

The Baeyer-Villiger Reaction of Polycyclic Aromatic Aldehydes: Preparation of Polycyclic Phenols

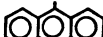
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Synopsis. Baeyer-Villiger reactions of such polycyclic aromatic aldehydes as 2-dibenzofurancarbaldehyde with various peroxy compounds have been studied in detail, giving predominantly the corresponding phenols.

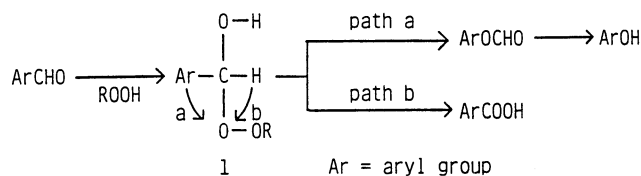
In contrast to simple benzenoid aromatics, only a little attention has been paid to such polycyclic aromatic compounds as naphthalene, dibenzofuran, anthracene and so on, though they have attractive attributes, i.e., their rigid ring skeletons and rich π -electron systems. We have been interested in the reaction characteristic of the polycyclic aromatic systems to provide a variety of useful derivatives. In this paper, we wish to report on the Baeyer-Villiger reaction (B-V reaction)¹⁾ of polycyclic aromatic aldehydes yielding a series of polycyclic phenols.

Table 1. B-V Reaction of Polycyclic Aromatic Aldehydes with MCPBA

Run No.	Ar	$X^a)$	Yield/%	
		%	ArOH	ArCOOH
1		81	32	42
2		95	80	2
3		75	48	16
4		97	79	2
5		94	85	2
6		97	86	1
7		99	92	2

a) X is the conversion of the aldehyde.

Several kinds of polycyclic aromatic aldehydes²⁾ were allowed to react with *m*-chloroperbenzoic acid (MCPBA) in dry dichloromethane at room temperature under an argon atmosphere. The results are shown in Table 1. Polycyclic aromatic aldehydes gave the corresponding phenols predominantly, while benzaldehyde yielded a mixture of phenol and benzoic acid. This difference can be attributed to a difference in the electron-donative nature between the polycyclic aromatic ring and the benzene ring. The mechanism shown in Scheme 1 is generally proposed.³⁾ A peroxy compound (ROOH) attacks the carbonyl group of an aldehyde (ArCHO) to afford an intermediate **1**, followed by a migration of the aryl group, Ar, (path a) or the hydride, H, (path b). The relative migratory aptitude of Ar and H depends on their electron-donative nature, so that the more electron-donative polycyclic aromatic ring migrates predominantly to give the formate, which is transformed into the phenol, ArOH, by alkaline hydrolysis. Thus, this work presents a new synthetic method regarding polycyclic phenols.



Scheme 1.

Many kinds of peroxy compounds were examined as oxidants instead of MCPBA in this B-V reaction of 2-dibenzofurancarbaldehyde (**2**). Table 2 shows the results of a reaction of **2** with aqueous hydrogen peroxide (30 wt%) in the presence of various acids to yield 2-dibenzofuranol (**3**) and 2-dibenzofurancarboxylic acid (**4**). The reaction was strongly affected by the

Table 2. B-V Reaction of **2** with Aqueous Hydrogen Peroxide

Run	H ₂ O ₂ /2	Solvent	T ^{a)}	t ^{b)}	X ^{c)}	Yield/%	
No.	mol/mol		°C	h	%	3	4
8	2.0	CH ₃ COOH	40	168	50	2	47
9	1.3	HCOOH	20	20	98	76	3
10	1.0	HCOOH	20	20	95	81	1
11	1.2	CF ₃ COOH	20	20	85	13	1
12	1.2	CH ₃ COOH-H ₂ SO ₄ (5%) ^{d)}	40	24	86	49	4
13	1.1	CH ₃ COOH-CH ₂ ClCOOH (5%) ^{d)}	40	20	80	66	7
14	1.2	CH ₃ COOH-CF ₃ COOH (5%) ^{d)}	40	20	60	34	13
15	2.0	CH ₃ OH-HCOOH (30%) ^{d)}	40	24	41	2	22
16	1.2	CH ₃ OH-H ₂ SO ₄ (5%) ^{d)}	40	48	100	36	64
17	1.3	(CH ₃) ₂ CO-H ₂ SO ₄ (5%) ^{d)}	40	24	78	1	55

a) *T* is the reaction temperature. b) *t* is the reaction time. c) *X* is the conversion of **2**. d) The concentration of the second material.

