mined. They are broadly similar, and that may be taken as an indication that the rates of protonation of anions **4b** and **4c** (Scheme II) are relatively high as compared to the rates of halide ion loss to form aryne **6**.

## Experimental Section

**Materials.** *p*-Methoxybenzophenone and *o*-benzoylbenzoic acid were commercial products whose identity was verified by melting point determination. 2-Chloro-4-methylbenzophenone was a sample prepared by Hrutfiord.[3] *p*-Fluorobenzophenone, mp 49.1–50.0 °C (lit.[13] mp 47–49 °C), was synthesized after McCarty et al. *o*-Methoxybenzophenone, mp 35.5–36.5 °C (lit.[14] mp 39 °C), was synthesized analogously by addition of *o*-methoxyphenylmagnesium bromide to benzonitrile and ensuing hydrolysis, in 50% yield. *o*-Bromobenzophenone, mp 29.2–29.6 °C, was synthesized in 78% yield by $AlCl_3$-catalyzed reaction of *o*-bromobenzoyl chloride with benzene.

*m*-Fluorobenzophenone was obtained in 70% yield by reaction of *m*-fluorobenzoyl chloride with a 2-mol proportion of $AlCl_3$ in excess benzene at reflux. The crude product was distilled at reduced pressure [bp 125–135 °C (12 mm)] and recrystallized from petroleum ether of bp 30–40 °C; mp 52.2–52.6 °C (lit.[15] mp 53 °C).

Anal. Calcd for $C_{13}H_9FO$: C, 77.99; H, 4.53. Found: C, 77.65; H, 4.45.

2-Bromo-4-methylbenzophenone was synthesized after DeTar and Relyea.[16] 2-Bromo-4-methylbenzoic acid, mp 150 °C, made by their method, was converted to its acid chloride by means of thionyl chloride, and the latter was combined with about a 1.8 molar proportion of $AlCl_3$ and heated at reflux in excess benzene for 3 h. The resulting 2-bromo-4-methylbenzophenone was crystallized from 95% ethanol; mp 41–42 °C.

**Reactions of Benzophenone Derivatives with Potassium Amide.** Reactions were conducted as previously described.[3] Four moles of $KNH_2$ were used per mole of ketone, and mixtures were in general held at reflux for 3 h before being quenched by addition of ammonium nitrate. However, when there was evidence of vigorous reaction in the form of strong boiling of the ammonia and strong color changes (as in all the cases in which cleavage occurred), the time of exposure was shorter, from 1 to 2 h. In some cases dry diethyl ether was present as a cosolvent, and in some such cases there were two liquid phases present. In several cases the starting benzophenone derivative was recovered from the reaction mixture and identified by melting point and mixture melting point in amounts as follows: *m*-fluorobenzophenone, 75%; *p*-fluorobenzophenone, 77%; *o*-methoxybenzophenone, 87%; *p*-methoxybenzophenone, 90%; *o*-benzoylbenzoic acid, 91%. From the cleavage of *o*-bromobenzophenone, benzoic acid (12%) and benzamide (62%) were identified by melting point and mixture melting point and aniline by comparison of its IR spectrum with that of an authentic sample.

The products of cleavage of 2-chloro- and 2-bromo-4-methylbenzophenone were separated into acidic, basic, and neutral fractions by extraction procedures. The acidic component was identified as benzoic acid by its melting point and mixture melting point. The neutral component was identified as benzamide by its melting point and mixture melting point. The basic fraction was an oil which was purified by distillation; bp 197 °C. Its infrared spectrum closely resembled that for a mixture of toluidine isomers.

