Table I. Alumina and Silica Gel as Triphase Catalysts[a]

reagent	reactant	product	temp, °C	time, h	yield, %[b] alumina	yield, %[b] silica gel
NaI	1-bromooctane	1-iodooctane	90	24	95	24
				44	100 (98)[d]	
KI	1-bromooctane	1-iodooctane	90	44	95	
LiCl	1-bromooctane	1-chlorooctane	90	68	10	9
NaCl	1-bromooctane	1-chlorooctane	90	68	1	0
KCl	1-bromooctane	1-chlorooctane	90	68	15	0
KCl	1-iodooctane	1-chlorooctane	90	68	4	
NH_4Cl	1-bromooctane	1-chlorooctane	90	68	30	2
NaCN	1-bromooctane	1-cyanooctane	90	68	38[c]	6
KCN	1-bromooctane	1-cyanooctane	90	68	65[c]	6
KCN	1-iodooctane	1-cyanooctane	90	68	6	
NaOAc	1-bromooctane	octyl acetate	90	68	0	0
KOAc	1-bromooctane	octyl acetate	90	100	89	7
KOAc	1-iodooctane	octyl acetate	90	68	13	
$KMnO_4$	cyclododecanol	cyclododecanone	25	20	95	
			25	40	100[e] (95)[d]	
$KMnO_4$	2-octanol	2-octanone	25	20	100	

[a] Unless stated otherwise, reactions were carried out by stirring 0.5 g of alumina, 5.0 mmol of reagent, plus 1.0 mmol of reactant dissolved in 4 mL of toluene in a 50-mL culture tube using the indicated temperature and reaction time. Control experiments carried out for each reaction in the absence of alumina showed no loss of starting material. [b] Yields were determined by GLC using internal standards. Mass balance in all cases was >95%. [c] A small yield (~10%) of 1-octanol plus an unidentified side product were also formed. [d] Isolated yield from preparative-scale reaction using procedures described in the text. [e] Control experiments carried out without alumina showed 3% oxidation when the concentration of alcohol was 0.1 M after 48 h and 20% oxidation of 0.5 M cyclododecanol in toluene after 72 h.

Table II. Solid-Liquid Phase-Transfer Catalyzed Displacement[a]

reagent	reactant	product	time, h	yield, %[b]
KI	1-bromooctane	1-iodooctane	4	85
KOAc	1-bromooctane	octyl acetate	20	70
KCl	1-bromooctane	1-chlorooctane	47	3
KCN	1-bromooctane	1-cyanooctane	47	23
KOAc	1-iodooctane	octyl acetate	20	34

[a] Reactions were carried out by stirring 1.0 mmol of the reactant, 5.0 mmol of reagent, plus 0.1 mmol of 18-crown-6 in 5 mL of toluene in a 50-mL culture tube at 90 °C for the indicated reaction time. [b] Yields were determined by GLC using internal standards. Mass balance in all cases was >95%.

neutral alumina plus 7.9 g (50.0 mmol) of $KMnO_4$ were suspended in 50 mL of toluene containing 1.84 g (10.0 mmol) of cyclododecanol and the reaction mixture was stirred at room temperature for 30 h, analysis of the liquid phase by GLC indicated complete conversion to cyclododecanone. The ketone was isolated by filtering the product mixture through Celite, washing the spent and unused reagent plus alumina with 100 mL of toluene, and removing the solvent from the combined filtrate under reduced pressure yielding 1.75 g (95%) of cyclododecanone as a colorless solid which melted at 58–59 °C.[13] The IR and ^1H NMR spectra were identical with those of an authentic sample.

Although we have only begun to examine the full scope of this chemistry, preliminary results reveal unusual selectivity features. Specifically, 1-bromooctane exhibits significantly greater reactivity toward nucleophilic displacement by chloride, cyanide, and acetate ion as compared to 1-iodooctane (Table I). Thus stirring 1 mmol each of 1-bromooctane and 1-iodooctane dissolved in 7 mL of toluene with crushed potassium acetate (0.5 g, 5.0 mmol) plus 0.5 g of neutral alumina converted 60% of the organic bromide and 0% of the organic iodide to octyl acetate.[14]

The mechanistic details underlying these complex three-phase reactions are not presently understood and kinetic as well as stereochemical studies are now underway in an effort to elucidate the nature of the catalysis. Nonetheless, the low cost and ready availability of alumina, coupled with the experimental simplicity associated with its use, strongly suggest that it will be of considerable value as a triphase catalyst.

