Table I
Hydrolysis and Catalytic Reduction of Benzyloxy Esters

Esters	Hydrolysis	Catalytic reduction	Product	% yield
$PhCO_2CH_2OCH_2Ph$	aq HCl–THF		$PhCO_2H$	98
$PhCO_2CH_2OCH_2Ph$		5% Pd/C–H_2	$PhCO_2H$	100
$C_5H_{11}CO_2CH_2OCH_2Ph$	aq HCl–THF		$C_5H_{11}CO_2H$	75
$C_5H_{11}CO_2CH_2OCH_2Ph$		5% Pd/C–H_2	$C_5H_{11}CO_2H$	69

5% sodium bicarbonate solution (500 ml) and water (500 ml) and dried over anhydrous magnesium sulfate. Filtration and concentration of the organic phase on a rotary evaporator yielded an oil. Distillation of the oil afforded 17.2 g (73%) of benzyloxymethyl hexanoate: bp 101–104° (0.08 mm); ir (neat) ester band at 1750 cm^{-1}; NMR (CCl_4) δ 7.44 (s, 5 H), 5.4 (s, 2 H), 4.71 (s, 2 H), 2.25 (t, 2 H), 1.1–2 (m, 6 H) and 0.9 (t, 3 H).

Anal. Calcd for $C_{14}H_{20}O_3$: C, 71.16; H, 8.53. Found: C, 71.31; H, 8.41.

Benzyloxymethyl Benzoate (IV). Sodium benzoate (18.7 g, 0.13 mol), benzyl chloromethyl ether (20.2 g, 0.13 mol), and hexamethylphosphoramide (75 ml) were stirred at room temperature for 48 hr and the reaction mixture was worked up by the above procedure. Distillation afforded 21.2 g (68%) of benzyloxymethyl benzoate: bp 122–124° (0.06 mm); ir (neat) ester band at 1725 cm^{-1}; NMR (CCl_4) δ 4.74 (s, 2 H), 5.67 (s, 2 H), 8.02–8.22 (m, 2 H), 7.20–7.50 (m) and 7.30 (s) [(m) + (s), 8 H].

Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.52; H, 5.89.

Ester Hydrolysis. Benzoic Acid VI. Benzyloxymethyl benzoate (IV, 1.0 g, 0.0041 mol) was dissolved in an aqueous HCl–THF solution (8 ml of concentrated HCl, 6 ml of H_2O, and 36 ml of THF) and the resulting solution was stirred at room temperature for 2 hr. The reaction solution was poured into 100 ml of H_2O and extracted with 2 × 100 ml of ether. The ether extracts were combined and extracted with 3 × 25 ml of 10% $NaHCO_3$. The aqueous basic layers were combined and washed with 75 ml of ether and then acidified carefully with concentrated HCl. The acidic layer was then extracted with 3 × 75 ml of $CHCl_3$ and the chloroform extracts were combined and dried over anhydrous magnesium sulfate. Filtration and removal of the solvent on a rotary evaporator afforded 490 mg (98%) of benzoic acid, mp 121–122° (lit.[5] mp 122.4°). The NMR and ir spectra of benzoic acid were identical with those of an authentic sample.

Hexanoic Acid V. Benzyloxymethyl hexanoate (III, 3.0 g, 0.0126 mol) was dissolved in an aqueous HCl–THF solution (6 ml of H_2O, 8 ml of concentrated HCl, and 51 ml of THF), the resulting solution was stirred at room temperature for 2 hr, and the reaction mixture was worked up by the above procedure. The organic solvent was removed by distillation at 1 atm and the resulting oil was then distilled under vacuum to afford 1.1 g (75%) of hexanoic acid, bp 115–123° (40 mm) [lit[6] bp 107° (15 mm)]. The NMR and ir spectra of hexanoic acid were identical with those of an authentic sample.

Catalytic Reduction. Benzoic Acid VI. To a solution of benzyloxymethyl benzoate (1.0 g, 0.0041 mol) in absolute ethanol (15 ml) was added 5% Pd/C (400 mg) and the resulting mixture was reduced with H_2 at 1 atm at room temperature. After a hydrogen uptake of 97.6 ml, the reaction mixture was filtered through Celite 545 and the Celite was washed with additional ethanol. The organic filtrate was dried over anhydrous magnesium sulfate; filtration followed by removal of the solvent afforded 500 mg (100%) of benzoic acid, mp 121.6–122.3° (lit.[5] mp 122.4°). The NMR and ir spectra of benzoic acid were identical with those of an authentic sample.