**Analysis of Toluidine Product Mixtures.** One gram of each toluidine mixture was dissolved in 5% aqueous HCl. Dilute (5%) aqueous NaOH was added until the solution became permanently cloudy. Several drops of dilute HCl were then added until the cloudiness just disappeared, chips of ice were added, and then 5 mL of acetic anhydride was added. The solution was shaken vigorously, 5 g of sodium acetate in 25 mL of water was added, and agitation of the solution was continued for several minutes. The brownish precipitate which settled out upon chilling of the mixture was collected, air-dried, and placed on the alumina column to which solvent systems were applied. Elution with a mixture of 3:1 diethyl ether–chloroform removed aceto-*m*-toluidide. Elution with a mixture of equal parts of ether and chloroform then removed aceto-*p*-toluidide. Finally, the ortho isomer was removed by a mixture of 1:3 ether–chloroform. After evaporation of the solvent from each fraction collected, the fraction was weighed, its melting point and IR spectrum determined, and a mixture melting point determined with an authentic sample of the indicated acetotoluidide. Separation of the isomers was remarkably clean except that the first sample of the ortho isomer melted a little low in each case, specifically, 100 °C (from the chloro ketone) and 103.5 °C (from the bromo ketone) vs. 110 °C for pure aceto-*o*-toluidide; that means that the yields of ortho isomers are slightly overestimated at the expense of the para isomer.

**Registry No.** Aniline, 62-53-3; $KNH_2$, 17242-52-3; *o*-methoxyphenyl bromide, 578-57-4; benzonitrile, 100-47-0; *o*-bromobenzoyl chloride, 1711-09-7; benzene, 71-43-2; *m*-fluorobenzoyl chloride, 1711-07-5; 2-bromo-4-methylbenzoic acid, 7697-27-0; 2-bromo-4-methylbenzoyl chloride, 53456-09-0; *m*-fluorobenzophenone, 345-69-7; *p*-fluorobenzophenone, 345-83-5; *o*-methoxybenzophenone, 2553-04-0; *p*-methoxybenzophenone, 611-94-9; *o*-benzoylbenzoic acid, 85-52-9; *o*-bromobenzophenone, 13047-06-8; benzoic acid, 65-85-0; benzamide, 55-21-0; 2-chloro-4-methylbenzophenone, 71549-60-5; 2-bromo-4-methylbenzophenone, 69617-43-2; aceto-*m*-toluidide, 537-92-8; aceto-*p*-toluidide, 103-89-9; aceto-*o*-toluidide, 120-66-1.

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# Synthesis of 2-[2-Aryl-2-(*p*-toluenesulfonyl)ethyl]-1,3-dioxolanes

Cornelus G. M. Janssen, Pieter M. van Lier, Henk M. Buck, and Erik F. Godefroi*

*Department of Organic Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands*

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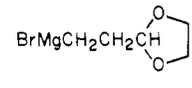
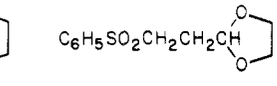
Umpolung of the intrinsic polarity of $\alpha,\beta$-unsaturated aldehydes is presently achieved by two means. Acrolein, for example, is converted in one step into 2-(2-bromoethyl)-1,3-dioxolane which is then transformed into the Grignard derivative **1**. The terminal carbon atom hereby




**1**




**2**

undergoes a changeover from an electrophilic to a nucleophilic center. The reagent has been used by Büchi in his synthesis of (±)-nuciferal[1] and by us as a synthon for constructing benzo[*b*]thiophenes,[2] benzimidazoles,[3] naphthalenes,[4] and 5-substituted butyrolactones.[5] A second approach makes use, in one way or another, of sulfur-stabilized carbanions,[6] the sulfur being brought on either the C-1 or the C-3 of the $\alpha,\beta$-unsaturated aldehyde. Sulfones are especially practical in this strategy. This is illustrated by the three-step conversion of acrolein to 2-[(2-phenylsulfonyl)ethyl]-1,3-dioxolane (**2**) ($C_6H_5SH$ addition, acetalization, and sulfur oxidation), whose corresponding anion was then both alkylated[7] and acylated.[8] The phenylsulfonyl group, having served its purpose, may later be removed by reduction or via $\beta$-elimination.[9]

