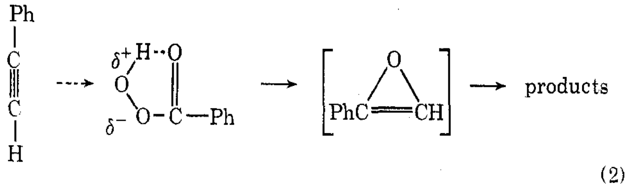
peroxidic oxygen to form the oxirene ring. Since PBA in benzene forms a five-membered intramolecular hydrogen bond, the mode of attack may be as follows.



(2)

The effect of substituents on the PBA epoxidation of styrenes[13] was reported to be correlated with the Yukawa–Tsuno equation[14] [$\log (k/k_0) = \rho (\sigma + r\Delta\sigma^+_R)$] ($\rho = -1.30$ and $r = 0.48$). The ratio of the ρ value for the PBA oxidation of phenylacetylenes to that for styrenes at 25.0° was 1.08. The ρ value (*vs.* σ^+) for acid-catalyzed hydration of phenylacetylenes[10] (−3.84) and that of styrenes[15] (−3.42) give a ratio of 1.12, which is close to the above ratio for the peracid oxidation. Hence, the attacks of peroxidic oxygen on triple and double bonds possess a polar effect analogous to that observed in protonation.

The r value in the Yukawa–Tsuno equation for our reaction is 1.0, which is larger than the r value of 0.48 for styrenes. The higher r value, *i.e.*, larger contribution of resonance for phenylacetylenes, shows that less (*ca.* $^1/_{60}$) reactive phenylacetylenes have a transition state stabilized more by conjugation between the reaction site and the phenyl group. One of the p orbitals of the triple bond, which is coplanar with the benzene ring, seems to participate in the reaction in the transition state. When its p-orbital electrons attack peroxidic oxygen, the positive charge generated on the reaction site is stabilized by delocalization to p orbitals of the benzene ring.

The solvent effect is shown in Table II. Addition of ethanol, a more basic solvent, to the nonpolar solvent benzene markedly decreases the rate. The peracid forms an intramolecular hydrogen bond in benzene.[16] The intramolecular bond changes to the intermolecular one by addition of more basic ethanol resulting in a decrease of rate. Strangely, the rate in aqueous ethanol is higher than that in benzene–ethanol. This suggests that the oxidation rate *via* an intermolecular hydrogen bonded peracid is increased by increasing solvent polarity as well as by decreasing solvent basicity. In fact, the same result has been obtained in the epoxidation of styrene.[17]

TABLE II

SOLVENT EFFECT ON THE SECOND-ORDER RATE CONSTANTS (k) FOR THE REACTION OF PHENYL- AND p-METHYLPHENYLACETYLENES WITH PERBENZOIC ACID AT 25.0 ± 0.1°

Solvent (v/v)	$C_6H_5C{\equiv}CH$, $10^5\,k$, $M^{-1}\,sec^{-1}$	p-$MeC_6H_4C{\equiv}CH$, $10^5\,k$, $M^{-1}\,sec^{-1}$
C_6H_6	2.5^a	6.8^a
C_6H_6:EtOH (75:25)	1.1^a	
C_6H_6:EtOH (50:50)	0.55^a	
EtOH	0.1^a	0.1^b
EtOH:H_2O (80:20)	0.2^b	0.5^b
EtOH:H_2O (50:50)	1.2^b $(1.5)^a$	2.7^b
EtOH:H_2O (40:60)	1.8^a	
EtOH:H_2O (50:50) buffered by 0.1 M Na_2CO_3	Very small ^{a,b}	Very small^{a,c}
EtOH:H_2O (40:60) buffered by 0.1 M Na_2CO_3	Very small^{a,b}	

[a] Rate constants were calculated from a decrease of perbenzoic acid. [b] Rate constants were calculated from a decrease of $RC_6H_4C{\equiv}CH$. [c] m-Bromophenylacetylene was used instead of p-methylphenylacetylene.

