Organotellurium Chemistry. 7. Reductive Removal of Electronegative α Substituents of Ketones and Acids by a Tellurolate Reagent

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Lithium and sodium 2-thiophenetellurolates have been used for the reductive dehalogenation of a variety of α-halo ketones and acids. Acetoxy, mesyloxy, and phenylthio groups were also successfully removed from the α position of an acetophenone. The reductions could in many cases be carried out by using sodium borohydride as the reducing agent in the presence of only a catalytic amount of the organotellurium reagent. Evidence is presented in support of a two-step mechanism involving the formation of α-aryltelluro carbonyl derivatives and enolate anions in succession.

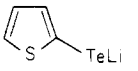
Methods for the selective removal of certain functional groups adjacent to a carbonyl have recently received considerable attention. In particular, a number of procedures have been developed to bring about the reductive dehalogenation of α-halo ketones. Zinc in acetic acid,[1] phosphines[2-5] and various inorganic phosphorus compounds,[6] sodium borohydride,[7] iodide ion,[8-11] thiols[12] and selenols,[13] titanium trichloride,[14] vanadium(II) chloride,[15] *N,N*-dimethylaniline,[16] organotin hydrides,[17] sodium dithionite,[18] and various metal carbonyls[19-21] are some of the reagents that have been used.

The recent report of the use of sodium hydrogen telluride for the debromination of *vic*-dibromides[22] and the early observation by Bergson[23] that sodium telluride and sodium ditelluride reduced chloroacetic acid to acetic acid suggested that anionic organotellurium reagents might be capable of effecting the reductive dehalogenation of α-halo carbonyl compounds. We now describe the reductions of some α-substituted ketones and carboxylic acids using lithium and sodium 2-thiophenetellurolate (1).

Results and Discussion

Lithium arenetellurolates are readily available by the insertion of elemental tellurium into the carbon–metal bond of various organolithium compounds. This reaction is especially effective when the aromatic moiety is heteroaromatic.[44]

We have found that a number of α-substituted ketones and carboxylic acids are readily reduced in good yields when treated with 2 equiv of lithium 2-thiophenetellurolate (1) in dry THF. A number of representative examples are



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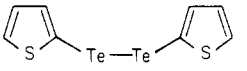

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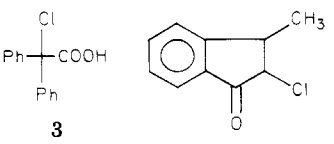
presented in Table I (procedure A). When solutions of α-chloro, α-bromo, or α-iodo ketones were added at room temperature to a solution of lithium 2-thiophenetellurolate, the deep red color of bis(2-thienyl) ditelluride (2) was observed immediately. Aqueous workup after 30 min afforded the parent ketone and bis(2-thienyl)ditelluride as the only product. Slightly improved yields were obtained by immediate protonation of the ketone enolates (vide infra) with acetic acid (Table I).

A number of other α substituents like acetoxy, mesyloxy, and phenylthio groups were also removed under the same mild reaction conditions, as can be seen from Table I. Phenacyl alcohol, however, did not react.

Sodium arenetellurolates are readily obtained by sodium borohydride reduction of diaryl ditellurides in ethanol.

Sodium 2-thiophenetellurolate, prepared in this manner by reduction of bis(2-thienyl) ditelluride,[44] reduced α-chloro, α-bromo, and α-iodo ketones in excellent yields at room temperature to the parent ketones (Table I, procedure B). α-Bromocarboxylic acids were debrominated, also in excellent yields, to give the parent carboxylic acids by using the same procedure. The workup is particularly easy in the latter case, since the acids can be extracted into base and separated from bis(2-thienyl) ditelluride, the only byproduct. α-Chlorodiphenylacetic acid (3), however, seemed to undergo α substitution by ethoxide and was best reduced by using procedure A mentioned above.