Our continued interest in three-carbon homologation units plus specific research requirements for large amounts of varied 3-aryl-3-(arylsulfonyl)propionaldehydes made us look for practical means of preparing 2-[2-aryl-2-(*p*-toluenesulfonyl)ethyl]-1,3-dioxolanes **3a–d**. The present

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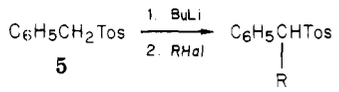
Ar = a, $C_6H_5$; b, $o$-$O_2NC_6H_4$; c, 2-furyl; d, 2-thienyl; Tos = $p$-toluenesulfonyl

report describes extremely simple entries into these systems as well as a one-step open-vessel procedure for converting acrolein directly into 2-[2-($p$-toluenesulfonyl)ethyl]-1,3-dioxolane (**4**).

Initial tryouts were performed on unsubstituted phenyl systems. Treatment of benzyl chloride with sodium $p$-toluenesulfinate (NaTos) in DMF gave **5**; this was anionized (BuLi) and then alkylated with either benzyl chloride or propargyl bromide in THF to provide **6a** and **6b**. The



5

**6a**, R = $CH_2C_6H_5$
**b**, R = $CH_2C{\equiv}CH$

anion in question, however, failed to react with bromoacetal under these conditions. This contrasts with results of Julia who did alkylate related sulfones with bromoacetal albeit in the presence of hexamethylphosphoramide (HMPA).[10] Suspected health risks associated with HMPA exposure[11] made us opt for other routes.

Aldehydes corresponding to **3a–d** formally represent 1,4-addition products of TosH to 3-arylpropenals; $\alpha,\beta$-unsaturated aldehydes, however, most frequently undergo 1,2- rather than 1,4-addition. Examination of the literature revealed only one instance of an aromatic sulfinic acid being added to cinnamaldehyde. Kohler and Reimer[12] in 1904 had described the reaction of cinnamaldehyde with TosH as giving a 1,4-addition product ("mp 78 °C, soluble in alcohol, ether and benzene, insoluble in water and ligroin") and a diaddition product ("mp at about 126 °C, soluble in benzene, alcohol and water" and "analyses gave no concordant results"). Their data tend to be vague and ambiguous. In our hands the action of equivalent amounts of TosH on cinnamaldehyde at room temperature caused instantaneous precipitation (43%) of a diadduct, mp 128–129 °C, insoluble in hot water or benzene. Analytical and spectral data (see Experimental Section) agreed with **7a**. With 2 equiv of TosH, cinnamaldehyde gave **7a** in 91% yield.

The diadduct was converted to aldehyde 8 in a variety of ways. These included aqueous $NaHCO_3$, $Et_3N$ in DMF, and, most advantageously, $Et_3N$ in water–ether. Physical data derived from 8 (mp 122–123 °C, soluble in benzene) are at variance with the literature,[12] but analytical and spectral data (see Experimental Section) leave no doubt as to the structure being correct. The aldehyde with