Catalytic Reduction. Hexanoic Acid V. To a solution of benzyloxymethyl hexanoate (III, 3.0 g, 0.0126 mol) in absolute ethanol (20 ml) was added 400 mg of 5% Pd/C, the resulting mixture was reduced at 1 atm at room temperature, and the reaction mixture was worked up by the above procedure. The organic solvent was removed by distillation at 1 atm. The oil residue was dissolved in 10% $NaHCO_3$ (50 ml) and extracted with 100 ml of ether. The ether phase was extracted with 35 ml of 10% $NaHCO_3$ and the basic layers were combined and carefully acidified with concentrated HCl. The acidified mixture was extracted with 3 × 150 ml of chloroform. The chloroform extracts were combined and dried over anhydrous magnesium sulfate. Filtration and removal of the solvent at 1 atm afforded an oil. Vacuum distillation of the oil afforded 1.0 g (69%) of hexanoic acid, bp 115–118° [lit.[6] bp 107° (15 mm)]. The NMR and ir spectra of hexanoic acid were identical with those of an authentic sample.

Registry No.—I, 10051-44-2; II, 532-32-1; III, 55887-43-9; IV, 55887-44-0; V, 142-62-1; VI, 65-85-0; benzyl chloromethyl ether, 3587-60-8.

References and Notes

(1) Undergraduate Research Participant.

(2) For a review of acid protecting groups see (a) M. Freifelder, "Practical Catalytic Hydrogenation", Wiley, New York, N.Y., 1971, p 398; (b) R. L. Augustine, "Catalytic Hydrogenation", Marcel Dekker, New York, N.Y., 1965; (c) *Org. React.*, **7**, 263 (1953).

(3) P. E. Pfeffer, T. A. Foglia, P. A. Barr, I. Schmeltz, and L. S. Silbert, *Tetrahedron Lett.*, 4063 (1972).

(4) J. E. Shaw, D. C. Kunerth, and J. J. Sherry, *Tetrahedron Lett.*, 689 (1973).

(5) F. W. Schwab and E. Wickers, *J. Research Natl. Bur. Stand.*, **25**, 747 (1950).

(6) H. Sato, K. Endo, M. Koga, and H. Shingu, *J. Chem. Soc. Jpn., Ind. Chem. Sect.*, **58**, 132 (1955).

Reactions of Oxetane with Imine Salts Derived from Cyclohexanone

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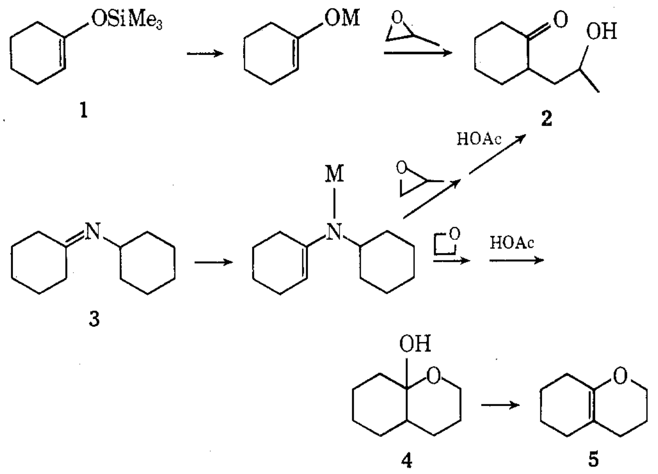
In connection with our interest in the use of α-methyleneoxetane[1] in nucleophilic ring-opening reactions, e.g., in the Robinson annelation, we have investigated the possibility of alkylating enolates or imine salts with oxetane (trimethylene oxide). For comparison, we have also studied the analogous reactions with an epoxide, propylene oxide. Ring-opening reactions of oxetanes with Grignard,[2–4] organolithium,[3,5] and organoaluminum[6] reagents are known, but few reactions with C-functional nucleophiles are reported.[7] Many nucleophilic ring-opening reactions of epoxides are reported, including reactions with imine salts and with enolates of β-dicarbonyl compounds.[7c,d,8–10]

We have been able to alkylate enolates of cyclohexanone with propylene oxide, but not with oxetane. However, we have found that the imine salt[11] of cyclohexanone is alkylated by both oxetane and propylene oxide in good yields.