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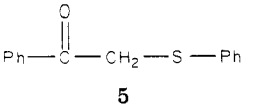

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We have also developed a catalytic procedure (procedure C) for reduction of both α-halo ketones and acids. Sodium borohydride was in this approach added dropwise under N_2 to a mixture of the α-halocarbonyl compound and a catalytic amount of bis(2-thienyl) ditelluride in ethanol, until the red color of the ditelluride disappeared. At this point, the system was opened up to the atmosphere and the small amount of sodium 2-thiophenetellurolate present

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Table I. Reduction of α-Substituted Carbonyl Compounds with Alkali 2-Thiophenetellurolates

substrate	procedure	product	yield	mp, °C	lit. mp, °C
phenacyl chloride	A	acetophenone	62		
	B	acetophenone	93		
phenacyl bromide	A	acetophenone	61		
	A[a]	acetophenone	70		
	B	acetophenone	87		
	C	acetophenone	90		
phenacyl iodide	A	acetophenone	69		
	B	acetophenone	93		
phenacyl phenyl sulfide	A[a]	acetophenone	88		
phenacyl acetate	A	acetophenone	52		
	A[a]	acetophenone	72		
phenacyl mesylate	A	acetophenone	55		
p-bromophenacyl bromide	A	*p*-bromoacetophenone	72	49-50	50-51[34]
	B	*p*-bromoacetophenone	98		
desyl chloride	C	desoxybenzoin	73	53-54	55-56[35]
2-bromocholestan-3-one	A	cholestan-3-one	90	127-128	127-128[36]
	B	cholestan-3-one	93		
2-chloro-3-methyl-1-indanone (*4*)	A	3-methyl-1-indanone	94	237-239[b]	239-241[37]
α-bromoacetanilide	A	acetanilide	94	113-115	114[38]
α-bromophenylacetic acid	B	phenylacetic acid	99	77	77[39]
	C	phenylacetic acid	98		
α-bromo-1-naphthylacetic acid	C	1-naphthylacetic acid	97	132-133	131[40]
α-chlorodiphenylacetic acid	A	diphenylacetic acid	93	145-146	146-147[41]
α-(2-thienyltelluro)acetanilide	A[a]	acetanilide	88	113-115	114[38]

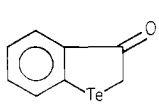
[a] 1 equiv of HOAc was added together with the α-substituted carbonyl compound in order to protonate the enolate immediately when formed. [b] m.p. of 2,4-dinitrophenyl hydrazone.

was allowed to oxidize back to ditelluride. Workup afforded excellent yields of carboxylic acids and surprisingly high yields of ketones (Table I).

Sodium borohydride apparently reduces the ditelluride preferentially over the carbonyl group, thus minimizing the formation of halohydrines, the expected reduction products from α-halo ketones. However, the sensitive α-halo ketone **4** gave a mixture of products due to overreduction. In this case, however, the general procedure A gave an excellent yield of the dehalogenated compound.

Phenacyl phenyl sulfide (**5**) failed to react with sodium 2-thiophenetellurolate in ethanol, indicating a lower nucleophilicity of the tellurolate anion in this solvent as compared to the reactions in THF. This may in part be due to complexation with boron species as previously suggested for sodium areneselenolates.[25]

It has previously been reported that reactions of α-halo ketones with thiolate and selenolate ions often give mixtures of reduction and substitution products, depending on the substrates and the amounts of reagents used.[12,13] In the present study, we were never able to isolate a substitution product from the reaction of an α-halo ketone with an alkali 2-thiophenetellurolate. The expected substitution products are α-telluro ketones, a class of compounds represented in the literature solely by the cyclic ketone **6**.[24] We felt, nevertheless, that α-telluro ketones



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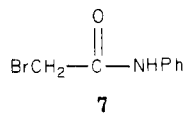

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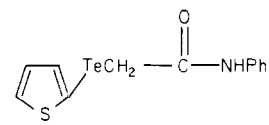

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might be intermediates in the α-halo ketone reductions. This supposition received indirect support by the isolation and chemical behavior of a related substance, namely an α-telluroamide.

