large sample of eicosanedioic acid was very generously furnished by the Shell Chemical Company. The determinations and analyses of the infrared spectra of samples of tetranonacontane obtained at various stages during the purification by Dr. John Y. Beach of the California Research Corporation is gratefully acknowledged. The viscosities and densities were determined by George H. Neff.

Oxidation of Alkylarenes with Aqueous Sodium Dichromate. A Useful Method for Preparing Mono- and Polyaromatic Carboxylic Acids[1]

L. Friedman,[2] D. L. Fishel, and H. Shechter

Department of Chemistry, The Ohio State University, Columbus 10, Ohio

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Mono- and polyalkyl-substituted polycyclic aromatic hydrocarbons are generally oxidized conveniently and in excellent yields to their corresponding polynuclear carboxylic acids by aqueous sodium dichromate at 225–250° in metal equipment. Selective conversion of hydrocarbons such as 1- and 2-methylnaphthalenes, 1,2- and 2,6-dimethylnaphthalenes, 4-methylphenanthrene, 2-methyltriphenylene, 6-methylcrysene, 3-picoline, and 3-methylthiophene to their aromatic or heterocyclic carboxylic acids illustrates the utility of sodium dichromate as an oxidant. Typical procedures for effecting oxidation in various types of equipment are described; the effects of excess oxidant and of buffers on the stoichiometry, selectivity, and rates of oxidation of various hydrocarbons have been investigated. Oxidations of benzene and naphthalene derivatives containing halogen, methoxyl, and nitro groups in various positions have been studied; general limitations of the oxidation method imparted by substituents and their positions have been defined.

Aromatic mono- and polycarboxylic acids are important intermediates in chemistry and considerable effort has been expended into developing methods[3] for their preparation. A particularly attractive method is the oxidation of side chains of mononuclear hydrocarbons[4] such as toluene to benzoic acid and *p*-xylene to terephthalic acid, etc. The oxidants usually used are air,[5a] acid or alkaline permanganate,[5b] chromic acid,[5c] nitric acid,[5d] potassium ferricyanide,[5e] and more recently sulfur and some of its oxidized derivatives.[5f] With the possible exceptions of potassium ferricyanide, the sulfur processes, and air oxidation, all of the aforementioned reagents are generally unsuccessful when applied to alkylated polynuclear aromatic systems because they result in extensive ring degradation. For example, 2-methylnaphthalene is oxidized by chromic acid to 2-methylnaphthoquinone[6a]; this reaction involves only nuclear oxidation. Similarly, anthracene is oxidized to anthraquinone[6b] and phenanthrene to phenanthraquinone,[6a,b] etc.

The problem of oxidizing 2-methylnaphthalene to 2-naphthoic acid is formidable. The common oxidizing agents[7a,b] either (a) completely destroy the compound, (b) attack the nucleus, or (c) effect electrophilic substitution.[7b,d] Potassium ferricyanide[7c] will slowly oxidize 2-methylnaphthalene to 2-naphthoic acid but the yield is poor and the product is accompanied by phthalic acid. These difficulties are common to all aromatic polycyclic systems.

The objective of the present investigation was to develop a general method for oxidation of alkylarenes to their corresponding acids. Oxidation of toluene,[8a] chlorotoluenes,[8b] xylenes,[8b] acenaphthene,[8b,c] and 3-picoline[8e] to their corresponding acids by aqueous sodium dichromate at elevated temperatures and pressures has been reported. Large excesses and high concentrations of sodium dichromate resulted in excessive nuclear destruction in oxidation of acenaphthene[8d]; yields of 1,8-naphthalic acid greater than 85% were obtained, however, at 200–210° using a 50% excess of 15–25% aqueous sodium dichromate.[8d]

A number of representative polynuclear hydrocarbons were thus subjected to 30% aqueous sodium dichromate at 250° for 15–18 hr. to determine their resistance to nuclear oxidation. Naphthalene, biphenyl, *o*-, *m*-, and *p*-terphenyls, phenanthrene, fluoranthene, and picene are essentially completely resistant under these conditions. *The stabilities of these hydrocarbons to aqueous sodium dichromate are quite remarkable in view*

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(1) (a) Abstracted in part from the Ph.D. Dissertations of L. Friedman, The Ohio State University, 1959, and D. L. Fishel, The Ohio State University, 1959; (b) presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, Abstracts, p. 66U, and in part of the 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1959, Abstracts, p. 22P.

