. *J. Org. Chem.* **1971**, *36*, 145.

Communications

Asymmetric Electrophilic Syntheses Using Chiral Acyclic Imidate Ester Enolates. Highly Enantioselective Syntheses of Carboxylic Acid Esters

Summary: Chiral imidate esters ($RCH_2C(OEt)=NR^*$; R = Me, Et; R* = (*S*)-$CH(CH_2Ph)CH_2OCH_3$, (*R*)-$CH(Ph)CH_2OCH_3$, (*S*)-$CH(i\text{-}Pr)CH_2OCH_3$) were prepared and deprotonated with various bases to give the corresponding lithio anion derivatives. Alkylations of the lithio derivatives proceeded in high synthetic yield and with good to excellent asymmetric induction to give α,α-disubstituted carboxylic acid derivatives. The structures of the imidate esters and their lithio derivatives are discussed.

Sir: Asymmetric synthesis is an area of synthetic methodology which has recently seen significant advances[2] including new methods for asymmetric carbon–carbon bond formation employing chiral nucleophiles which proceed with an efficiency and predictability such that they are now routinely useful in multistep natural product syntheses.[3] In this report, we describe a new class of chiral nucleophiles, acyclic imidate ester enolates.



(*S*)-**1**, R = CH_3; R* = $CH(CH_2Ph)CH_2OCH_3$
(*S*)-**2**, R = C_2H_5; R* = $CH(CH_2Ph)CH_2OCH_3$
(*R*)-**3**, R = CH_3; R* = $CH(Ph)CH_2OCH_3$
(*R*)-**4**, R = C_2H_5; R* = $CH(Ph)CH_2OCH_3$
(*S*)-**5**, R = CH_3; R* = $CH(i\text{-}Pr)CH_2OCH_3$
(*R*)-**6**, R = CH_3; R* = $CH(Ph)CH_3$

Chiral acyclic imidate esters **1**–**6** were readily prepared in 70–90% yield by modifications of literature procedures[4] either by treatment of an ortho ester with an amine or by alkylation of an amide with Et_3OBF_4. The chiral β-methoxy amines were available from amino acids.[5] The C=N stereochemistry of **1**–**6** was shown to be *E* (as drawn) by correlation of the ^1H and ^{13}C NMR spectra of **1**–**6** with spectra reported for other imidate esters, imines, and oxazolines. Of particular importance was the observation that $^{1,5}J_{H\text{-}H}$ across the C=N bond in both **1**–**6** and their alkylated products were <0.5 Hz, indicating $E_{C=N}$ stereochemistry.[6]

Chiral imidate ester enolates were generated at low temperatures by deprotonation of **1**–**6** using bases such as *n*-BuLi, *t*-BuLi, or lithium diethylamide (LDEA) and were

(1) Camille and Henry Dreyfus Teacher–Scholar, 1980–1985.
(2) Mosher, H. S.; Morrison, J. D. *Science (Washington, D.C.)* **1983**, *221*, 1013–1019; Bergbreiter, D. E.; Newcomb, M. in "Asymmetric Synthesis": Morrison, J. D., Ed.; Academic Press; New York, 1983; Vol 2, Part A, Chapter 9.
(3) Evans, D. A. *Aldrichimica Acta* **1982**, *15*, 23–32. Masamune, S.; Choy, W. *Ibid.* **1982**, *15*, 47–63.
(4) Neilson, D. G. In "The Chemistry of Amidines and Imidates": Patai, S., Ed.; Wiley: London, 1975; Chapter 9. Roger, R.; Neilson, D. G. *Chem. Rev.* **1961**, *61*, 179–211.
(5) Meyers, A. I.; Poindexter, G. S.; Brich, Z. *J. Org. Chem.* **1978**, *43*, 892–898.
(6) Meese, C. O.; Walter, W.; Berger, M. *J. Am. Chem. Soc.* **1974**, *96*, 2259–2260.

