The Reactions of Acidic Reagents with Diene–Quinone Adduct Epoxides

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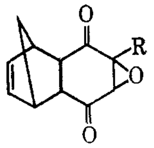
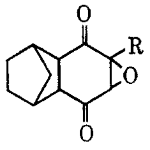
Received February 17, 1967

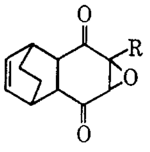
In 1960, Alder, *et al.*,[1] reported the preparation of cyclopentadiene–quinone adduct epoxides **1**. Since that time, additional examples have been prepared[2] and the configurations of these epoxides determined.[3] The present investigation is concerned with the acid treatment of aryl-substituted epoxides which affords ring-contracted acidic materials (see Tables I and II).



1a, R = C_6H_5
b, R = p-$CH_3C_6H_4$
c, R = p-$OCH_3C_6H_4$



2a, R = C_6H_5
b, R = p-$CH_3C_6H_4$



3a, R = C_6H_5
b, R = p-$CH_3C_6H_4$

When aryl-substituted epoxides such as **1**, **2**, or **3** were treated with boron trifluoride or mineral acids, crystalline materials were obtained whose elemental analyses indicated the loss of carbon monoxide from the original compounds. The material obtained from **1b** was soluble in bicarbonate solution and its infrared spectrum exhibited absorptions at 1560 (C=O) and 2560 cm^{-1} (OH · · · O), similar to the spectrum of the cyclopentadiene–cyclopentenedione adduct **5**,[4] which suggested that the indandione derivative **4** was its probable structure.

Alkylation with methyl iodide yielded both oxygen- (**6**) and carbon-methylated (**7**) products (Scheme I). As expected for a 2-disubstituted 1,3-diketone,[5] treatment of **7** with base cleaved the β-diketone to give keto acid **8**. The structure of **8** is supported by elemental analysis, infrared absorptions at 2400 (OH · · · O), 1705 (COOH), and 1690 cm^{-1} (C=O), and an nmr spectrum which showed the three $CHCH_3$ protons as a doublet at τ 8.62 and the $CHCH_3$ proton as a quartet at τ 6.14.

SCHEME I

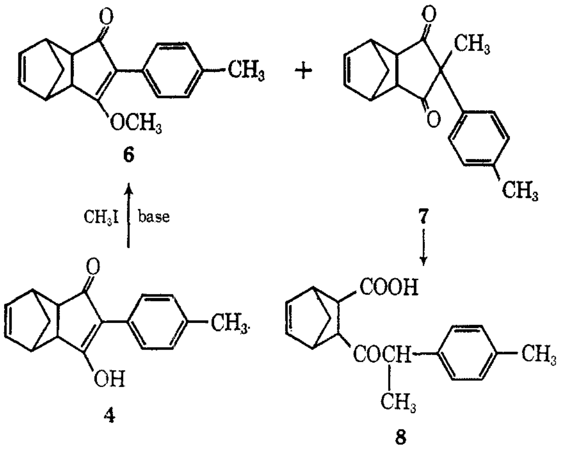
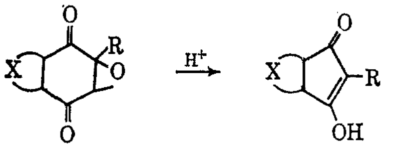


TABLE I

β-DIKETONES



Epoxide	Reaction conditions	Yield,[b] %	Mp, °C
1a[c]	93% H_2SO_4, 30 min, 0° reflux temp	44	245–246 dec
1a	$BF_3 \cdot OEt_2$–C_6H_6, 5 min, reflux	100	
1b[c]	50% H_2SO_4–dioxane, 4.5 min, 90°	71	243–245
1b	$BF_3 \cdot OEt_2$–C_6H_6, 5 min, reflux	95	
1c[a]	HCl–HOAc, 5 min, 90°	39	226.5–227.5 dec
2a[c]	$BF_3 \cdot OEt_2$–C_6H_6, 5 min, reflux	87	252–254
2b[a]	85% H_2SO_4, 2 hr, 90°	83	255.5–258
3a[c]	$BF_3 \cdot OEt_2$–C_6H_6, 5 min, reflux	81	249–251
3b[a]	HBr–HOAc, 35 min, 90°	58	260–262
11[a]	$BF_3 \cdot OEt_2$–C_6H_6, 3 min, reflux	87	147–149