When propylene oxide was treated with the lithium or bromomagnesium enolates of cyclohexanone,[12a] the alkylated product **2**[9b,10,14] was formed in low to moderate yields. However, when oxetane was treated with these enolates[12] under a variety of conditions, none of the expected alkylation products, **4**[15] or **5**,[15,16] was detected.[17]

The reaction of oxetane with the bromomagnesium salt of the imine (**3**) of cyclohexanone, followed by acetic acid hydrolysis,[11e] gave the hemiketal **4** in 80% isolated yield. A



M = Li, MgBr

similar reaction with the lithium salt of **3** gave a 38% yield by VPC.[18] The corresponding reactions of propylene oxide with the bromomagnesium and lithium imine salts produced keto alcohol **2** in 75% (isolated) and 43% (VPC) yields, respectively.

Harvey and Tarbell have reported the reaction of propylene oxide with the bromomagnesium salt of **3** followed by hydrochloric acid hydrolysis, giving **2** in only 36% yield.[10] In our initial studies of the reactions of oxetane with imine salts of **3**, we employed the hydrochloric acid hydrolysis procedure and obtained quite low (~20%) yields. The milder acetic acid hydrolysis method[11e] is clearly superior.

Nucleophilic ring-opening reactions of both oxetanes and epoxides are known to be greatly facilitated by coordination of the oxygen atom with Lewis acids.[19,20] In the reactions reported here, lithium and magnesium may facilitate the ring openings by acting as Lewis acids.[22] Although alkylations of oxetanes (and epoxides) with simple ketone enolates appear to have little synthetic value, alkylations with the more nucleophilic imine salts clearly have potential synthetic utility.

Experimental Section

Oxetane (Aldrich) and propylene oxide (Eastman) were used as received. Tetrahydrofuran (THF) was distilled from a deep purple solution prepared from sodium and benzophenone. 1,2-Dimethoxyethane (glyme) was distilled from lithium aluminum hydride. Petroleum ether was washed with sulfuric acid, dried (K_2CO_3), and distilled; the fraction of bp 38–41.5° was used. Methyllithium and butyllithium were obtained from Alfa Inorganics.

All reactions were carried out under a nitrogen atmosphere. Melting points were determined on a Fisher-Johns hot stage melting point apparatus. Infrared (ir) spectra were obtained using a Perkin-Elmer Model 137 spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained using a Varian T-60 spectrometer, using tetramethylsilane as the internal reference. Vapor phase chromatographic (VPC) analyses were performed on a Varian Aerograph Model 90-P instrument.[23]

Purification of Authentic Samples of Hemiketal 4 and Enol Ether 5. Following the procedure of Borowitz,[15] hemiketal **4** was obtained as a colorless oil which crystallized on standing: ir (CCl_4) 2.79, 2.95, 3.39, 3.50, 5.88 (very weak), 6.94, 9.28, 10.57 μ; NMR (CCl_4) δ 1.0–2.4 (broad, 13.8 H), 3.3–4.3 (broad, 2 H); 2,4-dinitrophenylhydrazone (from ethanol) mp 127.5–128.5° (lit.[16c] mp 126–128°). Portions of the product were recrystallized from pentane (yielding white crystals, mp 67–69°) and from aqueous ethanol (yielding white crystals, mp 75–78°). VPC analysis (145°)[23a] showed two peaks at 1.2 and 2.2 min in a ratio of 1:4.[18] The two components were separated by preparative VPC. The first, which on reinjection showed only one peak at 1.2 min, was identified as the enol ether **5**: ir (film) 5.91, 8.08, 8.69 μ; the NMR spectrum was identical with that reported.[16b–e] The second component was identified as hemiketal **4** (contaminated with a little **5**) by its ir and NMR spectra; on reinjection in the VPC, it showed two peaks at 1.2 and 2.2 min, indicating partial dehydration to the enol ether **5**.[18]