Registry No. Alumina, 1344-28-1; silica gel, 7631-86-9; 1-bromooctane, 111-83-1; 1-iodooctane, 629-27-6; 1-chlorooctane, 111-85-3; 1-cyanooctane, 2243-27-8; octyl acetate, 112-14-1; cyclododecanol, 1724-39-6; cyclododecanone, 830-13-7; 2-octanol, 123-96-6; 2-octanone, 111-13-7; KI, 7681-11-0; LiCl, 7447-41-8; NaCl, 7647-14-5; KCl, 7447-40-7; NH_4Cl, 12125-02-9; NaCN, 143-33-9; KCN, 151-50-8; NaOAc, 127-09-3; KOAc, 127-08-2; $KMnO_4$, 7722-64-7.

Silvio Quici, Steven L. Regen*
Department of Chemistry, Marquette University
Milwaukee, Wisconsin 53233
Received April 13, 1979

(13) An authentic sample from Aldrich Chemical Co. had mp 57–61 °C.

(14) Surprisingly, similar experiments carried out as solid–liquid phase-transfer reactions using 18-crown-6 gave identical results.

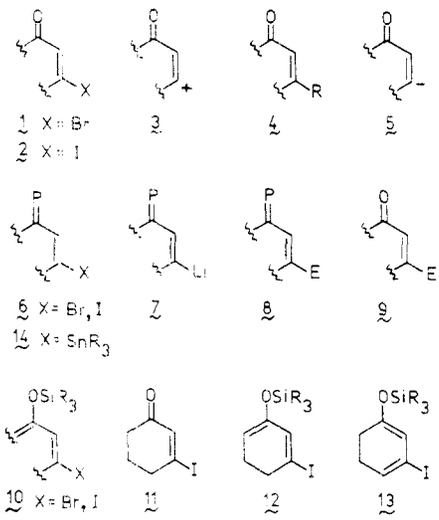
β-Acylvinyl Anion Equivalents: Preparation of 1-Lithio-3-(*tert*-butyldimethylsiloxy)-1,3-cyclohexadiene and Its Reaction with Electrophiles

Summary: 1-Lithio-3-(*tert*-butyldimethylsiloxy)-1,3-cyclohexadiene (**21**), conveniently prepared by transmetalation of the trialkylstannyl derivatives **18** and **20** with methyllithium and *n*-butyllithium, respectively, reacts smoothly with various electrophilic reagents to form, in excellent yields, the corresponding 1-substituted 3-(*tert*-butyldimethylsiloxy)-1,3-cyclohexadienes (**23**).

Sir: Previous work in our laboratory has demonstrated that β-bromo- (**1**) and β-iodo-α,β-unsaturated ketones (**2**)[1] serve as excellent synthetic equivalents of β-acylvinyl cations **3**.[2] For example, treatment of **1** and/or **2** with a

(1) E. Piers and I. Nagakura, *Synth. Commun.*, **5**, 193 (1975).

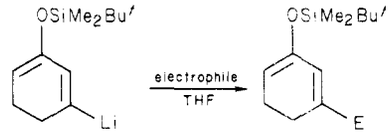
0022-3263/79/1944-3437$01.00/0



variety of cuprate reagents produces efficiently the corresponding β-substituted enones **4**, certain of which have proven to be very useful and versatile synthetic intermediates.[2,3] However, we have been intrigued also by the possibility that β-halo enones (**1**, **2**) might serve as suitable precursors of synthetic equivalents of β-acylvinyl anions **5**.[4] Presumably, putting this idea into practice would involve protection of the carbonyl group of **1** or **2**, followed by lithium–halogen exchange (e.g., alkyllithium) of the protected species **6** to produce **7** (the synthetic equivalent of **5**). Treatment of **7** with electrophilic reagents ("E^+") would afford, after removal of the protecting group from the initially formed products **8**, the β-substituted enones **9**. Clearly this (proposed) methodology, if successfully executed, would complement that involving treatment of **1** and/or **2** with nucleophilic reagents.

