Facile Oxidation of Polycyclic Arenes and Acetylenic Hydrocarbons with Bis(pyridine)silver Permanganate and Bis(2,2'-bipyridyl)copper(II) Permanganate Under Mild and Neutral Conditions

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The title compounds are used for the oxidation of polycyclic arenes and acetylenic hydrocarbons in dichloromethane at room temperature.

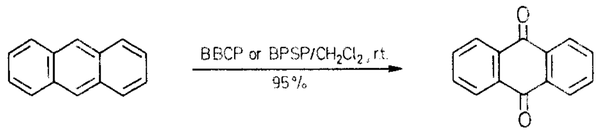
The oxidation of polycyclic arenes with the newly developed oxidants, ceric ammonium sulfate[1], manganese (III) sulfate[2] and phase-transfer permanganate agents[3] is reported to proceed well. Although the yields are good, these reagents encounter more or less the following drawbacks:

- the reaction media is partly aqueous and acidic and,
- the work up of the reaction mixture is tedious. In spite of its slight acidity, the ease of work-up and the mildness of the reaction condition make pyridinium fluorochromate[4], the recently reported oxidant, superior to the above mentioned methods for the oxidation of polycyclic arenes.

We have now found that the oxidation of polycyclic arenes and acetylenic hydrocarbons also proceed well with bis(pyridine)silver permanganate (BPSP)[5] and bis(2,2'-bipyridyl)copper(II) permanganate (BBCP)[6]. These reagents seem to be advantageous over the methods mentioned above, where neutrality, non-aqueous, aprotic media, good yields, and the mildness of the reaction condition are desired. Bis(pyridine)silver permanganate (BPSP) is an expensive and a moderately stable reagent and preferentially could be stored in a refrigerator for weeks. Bis(2,2'-bipyridyl) copper(II) permanganate (BBCP) is stable at room temperature, but precaution in handling of the completely dried reagent should be excercised[7].

Oxidation of anthracene (**1**) and phenanthrene (**3**) with BPSP and BBCP gave their corresponding 9,10-quinones **2** and **4** in high yields (Table). 1,2-Diphenylnaphtho[*b*]cyclobutadiene (**7**) and 1,2-diphenylanthra[*b*]cyclobutadiene (**9**) produced 2,3-dibenzoylnaphthalene (**8**) and 2,3-dibenzoyl anthracene (**10**) respectively in high yields. The yields obtained are much higher than those reported by other methods[8,9].

Oxidation of 2,3-diphenylanthra[*b*]cyclobutadiene (**9**) into 2,3-dibenzoyl-9,10-anthraquinone (**11**) also proceeded very well with these two reagents. 2,3-Dibenzoylanthracene (**10**) afforded 2,3-dibenzoyl-9,10-anthraquinone (**11**) in high



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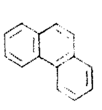
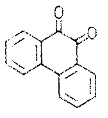
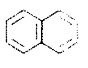
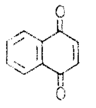
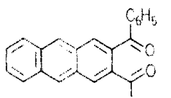
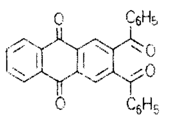
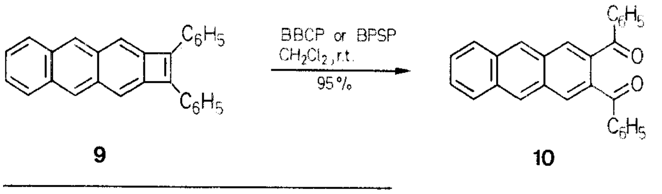
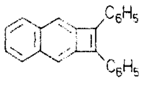
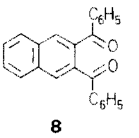
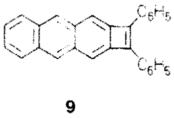
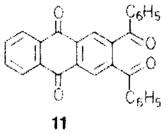
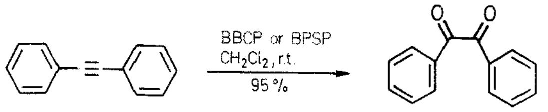
 **3**	 **4**
 **5**	 **6**
 **10**	 **11**