β-Diketone from epoxide	ν_{max}^{KBr}, cm^{-1}	Calcd, %		Found, %	
		C	H	C	H
1a	1550, 2500	80.6	5.9	80.5	5.6
1b	1560, 2560	80.9	6.4	80.9	6.6
1c	1560, 2600	76.1	6.0	75.8	6.1
2a	1550, 2500	80.0	6.7	79.6	6.9
2b	1555, 2600	80.3	7.1	80.5	7.4
3a	1560, 2580	80.9	6.4	80.6	6.7
3b	1560, 2620	81.2	6.8	81.5	7.1

[a] See Table II. [b] Yield of product after recrystallization from ethanol. [c] See ref 2.

TABLE II

NEW EPOXIDES[a]

Epoxide	Yield,[b] %	Mp, °C	ν_{max}^{KBr}, cm^{-1}	Calcd, %		Found, %	
				C	H	C	H
1c	88	164–165	1702	73.0	5.4	73.0	5.5
2b[c]	98	143–145	1710	76.5	6.4	76.4	6.2
3b	41	167–168	1702	77.5	6.2	77.2	6.5
11	64	63–64	1700	76.8	4.0	77.1	4.0

[a] All epoxides prepared by the procedure of Alder, *et al.*[1] See Experimental Section for new epoxide precursors. [b] Yield of product after recrystallization from ethanol. [c] See Experimental Section.

Confirmation of the structure of the ring-contracted products obtained in these reactions was provided by the synthesis given by eq 1. β-Diketone **9**, obtained from **1a**, was treated with diphenyliodonium chloride[6] to afford a product, **10**, identical with material obtained

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[1] K. Alder, F. H. Flock, and H. Beumling, *Chem. Ber.*, **93**, 1896 (1960).

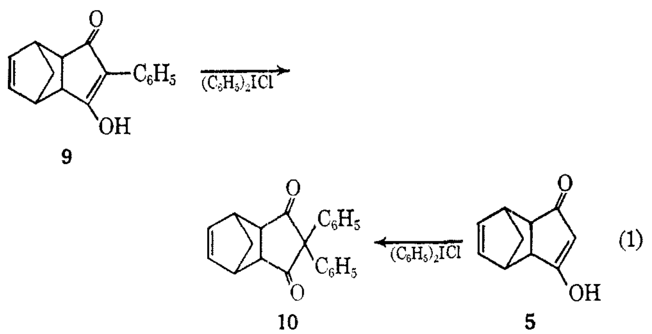
[2] H. S. Wilgus, III, E. Frauenglass, P. P. Chiesa, G. H. Nawn, F. J. Evans, and J. W. Gates, Jr., *Can. J. Chem.*, **44**, 603 (1966).

[3] D. F. O'Brien and J. W. Gates, Jr., *J. Org. Chem.*, **30**, 2593 (1965).

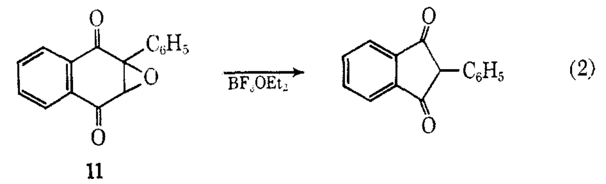
[4] C. H. DePuy and E. F. Zaweski, *J. Am. Chem. Soc.*, **81**, 4920 (1959).

[5] For examples, see W. Bradley and R. Robertson, *J. Chem. Soc.*, 2356 (1926); C. R. Hauser, F. W. Swamer, and B. I. Ringler, *J. Am. Chem. Soc.*, **70**, 4023 (1948); H. O. House and R. L. Wasson, *ibid.*, **78**, 4394 (1956).

[6] F. M. Beringer, E. J. Geering, I. Kuntz, and M. Mausner, *J. Phys. Chem.*, **60**, 141 (1956); F. M. Beringer, P. S. Forgione, and M. D. Yudis, *Tetrahedron*, **8**, 49 (1960).



by the diarylation of **5**.[4] As further confirmation of this reaction course, 2-phenyl-2,3-oxide 1,4-naphthoquinone, **11**, was synthesized and treated with boron trifluoride to produce 2-phenyl-1,3-indandione (eq 2).