Although a variety of carbonyl protecting groups (cf. **6**–**8**) could be envisaged, we felt that an enol silyl ether functionality (cf. **10**) might be a good choice. This functional group, in addition to being amenable to introduction and removal under mild reaction conditions, is itself synthetically very versatile.[5] However, attempted conversion (LDA,[6] THF; R_3SiCl) of 3-iodo-2-cyclohexen-1-one (**11**)[1] into the corresponding enol silyl ethers **12**, under a variety of experimental conditions, failed to produce synthetically useful yields of the desired product. Spectral analysis of the materials isolated from the various attempts indicated that varying amounts of the isomer **13** were formed in addition to **12**. Furthermore, these compounds proved to be quite unstable.[7]

Table I. Reaction of 1-Lithio-3-(*tert*-butyldimethylsiloxy)-1,3-cyclohexadiene (21) with Electrophiles

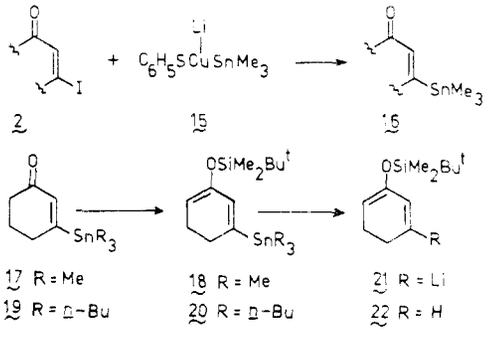


21 **23**

precursor of **21**	electrophile	product, E in **23** (% yield)[a]
20	CH_3I	CH_3- (86)
18	$CH_3(CH_2)_3Br$	$CH_3(CH_2)_3$- (72)
20	$R(CH_2)_2Br$[b]	$R(CH_2)_2$-[b] (72)
20	$Cl(CH_2)_4Br$	$X(CH_2)_4$-[c] (78)
18, 20	cyclohexanone	1-hydroxycyclohexyl (92, 91)
18, 20	cyclopentanone	1-hydroxycyclopentyl (88, 81)
20	2-cyclohexen-1-one	1-hydroxy-2-cyclohexenyl (84)
20	C_6H_5CHO	$C_6H_5CH(OH)$- (90)

[a] Yield of distilled, purified product. [b] R = 2-cyclopentenyl. [c] This product consisted of a mixture of the bromide (X = Br) and the chloride (X = Cl) in a ratio of 13:87, respectively.

The formation of vinyl anions by transmetalation of trialkylvinylstannanes is a well-known process.[8] Therefore, in view of the observations summarized above, the (projected) formation of β-acylvinyl anion equivalents **7** via transmetalation of the protected trialkylstannyl derivatives **14** became an attractive possibility. In this connection, we have recently shown[9] that β-iodo enones **2** can be transformed efficiently into the corresponding β-trimethylstannyl derivatives **16** by reaction of the former materials with lithium phenylthio(trimethylstannyl)cuprate (**15**).



Treatment of 3-(trimethylstannyl)-2-cyclohexen-1-one (**17**)[9] with LDA in THF (−78 °C, 1 h; 0 °C, 30 min), followed by addition of *tert*-butyldimethylsilyl chloride in HMPA (−78 °C to room temperature, 2 h), afforded (96%) the enol silyl ether **18**.[10] In similar fashion, the tri-*n*-butylstannyl derivative **19**[11] was converted into **20** (94%).