When sodium 2-thiophenetellurolate was generated carefully in the presence of excess α-bromoacetanilide (**7**),

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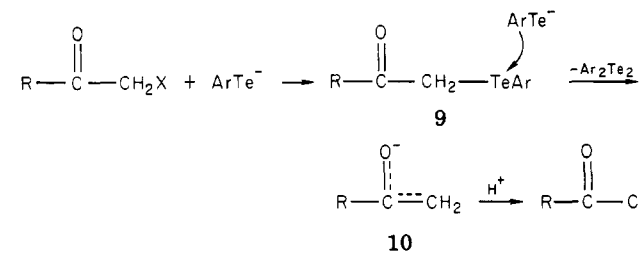
Scheme I



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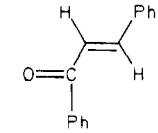
we were able to isolate α-(2-thienyltelluro)acetanilide (**8**) in 64% yield as stable yellow crystals. Attempts to use stoichiometric amounts of the bromoamide and the reagent resulted only in the formation of acetanilide product and bis(2-thienyl) ditelluride. Compound **8** was found to react rapidly with lithium 2-thiophenetellurolate to give acetanilide in 88% yield.

The above-mentioned experiments suggest that substitution products **9** (Scheme I) are probably involved in the reduction of α-halo ketones. Nucleophilic attack of a second molecule of tellurolate ion on the tellurium atom of **9** would then produce the enolate **10** in addition to bis(2-thienyl) ditelluride. The enolate would, of course, be protonated immediately in ethanol, but only during workup in a THF reaction, unless an external proton source has been added.

Evidence for the formation of intermediary enolates was obtained in experiments using benzaldehyde as a trapping agent.

When a mixture of phenacyl bromide and benzaldehyde was added to a solution of lithium 2-thiophenetellurolate in dry THF, chalcone (**11**) could be isolated in 48% yield after the usual work-up. Compound **8** gave a 60% yield of the hydroxyamide **12** under similar reaction conditions.



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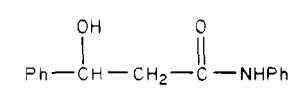

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It is also possible that reduction may proceed at least in part by direct attack of the tellurolate anion on the halogen of the α-halocarbonyl compound, as suggested earlier for some similar selenolate reactions.[25] This process would directly give the enolate **12** and a transient aryltellurenyl halide that would undergo further reaction with tellurolate ion to give a diaryl ditelluride.

This type of mechanism is, however, quite unlikely in the cases of phenacyl acetate and phenyl mesylate. Tellurolate attack on the chlorine of the tertiary halide **3** appears more attractive, but this highly reactive halo acid could also well give an α-tellurocarboxylate intermediate by a unimolecular solvolysis mechanism.

Conclusion

Although numerous methods are available for the reductive dehalogenation of α-halo ketones, we consider the present procedure a simple and useful addition to this type of methodology.

A variety of α-chloro, α-bromo, and α-iodo ketones as well as α-halo acids were reduced in consistently good yields, often by using only a catalytic amount of the organotellurium reagent. In addition, a number of other α substituents, i.e., acetoxy, mesyloxy, and aryl thio groups, could be selectively removed from a ketone.

Finally, the tellurolate dehalogenation of an α-halo ketone affords a mild new method for the generation of a ketone enolate. We hope to explore the utility of this reaction in synthesis as a potentially new procedure for the generation and trapping of regiospecifically generated enolates.

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. Mass spectra were recorded by using a Perkin-Elmer 270B instrument, and NMR spectra were obtained with a Varian EM-360 instrument. α-Bromo-1-naphthylacetic acid,[26] desyl chloride,[27] α-bromoacetanilide,[28] 2-bromocholestan-3-one,[29] phenacyl mesylate,[5] phenacyl acetate,[30] phenacyl iodide,[13] phenacyl alcohol,[31] and phenacyl sulfide[32] were all synthesized according to literature procedures. 2-Chloro-2,3-dihydro-3-methyl-1*H*-indan-1-one (**4**) was obtained by treatment of 2-diazo-3-methylindan-1-one[33] with HCl in dry ether as a mixture of cis and trans isomers, bp 100 °C (0.3 mmHg), yield 84%.

Three typical reductions of α-halo ketones and acids are described in the following paragraphs, exemplifying the three general procedures used (A, B, and C).