The mechanism of this reaction is probably analogous to the acid-catalyzed rearrangements of α,β-epoxy ketones which result in ring contraction, followed by deformylation.[7]

Experimental Section

Infrared spectra were obtained with Baird Models Ak-1 or NK-1 or Perkin-Elmer Infracord Model 137 instruments as KBr pressings. Nmr spectra were measured with a Varian A-60 spectrometer with TMS as an internal standard (taken as τ 10).

4-*p*-Tolyltricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (4). With Sulfuric Acid.—To a warmed (75°) solution of 13.3 g (48 mmoles) of epoxide **1b** in 100 ml of dioxane was added 65 ml of warm 1:1 sulfuric acid–water. The solution was heated on a steam bath; it turned dark after 2 min. After an additional 2.5 min, the solution was poured into ice water. The filtered solid was treated with aqueous sodium bicarbonate for 15 min and filtered, and the solution acidified to afford 8.6 g of solid. After recrystallization from ethanol, there was obtained 8.5 g (71%) of product, mp 243–245°.

With Boron Trifluoride.—A solution of 5 g (18.8 mmoles) of epoxide **1b** in 100 ml of benzene was heated at reflux when 3 ml of boron trifluoride etherate was added. Heating was continued for 5 min and then about 50 ml of water was added. The benzene was removed *in vacuo* and the product filtered from the aqueous solution. Recrystallization from ethanol yielded 4.8 g (95%), mp24 3–245°. The nmr spectrum (DMSO-d_6) showed peaks at τ 8.49 (2 H multiplet), 7.81 (3 H singlet), 6.98 (4 H br singlet), 4.15 (2 H singlet), and 2.70 (center of 4 H A_2B_2).

5-Methoxy-4-*p*-tolyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (6) and 4-Methyl-4-*p*-tolyltricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (7).—Barium hydroxide as its octahydrate (42 g, 0.132 mole) was mixed with water (500 ml) and 4-*p*-tolyltricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (43.5 g, 0.172 mole) and the resulting slurry warmed to 85°. The water was removed on a rotary evaporator at 60° (20 mm). A solution of methyl iodide (49 g, 0.344 mole) in dimethyl sulfoxide (150 ml) was added, with some generation of heat. After 3 days, the yellow slurry was poured into water. The residue was washed successively with 1 *N* HCl, 0.5 *N* NaOH, and water. The solid was dissolved in ether–acetone, filtered, and the solvents were removed to give 44.1 g of solid. The solid was dissolved in benzene and chromatographed on silica gel to give 17.8 g (39.0%) or the β-diketone **7**; it melted at 128–130° after a rinsing with ether–petroleum ether (bp 40–60°). The enol ether **6** was obtained by elution with chloroform, 25.3 g (55.5%), and melted at 138–140° after a rinsing with ether–petroleum ether. Both samples were recrystallized from chloroform–petroleum ether to give melting points of 131–132° for **7** and 140.5–141.5° for **6**; for **6**, ν_{max}^{KBr} 1675 cm^{-1}, **7** 1712 and 1770 cm^{-1} (sh). The nmr spectrum ($CDCl_3$) for **6** showed peaks at τ 8.34 (2 H multiplet), 7.75 (3 H singlet), 6.84 (4 H multiplet), 6.12 (3 H singlet), 4.06 (2 H multiplet), and 2.82 (4 H multiplet). For **7**, τ 8.57 (3 H singlet), 8.43 (2 H multiplet), 7.75 (3 H singlet) 6.50 (4 H multiplet), 4.00 (2 H multiplet), and 2.92 (4 H singlet).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8. Found for **6**: C, 81.1; H, 7.0. For **7**: C, 81.1; H, 7.1.

3-(2′-*p*-Tolylpropionyl)norborn-5-ene-2-carboxylic Acid (8).—An ethanol solution (100 ml) of 5 g (19 mmoles) of dione **7** and 2.5 g of potassium hydroxide was refluxed for 12 hr, cooled, and acidified with 6 *N* hydrochloric acid. A white precipitate was collected (2.5 g, 47%; mp 133–145°), dissolved in sodium bicarbonate solution, filtered, and reacidified. The product was recrystallized from benzene–ligroin: mp 151–153°. Spectral data are given in the discussion.

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.1; H, 7.1. Found: C, 76.3; H, 7.0.