**Table I. Preparation and Physical Properties of Compounds 7b–d and 3b–d**

| compd | exptl conds[a] | yield, %[b] | mp, °C (recrystn solvent)[c] | $^1$H NMR, $\delta$ |
|---|---|---|---|---|
| **7b** | a | 86 | 109–111 (THF–petroleum ether) | 2.22–2.68 (m, 2, $CH_2$), 2.41 (2 s, 6, 2 TosC$H_3$), 3.29–3.58 (m, 1, OH), 3.58–4.82 (m, 2, CHTos and OCHTos), 6.95–8.02 (m, 7, ArH) |
| **7c** | a | 61 | 98–101 (acetonitrile–isopropyl ether) | 2.22–2.82 (m, 2, $CH_2$), 2.40 (2 s, 2 TosC$H_3$), 3.30–3.52 (m, 1, OH), 3.92–4.74 (m, 2, CHTos and OCHTos), 6.06–7.67 (m, 7, ArH) |
| **7d** | a | 43 | 107–109 (acetonitrile–isopropyl ether) | 2.26–2.64 (m, 2, $CH_2$), 2.41 (2 s, 6, 2 TosC$H_3$), 3.01–3.45 (m, 1, OH), 3.87–5.27 (m, 2, CHTos and OCHTos), 6.06–7.67 (m, 11, ArH) |
| **3b** | b | 77 | 111–112 (benzene–isopropyl ether) | 2.38 (s, 3, TosC$H_3$), 2.46–2.75 (m, 2, $CH_2$), 3.41–4.00 (m, 4, $(OCH_2)_2$), 4.76 (t, 1, $CH(OC)_2$), 5.37–5.67 (m, 1, CHTos), 7.00–7.98 (m, 8, ArH) |
| | c | 60 | | |
| **3c** | b | 77 | 126–127 (benzene–petroleum ether) | 2.29–2.62 (m, 2, $CH_2$), 2.39 (s, 3, TosC$H_3$), 3.64–3.95 (m, 4, $(OCH_2)_2$), 4.28–4.91 (m, 2, CHTos and $CH(OC)_2$), 6.08–7.34 (m, 7, ArH) |
| **3d** | b | 80 | 139–140 (benzene–isopropyl ether) | 2.14–2.73 (m, 2, $CH_2$), 2.34 (s, 3, TosC$H_3$), 3.48–4.06 (m, 4, $(OCH_2)_2$), 4.29–5.00 (m, 2, CHTos and $CH(OC)_2$), 6.54–7.74 (m, 7, ArH) |
| | c | 69 | | |

[a] (a) Reaction of appropriate 3-arylpropenals with 2 equiv of TosH at 18 h at room temperature as for **7a**; (b) identical with method A, given for **3a**; (c) method B, as described for **3a**. [b] Figures correspond to crude yields of material melting not less than 5 °C below the analytical melting point. [c] Satisfactory C, H analyses (±0.30%) were reported.

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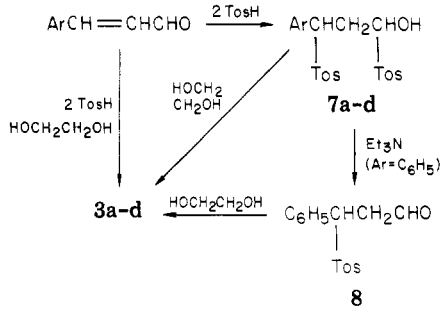



8

ethylene glycol in refluxing benzene gave acetal **3a**; this was also obtained directly from **7a** in excess boiling ethylene glycol in an unexpectedly fast reaction (method A).

The effect of aryl variation on TosH addition to 3-arylpropenals was then briefly examined. This involved the *o*-nitrophenyl, the 2-furyl, and the 2-thienyl analogues and gave, after 18 h at ambient temperatures, **7b–d** in 86, 58, and 43% yields. Extending the contact times did, in the one case studied, improve the yield: 3-(2-furyl)propenal with 2 equiv of TosH for 42, 66, and 168 h gave 67, 73, and 76% yields, respectively, of **7c**. Like **7a**, **7b–d** reacted extremely rapidly with ethylene glycol to furnish **3b–d** in good yields.

The experience gained earlier[2-5] in the concomitant HBr addition and acetalization of acrolein plus the ease of converting **7a–d** into acetals **3a–d** prompted efforts to convert the 3-arylpropenals directly into the desired dioxolanes. Cinnamaldehyde was therefore treated with 2 equiv of TosH in ethylene glycol at 125 °C to furnish, after 3 min, **3a** in 90% yield (method B). The *o*-nitrophenyl- and 2-thienylpropenals reacted likewise to give **3b,d**; the 2-furyl analogue, on the other hand, produced intractable tars. Reaction conditions appear to be critical and differ from case to case. In the thienyl series, for example, a contact time of 10 min at 125 °C or 5 min at 155 °C brought about total decomposition. The process most likely proceeds via the aforementioned ditosyl adducts, thus requiring participation of at least 2 equiv of TosH. This would certainly be substantiated by the observation that the use of but 1 equiv of TosH lowered the yield of **3d** to 25%. Specific data related to the mode of preparation of **7b–d** and **3b–d** and their physical properties are presented in Table I.