Procedure A. Reduction of 4-Bromophenacyl Bromide in Dry THF. *n*-Butyllithium (7.5 mL, 1.6 M, 12.0 mmol) was added under N_2 to a stirred solution of thiophene (1.12 g, 13.3 mmol) in dry THF (50 mL) at 0 °C. After 50 min at room temperature, finely ground elemental tellurium (1.50 g, 11.8 mmol) was added rapidly. A brisk stream of nitrogen was passed through the open system during the addition in order to prevent any introduction of oxygen. After 30 min all tellurium was consumed, and a solution of 4-bromophenacyl bromide (1.6 g, 5.75 mmol) in THF (5 mL) was added dropwise during 10 min. The solution changed from faint yellow to deep red as bis(2-thienyl) ditelluride was formed. After 30 min, the solvent was evaporated, and the residue was dissolved in water/ethyl ether. The organic phase was separated, dried ($CaCl_2$), and evaporated to give a red solid. Chromatography (silica, 1:1 CH_2Cl_2/hexane) afforded 0.82 g (72%) of 4-bromoacetophenone, mp 49–50 °C (lit. mp 50–51 °C).[34]

Procedure B. Reduction of 2-Bromocholestan-3-one in Ethanol. A solution of $NaBH_4$ (5% in 5% aqueous NaOH) was added dropwise to a stirred suspension of bis(2-thienyl) ditelluride[44] (0.75 g, 1.78 mmol) in ethanol under N_2, until the red of the solution just disappeared. 2-Bromocholestan-3-one (0.80 g, 1.72 mmol) in EtOH (5 mL) was then added dropwise during 10 min, causing an immediate red coloration. After 30 min the reaction mixture was poured into water/ethyl ether and the organic phase extracted several times with water. Drying ($CaCl_2$), evaporation, and chromatography (silica, CH_2Cl_2) yielded 0.62 g (93%) of cholestan-3-one, mp 127–128 °C (lit. mp 127–128 °C).[36]

Procedure C. Catalytic Reduction of α-Bromophenylacetic Acid in Ethanol. $NaBH_4$ (5% in 5% aqueous NaOH) was added dropwise under N_2 to a solution of α-bromophenylacetic acid (1.50 g, 7.0 mmol) and bis(2-thienyl) ditelluride (0.30 g, 0.71 mmol) in ethanol (40 mL) until the red of the ditelluride just disappeared. At this point air was introduced into the system to oxidize the catalyst back to the ditelluride state. The reaction mixture was then dissolved in ethyl ether/NaOH (5% aqueous). The aqueous phase was separated, acidified with HCl (aqueous 2 M), and extracted several times with ethyl ether. Drying ($CaCl_2$) and evaporation afforded phenylacetic acid, 0.93 g (98%), mp 77 °C (lit. mp 77 °C).[39]

α-(2-Thienyltelluro)acetanilide (8). Bis(2-thienyl) ditelluride (1.76 g, 4.2 mmol) was added in six equal portions to a solution of α-bromoacetanilide (3.0 g, 14.0 mmol) in ethanol (150 mL) kept under N_2. After each addition of ditelluride, $NaBH_4$ (5% in 5% aqueous NaOH) was added dropwise until the red of the ditelluride disappeared. After the sixth addition of $NaBH_4$ the yellowish solution was poured into water/ethyl ether and the organic phase washed several times with water. Drying ($CaCl_2$) and evaporation yielded a semisolid, which was submitted to chromatographic purification (silica, CH_2Cl_2). α-(2-Thienyltelluro)acetanilide, 1.84 g (64%), was obtained as a faint yellow oil that solidified upon standing: mp 87–88 °C (EtOH); NMR ($CDCl_3$, Me_4Si) δ 3.51 (s, 2 H), 6.93–6.97 (m, 1 H), 7.04–7.10 (m, 1 H), 7.22–7.55 (several peaks, 7 H); MS, *m/e* (rel intensity) 347 (7), 254 (4), 213 (19), 93 (100), 84 (45). Anal. Calcd for $C_{12}H_{11}NOSTe$: C, 41.79; H, 3.21. Found: C, 41.85; H, 3.29.