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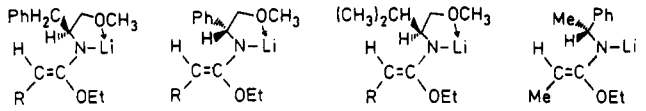
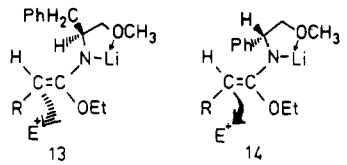
then alkylated with various alkyl halides. Imidate ester enolates could be handled for 1 h at 20 °C without significant decomposition and are more stable than enolates derived from oxazolines.[7] The stereochemistry of the imidate ester enolates was also studied and deduced to be $Z_{C=C},E_{C=N}$ for 7–12 as shown. This stereochemical as-



7, R = CH_3 9, R = CH_3 11, R = CH_3 12
8, R = C_2H_5 10, R = C_2H_5

signment is based on several data. First, ^{13}C NMR spectra of enolate 9 or 12 derived from $^{13}CH_3$-labeled starting material had only one detectable ^{13}C-labeled methyl signal. The simplest explanation for this observation is that only one C=C, C=N stereoisomer is present. Second, products of alkylation of 7–12 have $E_{C=N}$ stereochemistry (vide supra). We and others have found that C=N stereochemistry in electrophilic substitution products correlates well with C–N stereochemistry in azaallyllithium reagents.[8] Third, the postulated C–N stereochemistry is analogous to the experimentally and theoretically determined more stable syn stereochemistry in other azaallyllithium reagents.[9] Fourth, consideration of possible 1,3-allylic interactions in the transition states for deprotonation (in analogy to other enolate chemistry) predicts the postulated $Z_{C=C}$ stereochemistry.[10] Finally, $Z_{C=C},E_{C=N}$ stereochemistry is implicated by a simple model that predicts the direction of asymmetric induction in alkylation reactions (vide infra).

Alkylation of 7–11 proceeded with high stereoselectivity and in high yield (Table I). Further conversion of some of the alkylated imidate esters to the corresponding ethyl esters allowed us to examine the efficiency and sense of the asymmetric induction. The results listed in Table I indicate that the predominant enantiomer is that predicted by transition state models 13 and 14. The importance of



13 14

the chelating methoxy group was demonstrated by the observation that alkylation of 12 with iodoethane led to a mixture of diastereomers with 66% de. Under the same conditions, enolate 9 gave alkylated products with 90% de. It is reasonable to assume that chelation of lithium by the methoxy group increases the diastereofacial bias in 9 relative to that in 12 where the chiral auxiliary is less rigid.

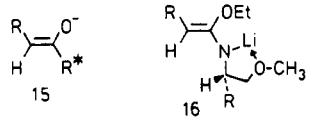
In comparison to other asymmetric syntheses of carboxylic acid derivatives, the use of chiral acyclic imidate esters offers advantages in the ease of preparation of reagents, the stability of the intermediate enolates, and the high diastereoselectivity observed in alkylations with a variety of conventional alkyl halides. In addition, both

Table I. Reactions of Chiral Imidate Ester Enolates with Alkyl Halides[a]

reagent	electrophile	% yield	ratio[b]	% o.p.	config[b]
7	EtI[c]	70–80	19:1	89[d]	*R*
	i-PrI	85	99:1		
	$PhCH_2Br$	80–85	32:1	95,[e] 93[d]	*R*
8	MeI[c]	44	6:1		*S*[f]
	n-PrBr	70	41:1		
	n-BuBr	90	30:1		
9	EtBr[c]	87	41:1		
	EtI	87	58:1		
	n-PrI	51	32:1		
	n-BuBr	80	32:1	94[d]	*S*[g]
	i-PrI	72	>99:1		
	$PhCH_2Br$	80	4:1	63,[e] 56[d]	*S*
10	MeI[c]	90	5:1		
	n-PrBr	90	31:1		
	n-BuBr	93	28:1		
11	EtI	60	6:1		

[a] Imidate esters were deprotonated with excess $LiNEt_2$ in THF at −78 °C or −23 °C; alkylations were performed at −78 °C. Imidate products were isolated by distillation after a conventional extractive workup. The indicated ethyl esters were prepared by alcoholysis of the imidate (H_2SO_4, EtOH) or by treatment with silica gel in ether. [b] Diastereomer ratios were determined by GC analysis of the crude alkylation products. Configurations were determined by optical rotation of the ethyl esters. [c] For these two pairs of diastereomers, reversing the R groups of the imidates and the electrophiles resulted in reversals of the predominant diastereomer. [d] % optical purity of the ethyl ester determined by NMR with a chiral shift reagent. [e] % optical purity of the ethyl ester determined by rotation.[11] [f] Configuration determined by correlation of the diastereomeric products to those formed by ethylation of 7. [g] Assuming that the (+) rotating enantiomer has *S* stereochemistry.[11]

enantiomers of a product are available either by using two precursors with different configurations at the chiral carbon of an auxiliary (i.e., 7 and 9) or by using one precursor and reversing the order of introduction of alkyl groups at the new chiral center. Another potentially important feature of chiral imidate ester enolates is that while other successful chiral nucleophiles have structure 15 with