(2) From whom reprints may be obtained: Department of Chemistry, Case Institute of Technology, Cleveland, Ohio 44106.

(3) The preparation of carboxylic acids has been reviewed in "Methoden der Organischen Chemie" [Vol. VIII, part 3, E. Muller, Ed., George Thieme Verlag, Stuttgart, 1952].

(4) H. Henecka, ref. 3, pp. 384–400.

(5) For leading references: (a) D. E. Burney, G. H. Weiseman, and N. Fragen, Proceedings of the 5th World Petroleum Congress, New York, N. Y. 1959, Vol. IV, p. 197; A. Saffer and R. S. Barker, U. S. Patent 2,833,817 (1958); (b) W. H. Mills, *J. Chem. Soc.*, 3191 (1912); C. F. Cullis and J. W. Ladbury, *ibid.*, 4196 (1953); (c) O. Jacobsen, *Chem. Ber.*, **18**, 1701 (1885); (d) H. Meyer and K. Bernhauer, *Monatsh. Chem.*, **53/54**, 742 (1929); E. Zaugg and R. T. Rapalla, *Org. Syn.*, **27**, 84 (1947); (e) W. A. Noyes, *Am. Chem. J.*, **11**, 161 (1889); (f) W. G. Toland, D. C. Hagmann, J. B. Wilkes, and F. J. Boutscky, *J. Am. Chem. Soc.*, **80**, 5423 (1958); W. G. Toland, *ibid.*, **82**, 1911 (1960).

(6) (a) L. F. Fieser, W. P. Campbell, E. M. Fry, and M. D. Gates, Jr., *J. Am. Chem. Soc.*, **61**, 3218 (1939); (b) K. H. Klipstein, *Ind. Eng. Chem.*, **18**, 1327 (1926); (c) R. P. Linstead and P. Levine, *J. Am. Chem. Soc.*, **64**, 2023 (1942).

(7) (a) For the action of chromic acid, see ref. 6a. Potassium permanganate or air oxidize 2-methylnaphthalene to phthalonic and phthalic acids. (b) Nitric acid gives nitro compounds, phthalic acid, and 2-naphthoic acids: I. N. Nazarov, N. V. Kuznetzov, and A. V. Semenovskii, *Dokl. Akad. Nauk. SSSR*, **99**, 1003 (1954). (c) R. Weissgerber and O. Kruber, *Chem. Ber.*, **52**, 346 (1919). (d) Note Added in Proof.—Recently, it was shown that alkyl aromatics, such as 2,6-dimethylnaphthalene, can be selectively oxidized by nitrogen dioxide and selenium dioxide (cooxidant or catalyst) to the corresponding aromatic acids in high yield: H. J. Peterson, A. P. Stuart, and W. D. Vanderwerff, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 230 (1964).

(8) (a) Bozel-Maletra Soc. Ind. de Prod. Chim., German Patent 537,982 (1930); (b) *Bios*, Report No. 1786; (c) J. Ogilvie and R. S. Wilder, U. S. Patent 2,379,032 (1945); (d) S. Kato, H. Hashimoto, and H. Sugiyama, *J. Soc. Org. Syn. Chem. Japan*, **14**, 123 (1956); (e) J. Ogilvie and A. J. Sweet; U. S. Patent 2,415,147 (1947).