Table 3. B-V Reaction of **2** with Various Peroxy Compounds

Run No.	Peroxy Compound ^{a)}	Solvent	T	t	X	Yield/%	
			°C	h	%	3	4
18	<i>t</i> -BuOOH	HCOOH	40	48	11	3	0.2
19	<i>t</i> -BuOOH	CH ₃ OH-H ₂ SO ₄ ^{b)}	40	48	90	61	15
20	<i>t</i> -BuOO-COCH ₃	CH ₃ OH-H ₂ SO ₄ ^{b)}	40	24	43	29	9
21	$\begin{array}{c} \text{CH}_3 \\ \\ t\text{-BuOO}-\text{C}-\text{OO}-t\text{-Bu} \\ \\ \text{CH}_3 \end{array}$	CH ₃ OH-H ₂ SO ₄ ^{b)}	40	24	52	17	17
22	(PhCO) ₂ O ₂	CH ₃ OH-H ₂ SO ₄ ^{b)}	40	48	92	—	85
23	K ₂ S ₂ O ₈	CH ₃ OH-H ₂ SO ₄ ^{b)}	40	24	56	9	29
24	CH ₃ CO ₃ H	(CH ₃ CO) ₂ O	40	24	97	2	68

a) The molar ratio of the peroxy compound to **2** is 1.2. b) The concentration of H₂SO₄ is 5 wt%.

acidity of the acid used. The reaction in formic acid gave **3** in high yield (81%, Run 10) and high selectivity, while the reaction in acetic acid proceeded slowly and gave **4** (47%, Run 8). When the reaction was carried out in trifluoroacetic acid, the yield of **3** was low (13%) and tarry materials were obtained (Run 11). Acid catalysts yield the conjugate acids of aldehydes and accelerate the nucleophilic additions of peroxides to the protonated carbonyl groups (Scheme 1).³⁾ The acidity of formic acid ($pK_a=3.75$ at 25 °C) is stronger than that of acetic acid ($pK_a=4.76$); thus, a reaction in formic acid gives **3** predominantly. In the case of trifluoroacetic acid ($pK_a=0.23$), its acidity is so strong that **2** and products would be further converted to tarry materials. When sulfuric acid ($pK_a=1.99$, Run 12) or chloroacetic acid ($pK_a=2.87$, Run 13) was added to acetic acid solvent, the yield of **3** increased, while the addition of formic acid or sulfuric acid in methanol (Runs 15, 16) and acetone (Run 17) did not improve the yield of **3**.

Table 3 shows the results of a reaction of **2** with several kinds of peroxy compounds. The reaction of **2** with *t*-butyl hydroperoxide (*t*-BuOOH) in methanol-sulfuric acid (Run 19) proceeded more rapidly and gave **3** more dominantly than that in formic acid (Run 18). When *t*-butyl peracetate (Run 20) and 2,2-bis(*t*-butyldioxy)propane (Run 21) were used as oxidants, **3** was also obtained more than **4**. On the other hand, other peroxy compounds such as dibenzoyl peroxide (Run 22), potassium peroxodisulfate (Run 23) and peracetic acid (Run 24) gave **4** predominantly. These results indicate that the nature of the leaving group of the intermediate **1** may affect the relative migratory tendency of the aryl and the hydride groups.

To sum up, polycyclic phenols were obtained from the corresponding aldehydes under the system of MCPBA-CH₂Cl₂, H₂O₂-HCOOH, H₂O₂-CH₃COOH-CH₂ClCOOH or *t*-BuOOH-CH₃OH-H₂SO₄. This reaction provides a new method for the preparation of polycyclic phenols.

Experimental

All melting points were measured by a Yanagimoto micro melting point apparatus and were uncorrected. NMR spectra were taken on a JEOL JMN-FX90 spectrometer. Mass spectra were obtained with a Shimadzu QP-1000 spectrom-

eter. Gas chromatographs were obtained with a Shimadzu GC-9A. All aldehydes, except for **2**, were commercially available and purified by a column chromatography on silica gel with dichloromethane as the eluent. Solvents such as benzene and dichloromethane were dried on Molecular Sieves 3A. All peroxy compounds and acids, except for peracetic acid, were purchased commercially and were used without purification. Peracetic acid was prepared in situ by the reaction of acetic anhydride with aqueous hydrogen peroxide.⁴⁾

Preparation of 2-Dibenzofurancarbaldehyde (2). To a solution of 21.4 g (127 mmol) of dibenzofuran in 40 cm³ of dry benzene was added 38.3 g (287 mmol) of aluminum chloride and 1.2 g (12 mmol) of copper(I) chloride in a 200 cm³ autoclave. It was filled with carbon monoxide until the pressure reached 4.9 MPa; the mixture was then stirred at 40 °C for 3 h maintaining the pressure at 4.9 MPa. The mixture was poured onto 500 g of ice to hydrolyze the complex of the product and aluminum chloride. The aqueous layer was removed; then, the organic layer was washed with 100 cm³ of water and dried (magnesium sulfate). After evaporation in vacuo, the residue was purified by a column chromatography (silica gel, dichloromethane). The eluent was evaporated, and the residual solid was recrystallized from petroleum ether to afford 17.4 g of **2** (70% yield).