Propylene Oxide with Enolates of Cyclohexanone. A. Lithium Enolate. To a stirred solution of 30 ml (48 mmol) of methyllithium (1.6 *M* in ether) in 50 ml of glyme was added a solution of 6.22 g (36.5 mmol) of the silyl enol ether **1**[24] in 50 ml of glyme over a period of 1 hr.[12a] After 5 min, 5 ml (4.3 g, 74 mmol) of propylene oxide was added, and the resulting solution was stirred at room temperature for 48 hr. The reaction mixture was poured into saturated $NaHCO_3$ and extracted with three 100-ml portions of ether, and the combined extracts were washed with water, dried (Na_2SO_4, $MgSO_4$), concentrated, and distilled, yielding 1.716 g (30%) of **2** as a colorless liquid: bp 70–75° (0.2 mm) [lit.[10] bp 73–75° (0.2 mm)]; 2,4-dinitrophenylhydrazone (from ethanol) mp 106–109° (lit.[9b] mp 105–108°). VPC analysis (105°)[23a] of **2** showed one major peak (93% pure) at a retention time of 1.7 min. The ir and NMR spectra of **2** were essentially identical with those of an authentic sample of **2** prepared by the method of Harvey and Tarbell.[10]

VPC analysis[23b] of the product of a similar reaction employing decane as an internal standard indicated that a 40% yield of **2** was formed after 48 hr at room temperature.[25]

B. Bromomagnesium Enolate. The bromomagnesium enolate was prepared by treating the silyl enol ether **1**[24] with methylmagnesium bromide in refluxing glyme–HMPA (20:1 v/v) for 55 hr.[12a] Treatment of propylene oxide with this enolate (room temperature, 6 hr) in the presence of decane (internal standard) gave a 19% yield of **2** by VPC.[23b,25]

Oxetane with Imine Salts of Cyclohexanone. A solution of 10.87 g (60.7 mmol) of the imine **3**[26] in 40 ml of THF was added to 35 ml (70 mmol) of ethylmagnesium bromide (about 2 *M* in THF) heated at reflux. After 2 hr, the solution was cooled to 0°, and 5.5 ml (4.9 g, 84.7 mmol) of oxetane was added. The resulting yellow solution was stirred at 25° for 19 hr, then partitioned between ether and brine. The layers were separated and the brine layer was reextracted twice with ether. The combined ether layers were dried (Na_2SO_4) and concentrated, then stirred with 80 ml of petroleum ether and 100 ml of 1 *M* acetic acid for 2 hr at room temperature.[11e] Sodium chloride was added to saturate the aqueous layer, the layers were separated, and the aqueous layer was reextracted twice with ether. The combined organic layers were washed with saturated $NaHCO_3$ and brine, and were dried (Na_2SO_4, $MgSO_4$) and concentrated, yielding 9.5 g of brown oil which crystallized. The solid was separated and washed with petroleum ether, producing 5.57 g of white crystals, mp 74–76°. The combined mother liquor and washing liquid were concentrated, giving oil and crystals. The crystals were distilled (bulb to bulb, oven temperature 110°, oil pump vacuum) giving 1.13 g of white crystals, mp 67–70°; the oil was similarly distilled, giving 0.90 g of white, crystalline solid, mp 61–66° (total yield 80%). The ir spectra of all three fractions were identical with each other and with that of the authentic sample of hemiketal **4** (above). The NMR spectra were equivalent to that of **4**.

VPC analysis[23b] of the product of a similar reaction employing dodecane as an internal standard indicated that an 88% yield of enol ether **5**[18] was formed after 18 hr at 25°.[25]

VPC analysis[23b] of the product of the reaction of oxetane with the lithium salt of **3** (from **3** and *n*-butyllithium at 0°) employing dodecane as an internal standard indicated that a 38% yield of enol ether **5**[18] was formed after 18 hr at 25°.[25]