(2) E. Piers and I. Nagakura, *J. Org. Chem.*, **40**, 2694 (1975); E. Piers, C. K. Lau, and I. Nagakura, *Tetrahedron Lett.*, 3233 (1976); E. Piers and I. Nagakura, *ibid.*, 3237 (1976); E. Piers and C. K. Lau, *Synth. Commun.*, 495 (1977); E. Piers, I. Nagakura, and J. E. Shaw, *J. Org. Chem.*, **43**, 3431 (1978); E. Piers, I. Nagakura, and H. E. Morton, *ibid.*, **43**, 3630 (1978); E. Piers and E. Ruediger, *J. Chem. Soc., Chem. Commun.*, 166 (1979).

(3) For related, independently published studies, see J. P. Marino and L. J. Browne, *Tetrahedron Lett.*, 3241, 3245 (1976), and references cited therein; R. D. Clark and C. H. Heathcock, *J. Org. Chem.*, **41**, 636 (1976); P. A. Wender and M. P. Filosa, *ibid.*, **41**, 3490 (1976); P. A. Wender and S. L. Eck, *Tetrahedron Lett.*, 1245 (1977); P. A. Wender, M. A. Eissenstat, and M. P. Filosa, *J. Am. Chem. Soc.*, **101**, 2196 (1979).

(4) For recent reports related to β-acylvinyl anion equivalents, see K. Kondo and D. Tunemoto, *Tetrahedron Lett.*, 1007, 1397 (1975); K. Kondo, E. Saito, and D. Tunemoto, *ibid.*, 2275 (1975); K. Iwai, H. Kosugi, A. Miyazaki, and H. Uda, *Synth. Commun.*, **6**, 357 (1976); T. Cohen, D. A. Bennett, and A. J. Mura, Jr., *J. Org. Chem.*, **41**, 2506 (1976); A. Debal, T. Cuvigny, and M. Larchevêque, *Tetrahedron Lett.*, 3187 (1977); P. C. Conrad and P. L. Fuchs, *J. Am. Chem. Soc.*, **100**, 346 (1978); P. Bakuzis, M. L. F. Bakuzis, and T. F. Weingartner, *Tetrahedron Lett.*, 2371 (1978); J. C. Saddler, P. C. Conrad, and P. L. Fuchs, *ibid.*, 5079 (1978); D. Caine and A. S. Frobese, *ibid.*, 5167 (1978); W. R. Baker and R. M. Coates, *J. Org. Chem.*, **44**, 1022 (1979).

(5) T. Mukaiyama, *Angew Chem., Int. Ed. Engl.*, **16**, 817 (1977); E. W. Colvin, *Chem. Soc. Rev.*, **7**, 15 (1978).

(6) LDA = lithium diisopropylamide. Similar results were obtained when lithium 2,2,6,6-tetramethylpiperidide was employed as the base.

(7) The bromo compound corresponding to **12** (Br instead of I) also proved to be very unstable.

(8) For recent reports, and references cited therein, see: R. H. Wollenberg, *Tetrahedron Lett.*, 717 (1978); S. L. Chen, R. E. Schaub, and C. V. Grudzinskas, *J. Org. Chem.*, **43**, 3450 (1978); P. W. Collins, C. J. Jung, A. Gasiecki, and R. Pappo, *Tetrahedron Lett.*, 3187 (1978).

(9) E. Piers and H. E. Morton, *J. Chem. Soc., Chem. Commun.*, 1033 (1978).

(10) All new compounds which were sufficiently stable exhibited spectral data in full accord with assigned structures, and gave satisfactory elemental analysis and/or high-resolution mass spectrometric measurements.

Each of these reactions was very clean, producing a single enol silyl ether which could be purified by simple distillation. Furthermore, the products **18** and **20** were quite stable and, with reasonable precautions (e.g., exclusion of air), these compounds have been stored at <0 °C without change for fairly long periods of time (e.g., >2 months for **20**).

Transmetalation of compounds **18** and **20** was accomplished by treatment (THF, −78 °C, 1–1.5 h) of these substances with 1.1 equiv of methyllithium and *n*-butyllithium, respectively. Protonation (HOAc) of the resultant vinyllithium intermediate **21** afforded (84% from **18**, 87% from **20**) 2-(*tert*-butyldimethylsiloxy)-1,3-cyclohexadiene (**22**). More importantly, the intermediate **21** also reacted smoothly with a variety of other electrophilic reagents to produce the corresponding substituted 1,3-cyclohexadienes. Some of the results we have obtained are summarized in Table I.