TABLE I

OXIDATION OF SUBSTITUTED POLYCYCLIC AROMATIC HYDROCARBONS WITH AQUEOUS SODIUM DICHROMATE[a]

Hydrocarbon	Sodium dichromate,[b] % excess	Product	Yield, %[c]	M.p., °C.[d]
1-Methylnaphthalene	42	1-Naphthoic acid	95	160–161
2-Methylnaphthalene	55	2-Naphthoic acid	93	184–185
1,2-Dimethylnaphthalene	47	1,2-Naphthalic anhydride[e]	75	167–168
2,3-Dimethylnaphthalene	23	2,3-Naphthalenedicarboxylic acid	93	237–239
1,6-Dimethylnaphthalene	43	1,6-Naphthalenedicarboxylic acid	97	300[f]
2,6-Dimethylnaphthalene	43	2,6-Naphthalenedicarboxylic acid	99	300[f]
4-Methylbiphenyl	20	4-Biphenylcarboxylic acid	95	225–226
3-Methylfluorenone	34	Fluorenone-3-carboxylic acid	88	283–285
1-Methylphenanthrene	40	1-Phenanthroic acid	91	230–231
4-Methylphenanthrene	40	4-Phenanthroic acid	91	169–170
9-Methylphenanthrene	40	9-Phenanthroic acid	89	243–249
1-Methyl-7-isopropylphenanthrene	40[g]	1,7-Phenanthrenedicarboxylic acid[h]	89	300
9,10-Dimethylphenanthrene	40	9,10-Phenanthrenedicarboxylic anhydride[e]	92	317–318
2-Methylanthracene	42	2-Anthroic acid	98	274–276
2-Methylanthracene	55	Anthraquinone-2-carboxylic acid	95	285–287
2-Methylanthraquinone	40	Anthraquinone-2-carboxylic acid	96	285–287
2-Methyltriphenylene	50	2-Triphenylenecarboxylic acid	92	332–334[f]
6-Methylchrysene	40	6-Chrysenecarboxylic acid	88	308–310
5-Methylbenzo[*c*]phenanthrene	40	5-Benzo[*c*]phenanthrenecarboxylic acid	90	231–233
3-Methylfluoranthene	50	3-Fluoranthenecarboxylic acid	90	285–290[f]
Fluorene	70	Fluorenone	99	82–83
4H-Cyclopenta[*d,e,f*]phenanthrene	50	4-H-Cyclopenta[*d,e,f*]phenanthrene-4-one	95	169–170

[a] Rocking autoclave, 250°, 18 hr. [b] Based on stoichiometry of eq. 1. [c] Based on initial hydrocarbon. [d] Melting points are in agreement with values in Elsevier's "Encyclopaedia of Organic Chemistry," Elsevier Publishing Co., Inc., Amsterdam, and I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, or are otherwise indicated. [e] See Experimental. [f] Also characterized as the methyl ester. [g] The theoretical stoichiometry for oxidation of an isopropyl group requires 3 moles of sodium dichromate. [h] Esterification with methanol and sulfuric acid gave dimethyl 1,7-phenanthrenedicarboxylate, m.p. 148–149°; L. Ruzicka, G. B. R. Graaff, and J. R. Hosking [*Helv. Chim. Acta*, **14**, 238 (1931)] report m.p. 151–152°.

of the known effects of other oxidizing agents.[9] Fluorene was oxidized by sodium dichromate at 250° to fluorenone (99% yield), anthracene to anthraquinone (99%), 1,2-benzanthracene to 1,2-benzanthraquinone (96%), and 4H-cyclopenta[*d,e,f*]phenanthrene (4,5-methylenephenanthrene) to 4H-cyclopenta[*d,e,f*]phenanthren-4-one (94%). At 200–210° anthracene and 1,2-benzanthracene are essentially unattacked; pyrene and dihydropyrene are highly degraded however.