Propylene Oxide with Imine Salts of Cyclohexanone. A solution of 10.986 g (61.3 mmol) of the imine **3**[26] in 40 ml of THF was added to 35 ml (70 mmol) of ethylmagnesium bromide (about 2 *M* in THF) heated at reflux. After 2 hr, the solution was cooled to 0°, and 6.4 ml (5.5 g, 94.7 mmol) of propylene oxide was added. The resulting yellow solution was stirred for 1 hr at 0° and 1 hr at room temperature, then worked up and hydrolyzed by a procedure identical with that described for the reaction of oxetane with the bromomagnesium salt of **3** (above). The resulting brown oil was distilled through a 7-cm Vigreux column, producing 7.20 g (75% yield) of **2** as a colorless liquid, bp 66–73° (0.50 mm) [lit.[10] bp 73–75° (0.2 mm)]. VPC analysis (130°)[23b] showed one major peak (95% pure) at a retention time of 4.0 min. The ir and NMR spectra were identical with those of an authentic sample of **2** prepared by the method of Harvey and Tarbell.[10]

VPC analysis[23b] of the product of a similar reaction run at 25°, employing decane as an internal standard, indicated that a 67% yield of **2** was formed after 2 hr.[25]

VPC analysis[23b] of the product of the reaction of propylene oxide with the lithium salt of **3** (from **3** and *n*-butyllithium at 0°), employing decane as an internal standard, indicated that a 43% yield of 2 was formed after 1 hr at 25°.[25]

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Registry No.—**1**, 6651-36-1; **2**, 6126-52-9; **2** DNPH, 23260-65-3; **3**, 10468-40-3; **4**, 13377-10-1; **5**, 7106-07-2; methyllithium, 917-54-4; propylene oxide, 75-56-9; methyl bromide, 74-83-9; ethyl bromide, 74-96-4; oxetane, 503-30-0.

References and Notes

(1) P. F. Hudrlik and A. M. Hudrlik, *Tetrahedron Lett.*, 1361 (1971); P. F. Hudrlik, A. M. Hudrlik, and C.-N. Wan, *J. Org. Chem.*, **40**, 1116 (1975).

(2) C. G. Derick and D. W. Bissell, *J. Am. Chem. Soc.*, **38**, 2478 (1916).

(3) S. Searles, *J. Am. Chem. Soc.*, **73**, 124 (1951).

(4) (a) W. Steudel and H. Gilman, *J. Am. Chem. Soc.*, **82**, 6129 (1960); (b) T. Cuvigny and H. Normant, *C. R. Acad. Sci., Ser. C*, **254**, 316 (1962); (c) E. N. Marvell, D. Sturmer, and R. S. Knutson, *J. Org. Chem.*, **33**, 2991 (1968); (d) R. D. Westland, J. L. Holmes, M. L. Mouk, D. D. Marsh, R. A. Cooley, Jr., and J. R. Dice, *J. Med. Chem.*, **11**, 1190 (1968); (e) S. H. Schroeter, *J. Org. Chem.*, **34**, 1188 (1969).

(5) (a) M. F. Ansell and B. Gadsby, *J. Chem. Soc.*, 3388 (1958); (b) L. L. Chan and J. Smid, *J. Am. Chem. Soc.*, **90**, 4654 (1968); (c) N. J. Foulger and B. J. Wakefield, *J. Chem. Soc., Perkin Trans. 1*, 871 (1974).

(6) D. B. Miller, *J. Organomet. Chem.*, **14**, 253 (1968).

(7) (a) Pyrrole Grignard: L. R. Kray and M. G. Reinecke, *J. Org. Chem.*, **32**, 225 (1967). (b) Nitrile anion: L. L. Darko and J. G. Cannon, *J. Org. Chem.*, **32**, 2352 (1967). (c) Isonitrile anion: D. Hoppe, *Angew. Chem., Int. Ed. Engl.*, **13**, 789 (1974). (d) 2-Lithio-1,3-dithiane: D. Seebach and E. J. Corey, *J. Org. Chem.*, **40**, 231 (1975).