In connection with the data tabulated in Table I, the following points should be noted. (a) Although the reaction of the lithio derivative **21** with carbonyl compounds proceeded to completion at −78 °C (~1 h), the alkylation reactions were carried out for 1 h at −78 °C and 1 h at room temperature. (b) In general, each of the products could be purified by means of a simple distillation. Of the two precursors (**18**, **20**) of the lithio intermediate **21**, the use of **18** was somewhat more convenient, since the relatively volatile tetramethyltin could be separated very easily from the various products **23**. (c) Hydrolysis (1 N hydrochloric acid in THF, room temperature) of the enol silyl ether functionality of the products **23** proceeded without incident, producing the corresponding β-substituted enones in good yield.

A typical experimental procedure follows. To a cold (−78 °C), stirred solution of **18** (100 mg) in 5 mL of dry THF, under an atmosphere of argon, was added dropwise a solution of methyllithium in ether (0.23 mL, 1.28 M), and the resultant yellow solution was stirred at −78 °C for 1 h. Cyclohexanone (34 mg) was added and the reaction mixture was stirred for an additional period of 1 h. After successive addition of saturated aqueous sodium bicarbonate (~0.2 mL) and ether (30 mL), the mixture was allowed to warm to room temperature. The crude product (isolated with ether) was distilled [air-bath temperature 127–135 °C (0.07 Torr)], affording 76 mg (92%) of compound **23** (E = 1-hydroxycyclohexyl): UV λ_{max} (MeOH) 268 nm (ϵ 5250); IR (film) 3420, 1653, 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 6 H), 0.88 (s, 9 H), 1.22 (s, 1 H, exchanged with D_2O), 1.48–1.64 (broad unresolved signal, 10 H), 2.08–2.14 (m, 4 H), 4.82 (m, 1 H, $W_{1/2}$ = 8 Hz), 5.74 (m, 1 H, $W_{1/2}$ = 4 Hz); exact mass calcd for $C_{18}H_{32}O_2Si$ 308.2171, found 308.2174.

Work in this area is continuing.

Acknowledgment. Financial support from the National Sciences and Engineering Research Council Canada (NSERC) and a NSERC postgraduate scholarship (to H.E.M.) are gratefully acknowledged.

Registry No. **17**, 69519-95-5; **18**, 71106-30-4; **19**, 71106-31-5; **20**, 71106-32-6; **21**, 71106-33-7; **22**, 71106-34-8; **23** (E = CH_3), 71106-35-9; **23** (E = $CH_3(CH_2)_3$), 71106-36-0; **23** (E = 2-cyclopentenyl-$(CH_2)_2$), 71106-37-1; **23** (E = $Br(CH_2)_4$), 71106-38-2; **23** (E = $Cl(CH_2)_4$), 71106-39-3; **23** (E = 1-hydroxycyclohexyl), 71129-42-5; **23** (E = 1-hydroxycyclopentyl), 71106-40-6; **23** (E = 1-hydroxy-2-cyclohexenyl), 71106-41-7; **23** (E = $C_6H_5CH(OH)$), 71106-42-8; CH_3I, 74-88-4; $CH_3(CH_2)_3Br$, 109-65-9; 2-cyclopentenyl$(CH_2)_2Br$, 21297-99-4; $Cl(CH_2)_4Br$, 6940-78-9; cyclohexanone, 108-94-1; cyclopentanone, 120-92-3; 2-cyclohexen-1-one, 930-68-7; C_6H_5CHO, 100-52-7.

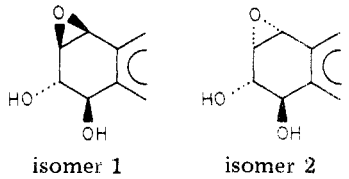
(11) Prepared by reaction of **11** with lithium phenylthio(tri-*n*-butylstannyl)cuprate (cf. ref 9).