Chalcone (11). A solution of lithium 2-thiophenetellurolate was prepared exactly as described in procedure A. A solution of phenacyl bromide (1.15 g, 5.8 mmol) and benzaldehyde (0.62 g, 5.8 mmol) in dry THF (4 mL) was added dropwise during 5 min, producing a deep red solution. After 30 min the THF was evaporated and the residue dissolved in water/ethyl ether. The organic phase was separated, dried ($CaCl_2$), and evaporated to give a semisolid. Chromatography (silica, 1:1 $CHCl_3$/hexane) afforded 2.37 g of bis(2-thienyl) ditelluride and 0.57 g (48%) of chalcone, mp 56–57 °C (lit. mp 57–58 °C).[42]

2-Hydroxy-2-phenylpropionanilide (12). A solution of α-(2-thienyltelluro)acetanilide (0.35 g, 1.02 mmol) and benzaldehyde (0.11 g, 1.09 mmol) in dry THF (3 mL) was added dropwise during 5 min to a solution of lithium 2-thienyltellurolate [prepared according to procedure A from thiophene (0.25 g, 3.0 mmol), butyllithium (1.5 mL, 1.6 M, 2.4 mmol), and elemental tellurium (0.30 g, 2.35 mmol) in dry THF (10 mL)]. The deep red solution was stirred for 30 min when the THF was evaporated and the residue dissolved in water/ethyl ether. The organic phase was dried ($CaCl_2$) and evaporated to give a solid as a mixture of the title compound **12** and acetanilide. Chromatographic separation (silica, CH_2Cl_2 + 5% MeOH) afforded 0.060 g of pure 2-hydroxy-2-phenylpropionanilide, mp 159–160 °C (lit. mp 160 °C)[43]

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and 0.72 g of a mixture of the two compounds, the relative amounts being determined by NMR. The total yield of compound **10** was 0.147 g (60%) and of acetanilide 0.033 g (24%).

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Registry No. 1, 82093-37-6; 2, 66697-24-3; 3, 7475-56-1; 4, 82093-38-7; 5, 16222-10-9; 7, 5326-87-4; 8, 82093-39-8; 11, 94-41-7; 12, 4198-15-6; $NaBH_4$, 16940-66-2; 4-bromophenacyl bromide, 99-73-0; 2-bromocholestan-3-one, 22164-15-4; α-bromophenylacetic acid, 4870-65-9; sodium 2-thiophenetellurolate, 82093-40-1; thiophene, 110-02-1; butyllithium, 109-72-8; tellurium, 13494-80-9; phenacyl chloride, 532-27-4; phenacyl bromide, 70-11-1; phenacyl iodide, 4636-16-2; phenacyl acetate, 2243-35-8; phenacyl mesylate, 20187-61-5; desyl chloride, 447-31-4; α-bromo-1-naphthylacetic acid, 72191-56-1; acetophenone, 98-86-2; p-bromoacetophenone, 99-90-1; desoxybenzoin, 451-40-1; cholestan-3-one, 15600-08-5; 3-methyl-1-indanone, 6072-57-7; acetanilide, 103-84-4; phenylacetic acid, 103-82-2; 1-naphthylacetic acid, 86-87-3; diphenylacetic acid, 117-34-0; benzaldehyde, 100-52-7.

Arenes Disubstituted with Primary Alkyl Groups from Xylylene Dianions

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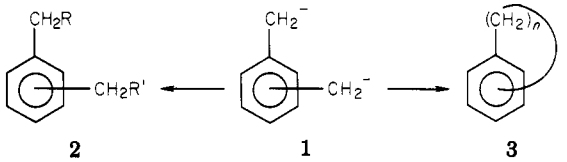
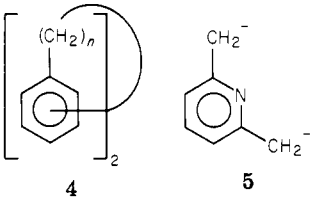
Xylenes were converted into dianions **1**. Reaction of dianions **1** with dialkyl sulfates gave symmetrical dialkylbenzenes **2** (R = R′), while methyl iodide caused oxidative coupling followed by alkylation to give **8**. Unsymmetrical dialkylbenzenes **2** (R ≠ R′) were made by an indirect route involving monoanions **9** and **11**. Reactions of dianions **1** with dihalides gave [*n*]cyclophanes *o*-**3** (*n* = 5, 6, 9), *m*-**3** (*n* = 8–10), and *p*-**3** (*n* = 9–11) and [*n.n*]cyclophanes *o*-**4** (*n* = 2, 5, 7, 9) and *m*-**4** (*n* = 2, 6, 7). Dianion **5** from 2,6-lutidine was used to prepare nitrogen analogues of **2** (R = R′) and *m*-**3** (*n* = 8–10).