Peracid becomes its anion in aqueous ethanol buffered by Na_2CO_3, but the reaction of phenylacetylenes with perbenzoate ion was not appreciable, probably because the electrophilicity of acetylene is rather weak and the anion may spontaneously decompose faster than its attack on the triple bond.

Experimental Section

Materials.—p-Methoxyphenylacetylene,[18a] bp 110–114° (24 mm), and m-nitrophenylacetylene,[18b] bp 120–123° (24 mm) [lit.[18b] bp 118–120° (20 mm)], were synthesized from the corresponding cinnamic acids. Other substituted phenylacetylenes were prepared from the corresponding acetophenones.[19] Substituent and melting point or boiling point were p-Cl, mp 46.5–47.0°; m-Br, 96–98° (22 mm); p-Me, bp 70.0–70.5° (23 mm) [lit.[19] bp 79–81° (31–33 mm)]; and unsubstituted, bp 46.5–47.0° (20 mm) [lit.[20] bp 137–139° (760 mm)]. They were identified by their ir spectra,[21] their purities being checked by glc. Perbenzoic acid was prepared by the reaction of benzoyl peroxide with hydrogen peroxide[22] and recrystallized from hexane.

Kinetics.—The rate of consumption of PBA was followed iodometrically. The rate of consumption of phenylacetylenes was determined by glc, using anisole as an internal standard with a column (2 m) of 3 wt % Apiezon grease L on Celite 545 (80–100 mesh) and N_2 as a carrier gas (20 ml/min) at the starting temperature of 50°, which was elevated at a rate of 6°/min. An aliquot was removed and added to a known amount of anisole, and the remaining PBA was decomposed by addition of dimethyl sulfoxide. The resulting benzene solution was washed with aqueous $NaHCO_3$ to remove acidic components, dried (Na_2SO_4), and analyzed by glc. This procedure was done for a mixture of two kinds of phenylacetylenes with the reaction time between 0 and 48 hr, the relative rate constant (k_R/k_H) being calculated from this competitive reaction. Assuming rate constants for two kinds of phenylacetylenes to be k_A and k_B, their initial concentrations, a and b, and their consumed concentrations at a given time, x and y, respectively, the relative rate constant (k_A/k_B) is given by eq 3.

$$k_A/k_B = \ln [(a - x)/a]/\ln [(b - y)/b] \quad (3)$$

Registry No.—PBA, 93-59-4

---

(13) Y. Ishii and Y. Inamoto, *Kogyo Kagaku Zassi*, **63**, 765 (1960).

(14) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 965 (1959).

(15) W. M. Schubert, B. Lamm, and J. R. Keeffe, *J. Amer. Chem. Soc.*, **86**, 4727 (1964).

(16) R. Curci, R. A. DiPrete, J. O. Edwards, and G. Modena, *J. Org. Chem.*, **35**, 740 (1970).

(17) Y. Ogata and Y. Sawaki, unpublished results.

(18) (a) J. D. Fulton and R. Robinson, *J. Chem. Soc.*, 1463 (1933); (b) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **41**, 1084 (1963).

(19) J. L. Jacobs, *Org. React.*, **5**, 50 (1949).

(20) H. Fiesselmann and K. Sasse, *Chem. Ber.*, **89**, 1775 (1956).

(21) A. D. Allen and C. D. Cook, *Can. J. Chem.*, **41**, 1084 (1963).

(22) Y. Ogata and Y. Sawaki, *Tetrahedron*, **22**, 3329 (1967).

Anodic Oxidations. V.[1] Aromatic Cyanation of Methoxydiphenylacetylenes

KUNIHISA YOSHIDA* AND TAKAYUKI FUENO

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan

Received March 27, 1972

We at first anticipated that, if the anodic oxidation of diphenylacetylene is conducted under the cyanation

---

(1) Part IV: K. Yoshida, T. Saeki, and T. Fueno, *J. Org. Chem.*, **36**, 3673 (1971).