The utility of aqueous sodium dichromate as a selective oxidant was indicated by its oxidation of 1-methylnaphthalene and 2-methylnaphthalene at 240–250° to 1-naphthoic acid (95% yield) and 2-naphthoic acid (93% yield, Table I). It is of importance to note the difference in products and the selectivity of this method with that of oxidation of 2-methylnaphthalene with other reagents.[6,7] Oxidation of a methyl group of an aromatic hydrocarbon to the corresponding carboxylic acid requires 1 mole of sodium dichromate (eq. 1).

$$\mathrm{Ar{-}CH_3 + Na_2Cr_2O_7 \longrightarrow Ar{-}CO_2Na + NaOH + Cr_2O_3 + H_2O} \quad (1)$$

Sodium hydroxide is formed during the conversion and slows oxidation. To minimize retardation it was of advantage to use up to 50% excess sodium dichromate as a buffer.[10] The stoichiometry of oxidation thus becomes as shown by eq. 2.

$$\mathrm{Ar{-}CH_3 + 1.5Na_2Cr_2O_7 \longrightarrow Ar{-}CO_2Na + Na_2CrO_4 + Cr_2O_3 + 1.5H_2O} \quad (2)$$

Under such conditions the initial pH of the reaction medium is 4.5–5, the final pH between 7 and 8, and little or no nuclear degradation occurs.

Oxidations with aqueous sodium dichromate were extended to various methy-l, polymethyl-, and alkyl-substituted polycyclic aromatic hydrocarbons (Table I). This method of oxidation is very effective and convenient for converting the hydrocarbons to their corresponding carboxylic acids. Typical of the selectivity of the oxidation method (Table I) is conversion of 1,6-dimethylnaphthalene, 4-methylphenanthrene, 2-methyltriphenylene, and 6-methylchrysene to 1,6-naphthalenedicarboxylic acid, 4-phenanthroic acid, 2-triphenylenecarboxylic acid, and 6-chrysenecarboxylic acid with no nuclear degradation. 3-Methylfluorenone and 2-methylanthraquinone are oxidized to fluorenone-3-carboxylic and anthraquinone-2-carboxylic acids, respectively; anthraquinone-2-carboxylic acid is also obtained from 2-methylanthraquinone. The conversions of 1,2- and 2,3-dimethylnaphthalenes to 1,2- and 2,3-naphthalenedicarboxylic acids are quite sensitive[11] to the amount of excess dichromate. The susceptibility of vicinal aromatic dicarboxylic acids to further oxidation is not unique to sodium dichromate.[12] It is emphasized that the quality of a crude acid obtained by acidification of a reaction mixture is excellent: the melting point is usually within one or two degrees of an

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(9) The literature of the occasional successes and the complications in oxidation of alkylated polyaromatic compounds to polyaromatic carboxylic acids is summarized in the dissertation of L. Friedman, *Dissertation Abstr.*, **20**, 3953 (1960) (University Microfilms, LC Card No. Mic 60-1181).

(10) Buffering can also be effected with carbon dioxide: J. Yamashita, K. Kurashima, and S. Kato, *Yuki Gosei Kagaku Kyokai Shi*, **20**, 277 (1962); *Chem. Abstr.*, **57**, 16512 (1962).

(11) Oxidation of 2,3-dimethylnaphthalene with 63% excess dichromate gave 2,3-naphthalenedicarboxylic acid in 55–65% yields; with larger excesses, more extensive ring destruction occurred and large quantities of carbon dioxide were formed. The best yield, 95%, was obtained with a 23% excess of dichromate. *Cf.* L. Friedman, *Org. Syn.*, **43**, 80 (1963).

(12) Compare with the actions of chromic acid or potassium permanganate on phthalic acid. *Cf.* R. Fittig and P. Bieber, *Ann.*, **156**, 242 (1870); B. W. Tronow and A. A. Grigorjewa, *J. Phys. Chem.* (USSR), **61**, 657 (1929).

accepted value, the neutralization equivalent agrees with theory, and the color is snow-white.[13]

Interest in 1,2-naphthalic acid was such that alternate routes for the preparation of it were developed. 1-Hydroxymethyl-2-methylnaphthalene[14a,b] was conveniently prepared from 2-methylnaphthalene *via* chloromethylation[14c] and hydrolysis. Oxidation of 1-hydroxymethyl-2-methylnaphthalene with sodium dichromate in the usual manner gave 1,2-naphthalic acid in 65–75% yields.[14d] Similarly, oxidation of 3-methyl-1-naphthoic acid[15] yields 1,2-naphthalic acid.