Benzenes **2–4**, disubstituted with primary alkyl groups, are quite difficult to prepare due to limitations in the Friedel–Crafts alkylation with primary halides.[1] We report simple preparations of many such compounds in two steps from the corresponding xylene via the readily prepared[2] dianions **1**. Some analogous reactions of new pyridine-containing dianion **5** are also presented.

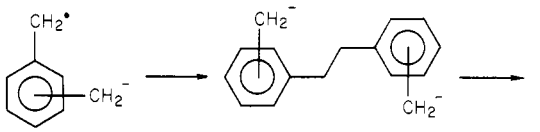


2 **1** **3**

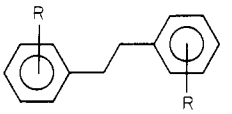


4 **5**

Symmetrical Dialkylation Products 2 (R = R′). Reaction of the disodium salt of *m*-**1** with excess methyl iodide was reported to give *m*-diethylbenzene (*m*-**2**, R = R′ = Me) as the major product by GC and NMR analyses.[2a] With the more ionic dipotassium salt of *p*-**1** and excess methyl iodide, we obtained almost none of the desired *p*-diethylbenzene (*p*-**2**, R = R′ = Me) but instead a 72% yield (based on *p*-xylene, thus nearly quantitative based on dianion *p*-**1**[3]) of *p*-**8** (R = Et), presumably formed by a one-electron oxidation (to *p*-**6**)–dimerization (to *p*-**7**)–dialkylation sequence.[4] *o*-Xylene and *m*-xylene gave



6 **7**



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the analogous dimeric products *o*-**8** (R = Et, 53%) and *m*-**8** (R = Et, 41%), along with the corresponding diethylbenzenes *o*-**2** (R = R′ = Me, 42%) and *m*-**2** (R = R′ = Me, 55%). Such electron transfers to methyl iodide have been previously observed with carbanions which are sufficiently good reducing agents;[5] apparently *p*-**1**, with the lowest calculated resonance energy of the three isomeric dianions,[2b–d] is also the best reducing agent.[6]

Dimeric products **8** were avoided by using dialkyl sulfates as the alkylating agents. With dimethyl sulfate, *p*-xylene was converted into *p*-diethylbenzene (*p*-**2**, R = R′ = Me) in 63% yield and with diethyl sulfate into *p*-di-*n*-propylbenzene (*p*-**2**, R = R′ = Et) in 65% yield.

(1) Price, C. *Org. React.* **1946**, *3*, 1.
(2) (a) Trimitsis, G. B.; Tuncay, A.; Beyer, R. D.; Ketterman, K. J. *J. Org. Chem.* **1973**, *38*, 1491. (b) Klein, J.; Medlik, A.; Meyer, A. Y. *Tetrahedron* **1976**, *32*, 51. (c) Klein, J.; Medlik-Balan, A. *J. Am. Chem. Soc.* **1977**, *99*, 1473. (d) Bates, R. B.; Hess, B. A., Jr.; Ogle, C. A.; Schaad, L. *Ibid.* **1981**, *103*, 5052.
(3) While *o*-**1** and *m*-**1** are produced essentially quantitatively from the corresponding xylenes, the *p*-**1** used in this work was formed in about 70% yield from *p*-xylene.[2d]
(4) An alternate route to *p*-**7** involving addition of dianion *p*-**1** to *p*-xylene is rendered less likely by the finding that *m*-xylene, whose intermediate *m*-xylylene is *much* less stable (Pollack, S.; Raine, B.; Hemre, W. *J. Am. Chem. Soc.* **1981**, *103*, 6308) and would presumably give other products, goes to *m*-**8** in only slightly diminished yield.
(5) Bahl, J.; et al. *J. Am. Chem. Soc.* **1977**, *99*, 6126.
(6) Bordwell, F.; Clemens, A. *J. Org. Chem.* **1981**, *46*, 1035.

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