15 16

the α-R group cis to the charge-bearing heteroatom, the imidate ester enolates have structure 16 with the α-R group trans to the charge-bearing heteroatom. This stereochemical difference could be important in the diastereoselectivity of aldol-like reactions, an area of current research interest in our laboratory.

Acknowledgment. This work was supported by the Robert A. Welch Foundation and an NIH-Biomedical Sciences support grant.

Registry No. (*S*)-1, 90553-87-0; (*S*)-2, 90553-88-1; (*R*)-3, 90553-89-2; (*R*)-4, 90553-90-5; (*S*)-5, 90553-91-6; (*R*)-6, 90553-92-7; 7, 90553-93-8; 8, 90553-94-9; 9, 90553-95-0; 10, 90553-96-1; 11, 90553-97-2; 12, 90553-98-3; $CH_3CH_2CH(CH_3)C(OEt)$=NCH-$(CH_2Ph)CH_2OCH_3$ (isomer 1), 90553-99-4; $CH_3CH_2CH(CH_3)C$-(OEt)=NCH$(CH_2Ph)CH_2OCH_3$ (isomer 2), 90554-12-4; $(CH_3)_2CHCH(CH_3)C(OEt)$=NCH$(CH_2Ph)CH_2OCH_3$ (isomer 1), 90554-00-0; $(CH_3)_2CHCH(CH_3)C(OEt)$=NCH$(CH_2Ph)CH_2OCH_3$ (isomer 2), 90554-13-5; $PhCH_2CH(CH_3)C(OEt)$=NCH-$(CH_2Ph)CH_2OCH_3$ (isomer 1), 90554-01-1; $PhCH_2CH(CH_3)C$-(OEt)=NCH$(CH_2Ph)CH_2OCH_3$ (isomer 2), 90554-14-6; CH_3-$(CH_2)_2CH(Et)C(OEt)$=NCH$(CH_2Ph)CH_2OCH_3$ (isomer 1), 90554-02-2; $CH_3(CH_2)_2CH(Et)C(OEt)$=NCH$(CH_2Ph)CH_2OCH_3$ (isomer 2), 90554-15-7; $CH_3(CH_2)_3CH(Et)C(OEt)$=NCH-

(7) Meyers, A. I. *Pure Appl. Chem.* **1979**, *51*, 1255–1268.
(8) Davenport, K. G.; Newcomb, M.; Bergbreiter, D. E. *J. Org. Chem.* **1981**, *46*, 3143–3144 and references therein.
(9) Houk, K. N.; Strozier, R. W.; Rondan, N. G.; Fraser, R. R.; Chauqui-Offermanns, N. *J. Am. Chem. Soc.* **1980**, *102*, 1426–1429.
(10) Heathcock, C. H.; White, C. T. Morrison, J. J.; VanDerveer, D. *J. Org. Chem.* **1981**, *46*, 1296–1309.
(11) Kenyon, J.; Phillips, H.; Pittman, V. P. *J. Chem. Soc.* **1935**, 1072–1084.

$(CH_2Ph)CH_2OCH_3$ (isomer 1), 90554-03-3; $CH_3(CH_2)_3CH(Et)C(OEt)=NCH(CH_2Ph)CH_2OCH_3$ (isomer 2), 90554-16-8; $CH_3CH_2CH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 1), 90554-04-4; $CH_3CH_2CH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 2), 90554-17-9; $CH_3(CH_2)_2CH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 1), 90554-05-5; $CH_3(CH_2)_2CH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 2), 90554-18-0; $CH_3(CH_2)_3CH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 1), 90554-06-6; $CH_3(CH_2)_3CH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 2), 90554-19-1; $(CH_3)_2CHCH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 1), 90554-07-7; $(CH_3)_2CHCH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 2), 90554-20-4; $PhCH_2CH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 1), 90554-08-8; $PhCH_2CH(CH_3)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 2), 90554-21-5; $CH_3(CH_2)_2CH(Et)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 1), 90554-09-9; $CH_3(CH_2)_2CH(Et)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 2), 90554-22-6; $CH_3(CH_2)_3CH(Et)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 1), 90554-10-2; $CH_3(CH_2)_3CH(Et)C(OEt)=NCH(Ph)CH_2OCH_3$ (isomer 2), 90554-23-7; $CH_3CH_2CH(CH_3)C(OEt)=NCH(i\text{-}Pr)CH_2OCH_3$ (isomer 1), 90554-11-3; $CH_3CH_2CH(CH_3)C(OEt)=NCH(i\text{-}Pr)CH_2OCH_3$ (isomer 2), 90554-24-8; EtI, 75-03-6; *i*-PrI, 75-30-9; $PhCH_2Br$, 28807-97-8; CH_3I, 74-88-4; *n*-PrBr, 106-94-5; *n*-BuBr, 109-65-9; EtBr, 74-96-4.