(8) For example, epoxides with the following. (a) Stabilized ester enolates: H. O. House, "Modern Synthetic Reactions", 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 300, 534–535. (b) Nitrile anions: N. R. Easton, J. H. Gardner, and J. R. Stevens, *J. Am. Chem. Soc.*, **69**, 2941 (1947); M. Mousseron and M. Canet, *C. R. Acad. Sci., Ser. C*, **232**, 637 (1951). (c) Carboxylic acid dianions: P. L. Creger, *J. Org. Chem.*, **37**, 1907 (1972). (d) Amide anions: W. Sucrow, M. Slopianka, and D. Winkler, *Chem. Ber.*, **105**, 1621 (1972). (e) Lithiodihydro-1,3-oxazines: A. I. Meyers, A. Nabeya, H. W. Adickes, I. R. Politzer, G. R. Malone, A. C. Kovelesky, R. L. Nolen, and R. C. Portnoy, *J. Org. Chem.*, **38**, 36 (1973). (f) β-Keto ester dianion: T. A. Bryson, *J. Org. Chem.*, **38**, 3428 (1973). (g) Lithio-1,3-oxazolines: A. I. Meyers, E. D. Mihelich, and R. L. Nolen, *J. Org. Chem.*, **39**, 2783 (1974). To our knowledge, the intermolecular reactions of epoxides with simple ketone enolates have not been reported.

(9) Epoxides with enamines: (a) P. Jakobsen and S.-O. Lawesson, *Tetrahedron*, **24**, 3671 (1968); (b) A. Z. Britten, W. S. Owen, and C. W. Went, *Ibid.*, **25**, 3157 (1969).

(10) Epoxides with imine salts: W. E. Harvey and D. S. Tarbell, *J. Org. Chem.*, **32**, 1679 (1967).

(11) For some other reactions of imine salts, see (a) G. Stork and S. R. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963); (b) G. Wittig and H. Reiff, *Angew. Chem., Int. Ed. Engl.*, **7**, 7 (1968); (c) G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **89**, 1217 (1970); (d) G. Stork and J. Benaim, *J. Am. Chem. Soc.*, **93**, 5938 (1971); (e) H. O. House, W. C. Liang, and P. D. Weeks, *J. Org. Chem.*, **39**, 3102 (1974).

(12) (a) Lithium and bromomagnesium enolates were prepared from the silyl enol ether **1** by reaction with methyllithium or methylmagnesium bromide: G. Stork and P. F. Hudrlik, *J. Am. Chem. Soc.*, **90**, 4464 (1968). (b) Bromomagnesium enolates were also prepared by the addition of magnesium bromide etherate[13] to solutions of the lithium enolate: H. O. House, R. A. Auerbach, M. Gall, and N. P. Peet, *J. Org. Chem.*, **38**, 514 (1973); H. O. House, D. S. Crumrine, A. Y. Teranishi, and H. D. Olmstead, *J. Am. Chem. Soc.*, **95**, 3310 (1973).

(13) M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances", Prentice-Hall, Englewood Cliffs, N.J., 1954, p 33.

(14) D. P. Brust and D. S. Tarbell, *J. Org. Chem.*, **31**, 1251 (1966).

(15) I. J. Borowitz, G. J. Williams, L. Gross, and R. Rapp, *J. Org. Chem.*, **33**, 2013 (1968).

(16) (a) H. Obara, *Nippon Kagaku Zasshi*, **82**, 60 (1961); *Chem. Abstr.*, **57**, 16426*d* (1962); (b) S. J. Etheredge, *J. Org. Chem.*, **31**, 1990 (1966); (c) I. J. Borowitz, G. Gonis, R. Kelsey, R. Rapp, and G. J. Williams, *J. Org. Chem.*, **31**, 3032 (1966); (d) C. D. Gutsche, I. Y. C. Tao, and J. Kozma, *Ibid.*, **32**, 1782 (1967); (e) R. G. Carlson and R. G. Blecke, *Ibid.*, **32**, 3538 (1967).

(17) In the reactions with the bromomagnesium enolate, 3-bromopropanol was formed. Treatment of oxetane with magnesium bromide is reported to give 3-bromopropanol.[3]

(18) The hemiketal **4** undergoes partial or complete dehydration to the enol ether **5** when subjected to VPC. VPC yields were obtained under conditions where dehydration was complete and are based on **5**.