Having acquired the above experimental know-how, we attempted the reaction of acrolein with an excess of TosH in ethylene glycol. The reaction proceeded at room temperature, was moderately exothermic, and produced compound 4 in 67% yield; this one-pot process offers a slight simplification of the recently reported preparation of **4**.[13]

## Experimental Section

**General Methods.** The authors thank Messrs. P. van den Bosch and H. Eding for microanalytical data. Nuclear resonance spectra (NMR) were recorded on a Varian EM 360A spectrometer. Melting points were determined on a Fisher-Johns block and are uncorrected. 3-Phenyl-, 3-(*o*-nitrophenyl)-, and 3-(2-furyl)propenal were obtained from Aldrich Europe. 3-(2-Thienyl)propenal was prepared from diethyl 2-(cyclohexylamino)vinylphosphonate[14] and thiophene-2-carboxaldehyde in 80% yield, paralleling directions for synthesizing cyclohexylideneacetaldehyde.[15]

**Phenyl-(*p*-toluenesulfonyl)methane (5).** To a stirred mixture of 142 g (0.800 mol) of NaTos in 170 mL of DMF was added 101 g (0.800 mol) of benzyl chloride. The temperature was adjusted to 110 °C, initiating an exothermic reaction which made the temperature climb to 140 °C. After an additional hour of stirring at ambient temperature the suspension was poured onto 800 mL of water. Product was collected by filtration and was then washed successively with water, cold ethyl alcohol, and ether to give 162 g (82%) of air-dried **5**: mp 145–146 °C (lit. mp 148–149 °C).[16]

**1,2-Diphenyl-1-(*p*-toluenesulfonyl)ethane (6a).** To 12.3 g (0.0500 mol) of **5** in 120 mL of dry THF was added, at −65 °C, 42 mL (0.0600 mol) of commercial 15% BuLi in hexane. After the mixture was stirred for 15 min, 7.48 g (0.0600 mol) of benzyl chloride was introduced at −65 °C. After 0.5 h the mixture was allowed to come to room temperature, and stirring was continued overnight. Addition of 500 mL of water and 100 mL of ether, filtration, and washing of the product with water furnished 11.3 g (67%) of air-dried material, mp 176–178 °C. Analytical material was prepared from toluene: mp 181–182 °C; NMR ($CDCl_3$) $\delta$ 2.32 (s, 3, $TosCH_3$), 3.03–4.36 (m, 3, $CH-CH_2$), 6.71–7.36 (m, 14, ArH).

Anal. Calcd for $C_{21}H_{20}O_2S$: C, 74.76; H, 5.99. Found: C, 75.23; H, 6.12.

**4-Phenyl-4-(*p*-toluenesulfonyl)but-1-yne (6b).** The anion of **5** was prepared as above from 1.23 g (0.005 mol) of **5** in 12 mL of dry THF and 4.2 mL (0.006 mol) of 15% commercial BuLi in hexane. Addition at −65 °C of 0.71 g (0.006 mol) of propargyl bromide and stirring for 0.5 h at −65 °C and then at room temperature for 18 h gave, on pouring into water, solid product. It was collected by filtration, was washed successively with water, ethyl alcohol, and ether, and was then air-dried [yield 0.85 g (60%)]. Recrystallization from isopropyl alcohol gave analytically pure product: mp 182–183 °C; NMR ($CDCl_3$) $\delta$ 1.72–1.90 (m, 1, CCH), 2.33 (s, 3, $TosCH_3$), 2.87–3.30 (m, 2, $CH_2$), 4.03–4.40 (m, 1, CHTos), 6.88–7.57 (m, 9, ArH).

Anal. Calcd for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67. Found: C, 71.77; H, 5.65.