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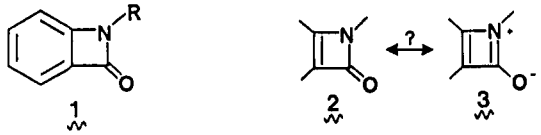
Azetinones Revealed

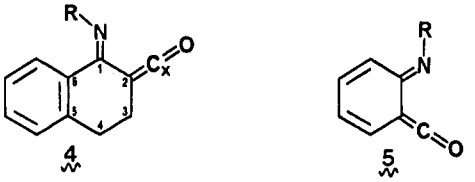
Summary: Chemical and spectral evidence for the formation of azetinones **11a–d** is presented.

Sir: While benzoazetinones **1** are known from work in this laboratory[1,2] and elsewhere,[3] no report of the synthesis of a simple azetinone (**2**) has survived the critical scrutiny

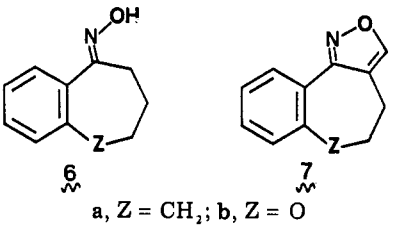


of the chemistry community. Announcements of success have been followed by disproofs,[4] and the literature is strewn with the conclusions of those who have conceded after clever attempts that **2** cannot be obtained.[5] Past interest in azetinones derives from their attractiveness as intermediates in the synthesis of medicinally useful α,β-functionalized β-lactams. As potentially antiaromatic compounds (**2** ↔ **3**), which can avoid violating Hückel's rule by bending R out of the ring plane, azetinones also are of theoretical importance.[6]

The present investigation was prompted by a hint that imino ketene **4** was generated in the chemistry of the related isoxazolium salt[7] and from indications that in solution **5** is a trace component in equilibrium with the benzoazetinone (**1**).[8] Thus, if N and C_x could be pushed together by pulling C_2–C_3 and C_1–C_6 apart while retaining the *s*-cis relationship at C_1–C_2, an azetinone might be observed.



To this end, the known *E* oximes[9] **6a,b** were converted to the respective isoxazoles (**7a**, C_3H at δ 8.15,[10] 77% yield; **7b**, δ 8.07, 74%) by the general acylation–cyclization process of Barber and Olofson.[11] These were alkylated either with a strong electrophile (CF_3SO_3Me or FSO_3Et) or with *t*-ROH/HX[12] to give the isoxazolium salts (**8a**, C_3H at δ 9.02, 94% yield; **8b**, δ 8.91, 6%; **8c**, δ 9.03, 92%; **8d**, δ 8.99, 9%; **8e**, δ 9.06, 24%; **8f**, δ 9.17, 90%). The latter process failed in the attempted *tert*-alkylation of **7b**.



a, Z = CH_2; b, Z = O

Treatment of **8** consecutively or simultaneously with tertiary amines and nucleophiles (MeOH or Et_2NH) nicely afforded the ring-opened products (**9a**, IR C=O at 6.15 μm; **9b**, 6.11; **9c**, 6.23; **9d**, 6.09) expected from addition of the nucleophile to an azetinone (**11**) or its assumed[8] imino ketene precursor (**10**). The anhydride (**9e**, C=O at 166.7 ppm) was obtained on reaction of **8f** with dicyclohexylethylamine (Cy_2NEt) in the presence of trace water.