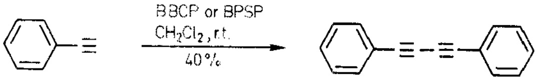
9 **10**

Substrate	Product
 **7**	 **8**
 **9**	 **11**

yield. Diphenylacetylene (**12**) afforded benzil (**13**), and phenylacetylene (**14**) gave 1,4-diphenyl-1,3-butadiyne (**15**) in moderate yield. In contrast, the same oxidation with permanganate/phase-transfer agent gave benzoic acid in high yield[3].



12 **13**



14 **15**

The results obtained in this investigation are listed in a Table along with some of those obtained from other oxidation methods[1,4].

Bis(pyridine)silver permanganate and bis(2,2'-bipyridyl)copper(II) permanganate were prepared according to our recently reported procedures[4,5]. All starting materials and products are known

Table. Oxidation of Polycyclic Arenes and Acetylenic Hydrocarbons with Bis(pyridine)silver Permanganate (BPSP) and Bis(2,2'-bipyridyl)copper(II) permanganate (BBCP), and their Yields in Comparison with Ceric Ammonium Sulfate (CAS), Manganese(III) Sulfate (MS), Phase-Transfer Permanganate Agents (PTP), and Pyridinium Fluorochromate (PFC) Oxidations

Reactant	Product	BPSP			BBCP					CAS[1]	MS[2]	PTP[3]	PFC[4]
		Oxidant Reactant	Reaction Conditions	Yield [%]	Oxidant Reactant	Reaction Conditions	Yield [%]	m.p. [°C]	Lit. m.p. [°C]	Yield [%]	Yield [%]	Yield [%]	Yield [%]
1	**2**	6	r.t./8h	95	4	r.t./16h	80	283–284	283.5–285[10]	–	80	75	68/98
3	**4**	6	r.t./16h	85	6	r.t./20h	70	207–208	209–211[10]	60	32	75	52/72
5	**6**	6	r.t./24h	0	6	r.t./24h	0	–	–	95	75	–	25
7	**8**	2	r.t./0.08h	80	2	r.t./0.08h	80	142–144	142–145[8]	–	–	–	–
9	**10**	2	r.t./0.08h	95	2	r.t./0.08h	90	189–191	189–191[9]	–	–	–	–
9	**11**	14	r.t./6h	70	16	r.t./24	60	242–244	244–245[9]	–	–	–	–
10	**11**	12	r.t./6h	70	14	r.t./24	70	242–244	244–254[9]	–	–	–	–
12	**13**	6	r.t./5h	95	6	r.t./18h	69	92–93	94–95[10]	–	–	93	–
14	**15**	2	r.t./2h	40	2	r.t./2h	30	83–85	86–87[10]	–	–	–	–

compounds. IR spectra were recorded on a Perkin-Elmer IR 157G. Melting points were determined in open capillaries on a Buchi 510 apparatus. Yields given in the Table refer to isolated products.

Oxidation of Diphenylacetylene (12) to Benzil (13); Typical Procedure:

To a solution of diphenylacetylene (178 mg, 1 mmol) in dichloromethane (25 ml), bis(pyridine)silver permanganate (3.23 g, 6 mmol) is added. The reaction mixture is stirred mangnetically at room temperature for 8 h. The progress of the reaction is monitored by TLC (eluent: benzene). The mixture is filtered and the filtrate is evaporated on a rotory evaporator. The resulting product is purified by column chromatography on silica gel using *n*-hexane (25 ml) and then benzene (50 ml) as eluents. Evaporation of the benzene fraction affords white crystals of benzil (**13**); yield: 190 mg (95%); m.p. 92–93 °C (Lit.[9], m.p. 94–95 °C).

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