**3-Phenyl-1,3-bis(toluenesulfonyl)propan-1-ol (7a).** To a stirred mixture of 13.2 g (0.100 mol) of 3-phenylpropenal in 200 mL of ether and 35.8 g (0.200 mol) of TosNa in 200 mL of water was added dropwise 200 mL of 1 N hydrochloric acid. A white precipitate formed immediately. Stirring was continued for 18 h; the solids were then filtered off and washed with water, ethyl alcohol, and ether to give, after air-drying, 40.5 g (91%) of product melting at 125–128 °C. Analytical material was obtained by recrystallization from THF–hexane: mp 128–129 °C; NMR ($Me_2SO$-$d_6$) $\delta$ 2.19–2.57 (m, 2, $CH_2$), 2.57 (2 s, 6, $TosCH_3$), 3.18–3.41 (m, 1, OH), 3.65–4.65 (m, 2, CHTos and OCHTos), 6.82–7.70 (m, 13, ArH).

Anal. Calcd for $C_{23}H_{24}O_5S_2$: C, 62.14; H, 5.44. Found: C, 62.39; H, 5.70.

**3-Phenyl-3-(*p*-toluenesulfonyl)propanal (8).** To a well-stirred suspension of 22 g (0.0500 mol) of **7a** in 150 mL of water and 100 mL of ether was added 5.05 g (0.0500 mol) of triethylamine. After 18 h of stirring, the solids were filtered off and were rinsed with water and ether. The dried material, 12 g (83%), melted at 122–123 °C. Analytical material was obtained on recrystallization from toluene–hexane: mp 122–123 °C; NMR ($CDCl_3$) $\delta$ 2.34 (s, 3, $TosCH_3$), 2.88–3.79 (m, 2, $CH_2$), 4.49–4.81 (m, 1, CHTos), 6.88–7.56 (m, 9, ArH), 9.58 (t, 1, CHO).

Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59. Found: C, 66.50; H, 5.49.

**2-[2-Phenyl-2-(*p*-toluenesulfonyl)ethyl]-1,3-dioxolane (3a). Method A. From 7a and Ethylene Glycol.** In a beaker containing 7 mL of boiling ethylene glycol was added 4.44 g (0.01 mol) of **7a**, immediately followed by 15 mL of ice-cold 2-propanol. The mixture was cooled on ice, and product was collected by filtration; it was rinsed with fresh isopropyl alcohol and then with diisopropyl ether to provide 2.5 g (75%) of dry product melting at 158–159 °C. Recrystallization from benzene gave analytical material: mp 158–159 °C; NMR ($CDCl_3$) $\delta$ 2.28–2.70 (m, 2, $CH_2$), 2.40 (s, 3, $TosCH_3$), 3.55–3.92 (m, 4, $(OCH_2)_2$), 4.08–4.85 (m, 2, CHTos and $CH(OC)_2$), 6.87–7.35 (m, 9, ArH).

Anal. Calcd for $C_{18}H_{20}O_4S$: C, 65.03; H, 6.06. Found: C, 65.15; H, 6.10.

**Method B. From 3-Phenylpropenal, TosH, and Ethylene Glycol.** To a solution of 3.12 g (0.02 mol) of dry TosH (prepared

(13) G. R. Cooper, and L. J. Dolby, *Tetrahedron Lett.*, 4675 (1976).
(14) W. Nagata, T. Wakabayashi, and Y. Hayase, *Org. Synth.*, **53**, 44–8 (1973).
(15) W. Nagata, T. Wakabayashi, and Y. Hayase, *Org. Synth.*, **53**, 104–7 (1973).
(16) E. A. Lehto and D. A. Shirley, *J. Org. Chem.*, **22**, 989 (1957).

freshly from the sodium salt) in 3 mL of ethylene glycol, preheated to 125 °C, was added 1.32 g (0.01 mol) of cinnamaldehyde. After 3 min more at 125 °C, 3 mL of isopropyl alcohol was added. Cooling, filtration and rinsing with isopropyl alcohol and isopropyl ether gave 2.9 g (90%) of material, mp 158–159 °C, identical with the product obtained via method A.