When anhydrous *i*-Pr_2NEt (1 equiv) was rapidly added to the *N*-ethyl salt **8a** in scrupulously dried CH_2Cl_2 kept at 5 °C, a bright yellow color instantly appeared. The solution immediately was analyzed by IR (cells dried in vacuo and stored at 5 °C). The spectrum contained a strong, short-lived C=O stretch absorption in the 5.5–5.6 μm range expected for the azetinone (**11a**, gone in ca. 4

(1) Olofson, R. A.; Vander Meer, R. K.; Hoskin, D. H.; Bernheim, M. Y.; Stournas, S.; Morrison, D. S. *J. Org. Chem.* **1984**, in press. First isolation: Olofson, R. A.; Vander Meer, R. K.; Stournas, S. *J. Am. Chem. Soc.* **1971**, *93*, 1543.

(2) Vander Meer, R. K.; Olofson, R. A. *J. Org. Chem.* **1984**, in press.

(3) Bashir, N.; Gilchrist, T. L. *J. Chem. Soc., Perkin Trans. 1* **1973**, 868. Burgess, E. M.; Milne, G. *Tetrahedron Lett.* **1966**, 93. Ege, G. *Chem. Ber.* **1968**, *101*, 3079. Ege, G.; Pasedach, F. *Ibid.* 3089.

(4) Recent publications where investigators have nicely disproved azetinone structures presented by earlier workers include: Gane, P. A. C.; Boles, M. O. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2664. Bachi, M. D.; Goldberg, O.; Gross, A.; Vaya, J. *J. Org. Chem.* **1980**, *45*, 1481. Abdulla, R. F.; Unger, P. L. *Tetrahedron Lett.* **1974**, 1781. While Henery-Logan and Rodricks [Henery-Logan, K. R.; Rodricks, J. V. *J. Am. Chem. Soc.* **1963**, *85*, 3524] have not been retracted, it is unlikely that 1,2-diphenyl-2-azetin-4-one is correctly described therein. The product had mp of 121 °C after *chromatography over alumina* and crystallization from acetone–*water* (IR CO stretch at 5.71 μm).

(5) For example: Barton, D. H. R.; Buschmann, E.; Haüsler, J.; Holzapfel, C. W.; Sheradsky, T.; Taylor, D. A. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1107. Allan, R. D.; Barton, D. H. R.; Girijavallabhan, M.; Sammes, P. G.; Taylor, M. V. *Ibid.* **1973**, 1182. Kretschmer, G.; Warrener, R. N. *Tetrahedron Lett.* **1975**, 1335. Sheradsky, T.; Zbaida, D. *J. Heterocycl. Chem.* **1983**, *20*, 245 and references therein. For other processes proceeding via **2**, see: Potts, K. T.; Ehlinger, R.; Nichols, W. M. *J. Org. Chem.* **1975**, *40*, 2596 and references therein.

(6) Benzoazetinone (**1**) is antiaromatic; all ring system atoms along with the attached exocyclic O and N–C are in the same plane.[1]

(7) Olofson, R.; Barber, G.; Hoskin, D., unpublished observation.

(8) The imino ketene **5** was proposed as a trace equilibrium intermediate from kinetic studies (in the dark and photochemically): Olofson, R. A.; Vander Meer, R. K. *J. Org. Chem.* **1984**, in press.

(9) **6a**: Kipping, F. S.; Hunter, A. E. *J. Chem. Soc.* **1901**, *79*, 602. **6b**: Bădilescu, I. I. *Rev. Roum. Chim.* **1975**, *20*, 761.

(10) New compounds identified by including some property (for spectral data, see supplementary material); mp **7a** 56.5–57 °C, **7b** (bp) 135–138 °C at 0.6 mm, **8a** 151–152 °C, **8b,c** solid ClO_4^- salts, **8d** 61–63 °C, **8e** 169–170 °C dec, **8f** 80–82 °C, **9b** 66.5–67.5 °C, **9c** 90.5–92 °C, **9a,d,e** oils.

(11) Barber, G. N.; Olofson, R. A. *J. Org. Chem.* **1978**, *43*, 3015. Hoskin, D. H.; Olofson, R. A. *Ibid.* **1982**, *47*, 5222.

(12) Woodward, R. B.; Woodman, D. J. *J. Org. Chem.* **1966**, *31*, 2039. Woodman, D. J. *Ibid.* **1968**, *33*, 2397. *t*-BuOH formed in situ from isobutene.

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