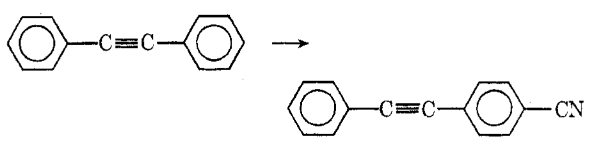
Table I

Anodic Cyanation of Diphenylacetylenes[a]

Reactant	Electricity, F	Conversion, %	Product	Current efficiency, %	Yield,[b] %
Diphenylacetylene	0.023	59	4-Cyanodiphenylacetylene	31	60
2-Methoxydiphenylacetylene	0.007	34	2-Cyanodiphenylacetylene	11	12
			2-Methoxy-4-cyanodiphenylacetylene	4	5
3-Methoxydiphenylacetylene	0.037	81	3-Cyanodiphenylacetylene		Trace
			3-Methoxy-4-cyanodiphenylacetylene	9	23
4-Methoxydiphenylacetylene	0.014	57	4-Cyanodiphenylacetylene	15	18

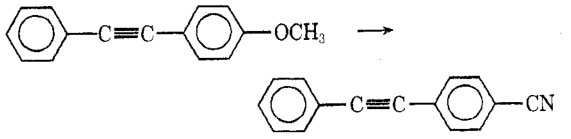
[a] [NaCN] = 0.8 *M;* [diphenylacetylene] = 0.2 *M* (3-methoxydiphenylacetylene did not give a homogeneous solution owing to its limited solubility); platinum electrode; two-compartment cell; anode potential, 2.0 V *vs.* sce; temperature, 25°; reaction time, 24 hr; current density, *ca.* 0.003 A/cm². [b] Based on consumed acetylene compounds.

conditions, the cyanide ion would attack the acetylenic bond to yield α-phenylcinnamonitrile derivatives. However, the product formed was found to be exclusively 4-cyanodiphenylacetylene, an aromatic substitution product (reaction type 1).[2]


(1)

We have extended the work to methoxydiphenylacetylenes. Oxidations were carried out in methanolic sodium cyanide at an anode potential of +2.0 V *vs.* sce. The results are summarized in Table I.

4-Methoxydiphenylacetylene underwent replacement of the methoxyl group by the nitrile group to yield 4-cyanodiphenylacetylene (reaction type 2).[3] With 3-methoxydiphenylacetylene, the product obtained was 3-methoxy-4-cyanodiphenylacetylene, which was formed by substitution of para hydrogen atom (reaction type 1). With 2-methoxydiphenylacetylene, both types of reactions, 1 and 2, occurred, the latter being somewhat prevalent. In all these cases, the yields of cyanated products were rather low, because of unavoidable side reactions giving a tarry residue.


(2)

By analogy with other anodic cyanations,[1,4] the primary electrode process is considered to be the oxidation of diphenylacetylene to a cationic species (most likely a cation radical) which subsequently reacts with cyanide ion.

Experimental Section

The electrochemical and spectroscopic instrumentation and techniques were as previously described.[4]

Materials.—Methanol was purified by fractional distillation from magnesium activated with iodine. Reagent grade sodium cyanide was used with no purification other than drying.

Acetylene compounds were prepared according to known procedures.[5,6] 3-Methoxydiphenylacetylene had mp 79–80° (from methanol); ir 2230 (C≡C), 1037 (COC), 866, 798, 770, and 686 cm^{-1} (mono- and 1,3 substitution); nmr (CCl_4) τ 2.45–3.35 (9 H, m) and 6.27 (3 H, s). 2-Cyanodiphenylacetylene had bp 130° (1 mm). 3-Cyanodiphenylacetylene had mp 70–71°.