**2-[2-*p*-(Toluenesulfonyl)ethyl]-1,3-dioxolane (4).**[13] Freshly distilled acrolein, 5.6 g (0.10 mol), was added with stirring to 34 g (0.20 mol) of TosH in 30 mL of ethylene glycol. The temperature rose within 4 min to 68 °C. Stirring was continued for 18 h whereupon the viscous slurry was poured onto 100 mL of ice–water containing 10 mL of ammonium hydroxide solution. The solids were filtered off; rinsing with water, cold isopropyl alcohol, and ether gave 16.1 g (67%) of crystals melting at 79–80 °C. Recrystallization from isopropyl alcohol furnished the analytical sample: mp 80–80.5 °C; NMR ($CDCl_3$) $\delta$ 1.80–2.29 (m, 2, $TosCCH_2$), 2.44 (s, 3, $TosCH_3$), 2.98–3.41 (m, 2, $CH_2Tos$), 3.57–4.07 (m, 4, $(OCH_2)_2$), 4.87 (t, 1, $CHO_2$), 7.10–7.69 (m, 4, ArH).

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.34; H, 6.33.

**Registry No. 3a**, 71370-80-4; **3b**, 71370-81-5; **3c**, 71370-82-6; **3d**, 71370-83-7; **4**, 63305-66-8; **5**, 5395-20-0; **6a**, 14902-09-1; **6b**, 71370-84-8; **7a**, 71370-85-9; **7b**, 71370-86-0; **7c**, 71370-87-1; **7d**, 71370-88-2; **8**, 71370-89-3; NaTos, 824-79-3; benzyl chloride, 100-44-7; propargyl bromide, 106-96-7; ethylene glycol, 107-21-1; TosH, 536-57-2; 3-phenylpropenal, 104-55-2; 3-(*o*-nitrophenyl)propenal, 1466-88-2; 3-(2-furyl)propenal, 623-30-3; 3-(2-thienyl)propenal, 14756-03-7; diethyl 2-(cyclohexylamino)vinylphosphonate, 20061-84-1; thiophene-2-ca-

**Supplementary Material Available:** Analytical data for compounds **3b–d** and **7b–d** (1 page). Ordering information is given on any current masthead page.

# *Communications*

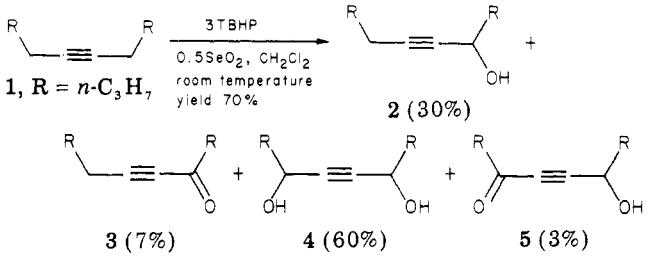
## Oxidation of Acetylenes with *tert*-Butyl Hydroperoxide Catalyzed by Selenium Dioxide. $\alpha,\alpha'$-Dioxygenation of Internal Alkynes

*Summary:* Unlike olefins, acetylenes show a strong tendency to undergo $\alpha,\alpha'$-dioxygenation upon reaction with $SeO_2$. The oxidation of ten different acetylenes allowed assignment of the reactivity sequence: $CH_2 \simeq CH > CH_3$. Alkynes bearing one methylene and one methine substituent afforded the enynone as the major product.