2-Dibenzofurancarbaldehyde (2): Mp 61–63 °C; ¹H NMR (CDCl₃) $\delta=7.1$ – 7.4 (4H, m), 7.6 – 7.8 (2H, m), 8.09 (1H, d, $J=2$ Hz) and 9.90 (1H, s, CHO); ¹³C NMR (CDCl₃) $\delta=111.71$, 111.81, 120.75, 122.54, 123.14, 123.30, 124.71, 127.96, 128.66, 131.91, 156.62, 159.27, and 190.69; MS (70 eV) m/z (rel intensity) 196 (M^+ ; 90), 195 (100), 167 (30), and 139 (58); Found: C, 79.62; H, 4.08%; Calcd for C₁₃H₈O₂: C, 79.61; H, 4.08%.

B-V Reaction of 2 with MCPBA. To a solution of 392 mg (2 mmol) of **2** in 5 cm³ of dry dichloromethane was added 414 mg (2.4 mmol) of MCPBA. The mixture was stirred at room temperature under an argon atmosphere for 20 h. An excessive amount of aqueous sodium thiosulfate solution was added to the reaction mixture and no remains of MCPBA were checked by potassium iodide-starch paper. After an addition of 10 cm³ of 2 mol dm⁻³ NaOH and 10 cm³ of methanol, the mixture was stirred for 0.5 h and neutralized to pH 7–8 with 1 mol dm⁻³ HCl and aqueous sodium hydrogencarbonate solution, then extracted with 30 cm³ of dichloromethane. The amounts of **2** and **3** in the organic layer were determined by gas chromatography (200 °C, Fuloxylate-K, 3 mm×2 m) using dimethyl 2,6-naphthalenedicarboxylate as an internal standard. After the organic layer was evaporated, **3** was isolated from the residue by column chromatography (silica gel, dichloromethane) and recrystallization from ethanol.

2-Dibenzofuranol (3): Mp 136–137 °C; $^1\text{H NMR}$ (CDCl_3) δ =4.82 (1H, s, OH), 6.95 (1H, dd, J =9 Hz, 3 Hz), 7.1–7.7 (5H, m), and 7.90 (1H, dd, J =9 Hz, 2 Hz); MS (70 eV) m/z (rel intensity) 184 (M^+ ; 100), 155 (9), 128 (17), and 127 (10); Found: C, 78.07; H, 4.35%; Calcd for $\text{C}_{12}\text{H}_8\text{O}_2$: C, 78.28, H, 4.34%.

The aqueous layer, which contained **4**, was acidified with concentrated HCl and extracted with 30 cm^3 of ethyl acetate. A diazomethane-ether solution was added to the organic layer to convert **4** into the methyl ester; then, the amount of the methyl ester was measured by gas chromatography. The methyl ester was isolated by column chromatography (silica gel, dichloromethane).

Methyl 2-Dibenzofurancarboxylate: $^1\text{H NMR}$ (CDCl_3) δ =3.97 (3H, s), 7.3–7.7 (4H, m), 7.9–8.2 (3H, m), and 8.60 (1H, d, J =2 Hz); MS (70 eV) m/z (rel intensity) 226 (M^+ ; 66), 195 (100), 167 (25), and 139 (31); Found: C, 74.30; H, 4.48%; Calcd for $\text{C}_{14}\text{H}_{10}\text{O}_3$: C, 74.33; H, 4.46%.

The products of the B-V reaction of other aldehydes (Table 1) were analyzed using the same method, except for the reaction of 9-anthracenecarbaldehyde. They were identified through a comparison of their respective retention times in gas chromatography and the mass spectra with those of commercially available chemicals. 9-Anthryl formate was isolated by column chromatography (silica gel, dichloromethane) without an alkaline hydrolysis of the reaction

mixture.

9-Anthryl Formate: Mp 90–91 °C; $^1\text{H NMR}$ (CDCl_3) δ =7.4–7.7 (4H, m), 7.9–8.2 (4H, m), 8.41 (1H, s), and 8.66 (1H, s); MS (70 eV) m/z (rel intensity) 222 (M^+ ; 20), 195 (16), 194 (100), 193 (18), 165 (75), and 163 (14); Found: C, 81.11; H, 4.66%; Calcd for $\text{C}_{15}\text{H}_{10}\text{O}_2$: C, 81.10; H, 4.50%.

References

- 1) The B-V reactions of ketones and aldehydes have been extensively studied, but there are only a few reports on the similar reactions of polycyclic aromatic compounds. a) Y. Ogata and Y. Sawaki, *J. Org. Chem.*, **34**, 3985 (1969). b) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Am. Chem. Soc.*, **80**, 6393 (1958). c) Y. Ogata and Y. Sawaki, *ibid.*, **94**, 4189 (1972).
- 2) Polycyclic aromatic hydrocarbons react with carbon monoxide in the presence of aluminum chloride and hydrogen chloride to yield the corresponding aromatic aldehydes. N. N. Crounse, "Organic Reactions," John Wiley & Sons, Inc., New York (1949), Vol. 5, Chap. 6, pp. 290–300.
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