Edward Piers,* Howard E. Morton
Department of Chemistry
University of British Columbia
Vancouver, British Columbia, Canada V6T 1W5
Received June 5, 1979

Benzo-Ring Diol Epoxides of Benzo[*e*]pyrene and Triphenylene

Summary: Synthesis and isolation of the first examples of conformationally rigid, diastereomeric pairs of diol epoxides from *trans*-dihydrodiols are described. Direct epoxidation of the bay-region benzo[*e*]pyrene 9,10-dihydrodiol and triphenylene 1,2-dihydrodiol produces ca. 1:1 mixtures of diastereomeric diol epoxides in which the benzylic hydroxyl group is either cis (isomer **1**) or trans (isomer **2**) to the epoxide oxygen. Relative stereochemistry is assigned through spectral methods, solvolysis to tetraols, and an alternate route of synthesis.

Sir: The bay-region theory[1] predicted that benzo-ring diol epoxides of polycyclic aromatic hydrocarbons, in which the epoxide group forms part of a bay region, should be among the chemically most reactive and presumably most biologically active metabolites of a given hydrocarbon. Evidence has been forthcoming which indicates that this is indeed the case for the eight hydrocarbons which have since been adequately studied.[2] For diol epoxides of benzo-ring *trans*-dihydrodiols, two diastereomers are possible in which the benzylic hydroxyl group is either cis (isomer **1**) or trans (isomer **2**) to the epoxide oxygen. In



isomer 1 isomer 2

the absence of conformational restraints imposed by a proximate bay region, the hydroxyl groups of non-bay-region dihydrodiols reside in a predominantly quasi-diequatorial conformation, as evidenced by the large values of J_{diol} in their ^{1}H NMR spectra.[3] As described in detail elsewhere,[4] the allylic quasi-equatorial hydroxyl group acts

(1) The simplest example of a bay region is the hindered area between the 4 and 5 positions in phenanthrene. For details of the theory see: D. M. Jerina and J. W. Daly in "Drug Metabolism", D. V. Parke and R. L. Smith, Eds., Taylor and Frances, London, 1976, pp 13–32; D. M. Jerina, R. E. Lehr, H. Yagi, O. Hernandez, P. G. Wislocki, A. W. Wood, R. L. Chang, W. Levin, and A. H. Conney in "In Vitro Metabolic Activation in Mutagenesis Testing", F. J. DeSerres, J. R. Fouts, J. R. Bend, and R. M. Philpot, Eds., Elsevier/North Holland Biomedical Press, Amsterdam, 1976, pp 159–177; D. M. Jerina and R. E. Lehr in "Microsomes and Drug Oxidations", V. Ullrich, I. Roots, A. G. Hildebrant, R. W. Estabrook, and A. H. Conney, Eds., Pergamon Press, Oxford, England, 1977. pp 709–720.

(2) For leading references see D. R. Thakker, M. Nordqvist, H. Yagi, W. Levin, D. Ryan, P. Thomas, A. J. Conney, and D. M. Jerina in "Polynuclear Aromatic Hydrocarbons", P. W. Jones and P. Leber, Eds., Ann Arbor Science Publishers, Ann Arbor, Michigan, 1979, pp 455–472; M. K. Buening, W. Levin, A. W. Wood, R. L. Chang, H. Yagi, J. M. Karle, D. M. Jerina, and A. H. Conney, *Cancer Res.*, **39**, 1310 (1979).

(3) D. M. Jerina, H. Selander, H. Yagi, M. C. Wells, J. F. Davey, V. Mahadevan, and D. T. Gibson, *J. Am. Chem. Soc.*, **98**, 5988 (1976); D. T. Gibson, V. Mahadevan, D. M. Jerina, H. Yagi, and H. J. C. Yeh, *Science*, **189**, 295 (1975); R. Lehr, M. Schaefer-Ridder, and D. M. Jerina, *J. Org. Chem.*, **42**, 736 (1977); J. M. Karle, H. D. Mah, D. M. Jerina and H. Yagi, *Tetrahedron Lett.*, 4021 (1977).