Procedure.—Acetylene compound (0.01 mol) in 50 ml of methanol–sodium cyanide (0.8 *M*) was electrolyzed at a controlled anode potential. The electrolyzed mixture was treated with water and the organic material was extracted with ether. The ether was removed by distillation and the residue was chromatographed on alumina using benzene as an eluent. Unreacted starting material was first eluted, followed by cyanated products.

Identification of Product.—Cyanated products were characterized by elemental analyses, by ir, nmr, and mass spectra, and by comparison with authentic samples.

2-Cyanodiphenylacetylene had bp 130° (1 mm); ir 2240 (CN and/or C≡C), 757, and 686 cm^{-1} (mono- and 1,2 substitution); nmr (CCl_4) τ 2.3–2.8 (m).

Anal. Calcd for $C_{15}H_9N$: C, 88.64; H, 4.46; N, 6.89. Found: C, 88.89; H, 4.53; N, 6.83.

3-Cyanodiphenylacetylene had mp 70–71° (from ethanol); ir 2240, 2230 (CN and C≡C), 890, 795 (1,3 substitution), 758, and 677 cm^{-1} (monosubstitution); nmr (CCl_4) τ 2.1–2.8 (m).

4-Cyanodiphenylacetylene had mp 108.5–109.5° (from ethanol); ir 2240, 2230 (CN and C≡C), 845 (1,4 substitution), 760, and 690 cm^{-1} (monosubstitution); nmr (CCl_4) τ 2.40 (4 H, s) 2.4–2.7 (5 H, m). *Anal.* Calcd for $C_{15}H_9N$: C, 88.64; H, 4.46; N, 6.89; mol wt, 203.24. Found: C, 88.67; H, 4.47; N, 6.88; mol wt, 203 (mass spectroscopy).

2-Methoxy-4-cyanodiphenylacetylene had mp 106–107° (from ethanol); ir 2240 (CN and/or C≡C), 1172, 1115, 1030 (COC), 879, 823 (1,2,4 substitution), 756, and 688 cm^{-1} (monosubstitution); nmr (CCl_4) τ 2.4–3.0 (8 H, m) and 6.7 (3 H, s). *Anal.* Calcd for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.00. Found: C, 82.35; H, 4.82; N, 5.90.

3-Methoxy-4-cyanodiphenylacetylene had mp 142.5–144.5° (from ethanol); ir 2240, 2230 (CN and C≡C), 1117, 1026 (COC), 859, 836 (1,2,4 substitution), 762, and 687 cm^{-1} (monosubstitution); nmr (CCl_4) τ 2.44–3.02 (8 H, m) and 6.03 (3 H, s). *Anal.* Calcd for $C_{16}H_{11}NO$: C, 82.38; H, 4.75; N, 6.00; mol wt, 233.27. Found: C, 82.26; H, 4.74; N, 6.01; mol wt, 233 (mass spectroscopy).

Registry No.—3-Methoxydiphenylacetylene, 37696-01-8; 2-cyanodiphenylacetylene, 32183-76-9; 3-cyanodiphenylacetylene, 37696-03-0; 4-cyanodiphenylacetylene, 29822-79-5; 2-methoxy-4-cyanodiphenylacetylene, 37696-05-2; 3-methoxy-4-cyanodiphenylacetylene, 37696-06-3.

Acknowledgment.—This work was partially supported by a grant (Shorei A) from the Ministry of Education.

---

(2) K. Yoshida and T. Fueno, *Chem. Commun.*, 711 (1970).

(3) A replacement of aromatic methoxyl by nitrile has been reported in the case of dimethoxybenzenes: S. Andreades and E. W. Zahnow, *J. Amer. Chem. Soc.*, **91**, 4181 (1969).

(4) K. Yoshida and T. Fueno, *J. Org. Chem.*, **36**, 1523 (1971).

(5) L. I. Smith and M. M. Falkof, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 350.

(6) R. D. Stephens and C. E. Castro, *J. Org. Chem.*, **28**, 3313 (1963).