(19) (a) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); (b) A. Rosowsky in "Heterocyclic Compounds with Three- and Four-Membered Rings", Part One, A. Weissberger, Ed., Interscience, New York, N.Y., 1964, pp 1–523; (c) S. Searles, Jr., *Ibid.*, Part Two, pp 983–1068; (d) R. J. Gritter in "The Chemistry of the Ether Linkage", S. Patai, Ed., Interscience, New York, N.Y., 1967, pp 373–443.

(20) Ring-opening reactions of oxetanes might be expected to be less facile than those of epoxides because of the difference in strain; however, catalysis by Lewis acids might be more effective with oxetanes, since oxetanes have been shown to be more basic than epoxides.[21]

(21) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951); see also S. Searles, Jr., and M. Tamres in ref 19d, pp 243–308.

(22) Several attempts to use compounds of aluminum, boron, or zinc in the reactions with oxetane were not fruitful.

(23) The following aluminum columns were used for VPC analysis: (a) 5% SE-30 on Chromosorb W, 5 ft × 0.25 in.; (b) 10% SE-30 on Chromosorb W, 10 ft × 0.25 in.

(24) (a) Belgian Patent 670,769 (1966); *Chem. Abstr.*, **65**, 5487*d* (1966); (b) A. Bazouin, J. Dunogues, and M. Lefort, French Patent 1,436,568 (1966); *Chem. Abstr.*, **66**, 18764z (1967).

(25) Analysis of several aliquots taken at different times suggested that this was approximately the optimum reaction time.

(26) E. D. Bergmann, E. Zimkin, and S. Pinchas, *Recl. Trav. Chim. Pays-Bas*, **71**, 168 (1952).

An Efficient Synthesis of 4,5-Benzotropone from *o*-Xylylene Dibromide

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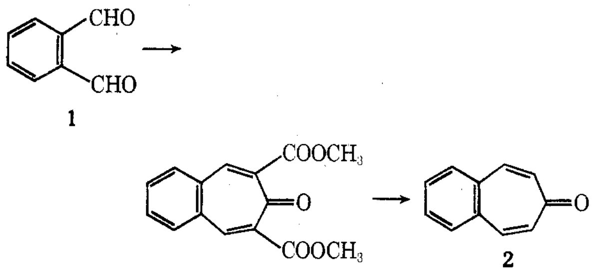
Our study of the chemical properties of benzazocine[1] and homobenzazocine systems[2] necessitated inter alia the availability of a ready, inexpensive, and plentiful source of 4,5-benzotropone (2). The original procedure of Thiele and Wertz[3,4] involves condensation of *o*-phthaldialdehyde (1) with dimethyl acetonedicarboxylate and subsequent hydrolysis and decarboxylation (eq 1). For large-scale synthesis, however, the cost of 1 becomes prohibitive and the requirements of an autoclave and 200° in the final stage is an unattractive feature. Srivastava and Dev[5] have examined selenium dioxide oxidation of benzocycloheptatriene (3) as a route to 2. Although 4,5-benzotropone is indeed formed (27%), the 2,3 isomer (4, 13% yield) contaminates the product (eq 2). Also, hydrocarbon 3 is not readily available. Battiste's recently discovered multistep route from the benzyne–furan adduct 5 to 2,[6] while novel and elegant in concept, has in our hands not proven amenable to convenient scale-up (eq 3).



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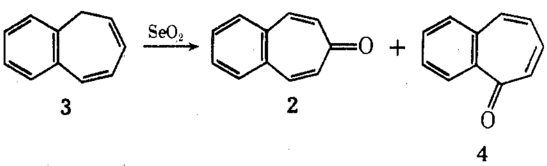

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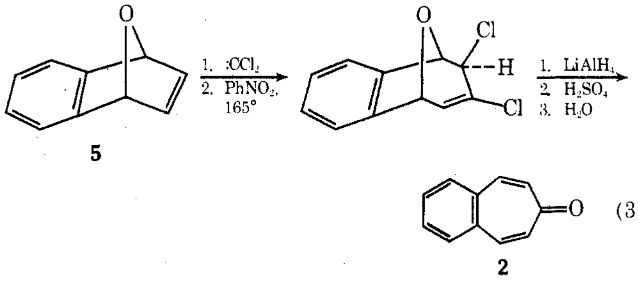

(3)