*Sir:* We have reported that *tert*-butyl hydroperoxide (TBHP), in the presence of $SeO_2$ as a catalyst, is a very effective system for the allylic oxidation of olefins.[1] A single acetylene (1-decyne) was examined in that earlier study[1] and it was noted that, like the olefins, it was readily $\alpha$-oxygenated.[2] More recently we had need for 5-decyn-4-ol (**2**) and set out to prepare it by oxidation of 5-decyne (**1**) with the $SeO_2$/TBHP procedure.[1] We were surprised to find that this internal acetylene showed a pronounced tendency for oxygenation on both sides of the acetylenic group (see Scheme I). Thus, in addition to the expected monooxygenated products **2** and **3**, substantial amounts of the $\alpha,\alpha'$-dioxygenated products **4** and **5** were also found. This pattern of oxidation (i.e. $\alpha,\alpha'$-attack) is very rare[3] with olefins and never accounts for the major products. Table I reveals that $\alpha,\alpha'$-oxidation is a general phenomenon with internal acetylenes.

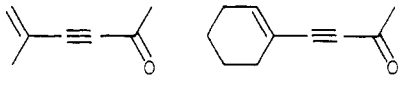
The results in Table I allow formulation of a set of selectivity rules for oxidation of unsymmetrical acetylenes analogous to the rules of Guillemonat.[4] The reactivity sequence for alkynes is $CH_2 \simeq CH > CH_3$.[5] Methine is

Scheme I




essentially identical in reactivity to methylene, but both are much more reactive than methyl.

In those cases (entries 4 and 5, Table I) where the acetylene bears one methylene and one methine substituent, the enynone (e.g. **6** and **7**) becomes an important product.



**6** **7**

Formation of the olefinic linkage in enynones **6** and **7** presumably results from dehydration at the diol and/or the ketol stage. Consistent with this speculation is the observation that the diol (isolated from case 5a, Table I) is transformed to enynone **7** when resubjected to the conditions of the reaction.

Diol **4** derived from 5-decyne was shown to be an approximately 1:1 mixture of the meso and *d,l* isomers.[6] By contrast, the diol derived from cyclododecyne appears to be a single isomer.[7] In considering this stereochemical point, it is worth pointing out an interesting difference between $SeO_2$ oxidations of olefins and acetylenes. In the case of olefins the allylic seleninic acid intermediate **8** can in principle give rise to allylic alcohol by a 2,3-shift to either

(1) Umbreit, M. A.; Sharpless, K. B. *J. Am. Chem. Soc.* **1977**, *99*, 5526. For a review on this and other metal-catalyzed oxidations with TBHP see Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, No. 4, in press.

(2) Reports of acetylene oxidations under the usual stoichiometric $SeO_2$ oxidation conditions are rare. Rabjohn's recent review cites only six examples (see Rabjohn, N. *Org. React.* **1976**, *24*, 261).

(3) We have encountered minor (almost trace), $\alpha,\alpha'$-dihydroxylation products of olefins in these $SeO_2$/TBHP systems (Umbreit, M. A. Ph.D. Dissertation, Massachusetts Institute of Technology, 1977).

(4) Guillemonat, A. *Ann. Chim. (Paris)* **1939**, *11*, 143.

(5) This contrasts with Guillemonat's rules for olefins which give the reactivity sequence as $CH_2 > CH_3 > CH$. However in the case of olefins the reactivity of methine groups varies so that examples are known where they are more reactive than methyl groups (see Büchi, G.; Wüest, H. *J. Org. Chem.* **1969**, *34*, 857).

(6) Diol **4** was converted (pyridine/$Ac_2O$) to the diacetate. The NMR spectrum of this compound was recorded in the presence of increasing amounts of the chiral shift reagent tris[3-heptafluoropropylhydroxymethylene-*d*-camphorato]europium(III). In the presence of 20% of the reagent, the singlet belonging to the acetate methyl at $\delta$ 2.00 becomes two doublets (at $\delta$ 3.46 and 3.55) of equal area. For a similar example see Gaudemer, A. In "Stereochemistry, Fundamentals and Methods"; Kagan, H. B., Ed.; Georg Thieme: Stuttgart, 1977; Vol. I, p 75.

(7) In the same type of experiment described in footnote 6 the NMR signal due to the methyl groups of the diacetate (mp 64–65 °C) split into two singlets in the presence of the chiral shift reagent.

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