4,4-Diphenyltricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (10). From Tricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (5).—To a solution of 0.7 g (0.03 mole) of sodium in 190 ml of *t*-butyl alcohol under nitrogen was added 5 g (0.03 mole) of dione **5**. After a few minutes, 9.7 g (0.03 mole) of diphenyliodonium chloride was added and the mixture heated at reflux for 18 hr. The solution was then steam-distilled to remove iodobenzene. After 4.15 g of potassium carbonate in 30 ml of water had been added, the solution was extracted with 1:1 benzene–ethylacetate. Acidification of the aqueous layer did not afford any of the monoarylated material. The organic layer was washed with water, dried, and the volume reduced to about 20 ml. Upon chilling the solution, two crops of yellow needles of **10** were obtained: mp 163–166°; yield, 2.2 g (46%). Recrystallization from ethyl acetate or ethanol afforded colorless needles: mp 169–170°, ν_{max}^{KBr} 1715 and 1755 cm^{-1} (sh). The nmr spectrum in $CDCl_3$ exhibited peaks at τ 8.40 (multiplet, 2 H), 6.42 (multiplet, 4 H), 3.72 (multiplet, 2 H), 3.18–3.4 (br multiplet, 2 H), and 2.70 (multiplet, 8 H).

Anal. Calcd for $C_{22}H_{18}O_2$: C, 84.1; H, 5.8. Found: C, 84.3; H, 5.8.

From 4-Phenyltricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (9).—In 160 ml of *t*-butyl alcohol was placed 0.95 g (8.4 mmoles) of potassium *t*-butoxide, 2 g (8.4 mmoles) of dione **9**, and 2.66 g (8.4 mmoles) of diphenyliodonium chloride. The solution was heated at reflux under nitrogen for 5 hr. The same procedure already described afforded 1.3 g (50%) of product, mp 169–170°, mixture melting point with material obtained above 169–170°. The infrared spectra of the materials obtained by both paths were identical.

4-*p*-Anisyltricyclo[6.2.1.0^{2,7}]undec-4,9-diene-3,6-dione was prepared from the quinone[8] by the general procedure of Porter, *et al.*,[9] in 90% yield after recrystallization from ethanol.

Anal. Calcd for $C_{18}H_{16}O$: C, 77.2; H, 5.7. Found: C, 77.4; H, 6.1.

Epoxide 2b.—A solution of 10 g of the *p*-tolyl-1,4-benzoquinone-cyclopentadiene adduct epoxide[2] in 250 ml of ethyl acetate was hydrogenated in a Parr shaker at 40 lb for 4 min, with Pd-C as catalyst. After filtration and removal of solvent, the epoxide was recrystallized from ethanol (see Table II).

4-*p*-Tolyltricyclo[6.2.2.0^{2,7}]dodec-4,9-diene-3,6-dione was prepared by the general procedure of Porter, *et al.*,[9] in 73% yield after recrystallization from ethanol.

Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.8; H, 6.5. Found: C, 81.9; H, 6.5.

Registry No.—**1a**, 13369-35-2; **1b**, 13369-36-3; **1c**, 13369-37-4; **2a**, 5826-65-3; **2b**, 13369-39-6; **3a**, 5895-23-8; **3b**, 13369-41-0; **4**, 13369-42-1; **6**, 13369-43-2; **7**, 13369-44-3; **8**, 13369-45-4; **10**, 13369-46-5; **11**, 13369-47-6.

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(7) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 737 (1959); A. Rosowsky in "Heterocyclic Compounds with Three- and Four-membered Rings," A. Weissberger, Ed., Interscience Publishers Inc., New York, N. Y., 1964, part I, p 1. For part VIII in a series on α,β-epoxy ketone rearrangements, see H. O. House and G. D. Ryerson, *J. Am. Chem. Soc.*, **83**, 979 (1961). J. W. Ager, F. A. Eastwood, and R. Robinson, *Tetrahedron Suppl.*, **7**, 277 (1966).

(8) P. Brassard and P. L'Ecuyer, *Can. J. Chem.*, **36**, 700 (1958).

(9) R. F. Porter, W. W. Rees, E. Frauenglass, H. S. Wilgus, III, G. H. Nawn, P. P. Chiesa, and J. W. Gates, Jr., *J. Org. Chem.*, **29**, 588 (1964).