Use of sodium dichromate was extended to heterocyclic and simpler aromatic compounds (Table II). Propenylbenzene and *trans*-stilbene are oxidized essentially quantitatively to benzoic acid; an aromatic ring and not just a double bond conjugated with a phenyl group is necessary for resistance to sodium dichromate. *t*-Butylbenzene is quite inert to alkaline dichromate; on reaction with a large excess of oxidant (18 hr.), only 15% was coverted to benzoic acid. Oxidation of *p*-*t*-butyltoluene yielded *p*-*t*-butylbenzoic acid (~86%) and minor amounts of terephthalic acid (~8%); the *meta* derivative gave *m*-*t*-Butylbenzoic acid (77–80%); the hindered derivative, *o*-*t*-butyltoluene, yielded *o*-*t*-butylbenzoic acid (>70%).[16] The lack of reactivity of *t*-butyl groups is consistent with the limited action of other oxidants on *t*-butylbenzene and related derivatives. It appears that oxidation with aqueous alkali dichromate at pH 4–7 probably involves free-radical attack at benzylic carbon.[17]

Table II

Oxidation of Substituted Benzenes with Aqueous Sodium Dichromate[a]

Compd.[b]	Sodium dichromate,[c] % excess	Sodium dichromate–water (w./w.)	Product	% yield[d]
m-*t*-Butyltoluene	66	0.60	*m*-*t*-Butylbenzoic acid	71
o-*t*-Butyltoluene	45	0.22	*o*-*t*-Butylbenzoic acid[e]	70
p-Cymene	50[f]	0.70	Terephthalic acid	92
o-Fluorotoluene	100	0.38	. . .[g]	
m-Fluorotoluene	50	0.50	*m*-Fluorobenzoic acid	35
p-Fluorotoluene	50	0.33	*p*-Fluorobenzoic acid[g]	21
p-Fluorotoluene	50 + B[h]	0.19	*p*-Fluorobenzoic acid	55
o-Chlorotoluene	100	0.23	*o*-Chlorobenzoic acid	98
m-Chlorotoluene	50	0.33	*m*-Chlorobenzoic acid	73
p-Chlorotoluene	50	0.33	*p*-Chlorobenzoic acid	88
o-Bromotoluene	50	0.30	*o*-Bromobenzoic acid	92
o-Nitrotoluene	. . .[i]	. .	. . .[g]	
m-Nitrotoluene	200 + B[j]	0.17	*m*-Nitrobenzoic acid	82
p-Nitrotoluene	200 + B[i]	0.17	*p*-Nitrobenzoic acid	94
2-Chloro-*p*-xylene	50	0.50	Chloroterephthalic acid	82
2-Bromo-*p*-xylene	22	0.40	Bromoterephthalic acid	68
2-Iodo-*p*-xylene	20	0.25	Iodeterphthalic acid	83
m-Methoxytoluene	150 + B[h]	0.17	*m*-Methoxybenzoic acid	70
2-Methoxy-*p*-xylene	25 + B[h]	0.25	Methoxyterephthalic acid	48
Phenyl *p*-tolyl ether	50	. .	*p*-Phenoxybenzoic acid	
Di-*p*-tolyl ether[k]	50	. .	Diphenyl ether 4,4′-dicarboxylic acid	

[a] Rocking autoclave, 250°, 18 hr. [b] Propenylbenzene (0.1 mole), sodium dichromate (0.5 mole), and water (250 ml.) gave benzoic acid (100%); *trans*-stilbene (0.056 mole), sodium dichromate (0.13 mole, 75% excess), and water (150 ml.) also gave benzoic acid (97%). [c] Based on stoichiometry of eq. 1. [d] Based on initial starting material; footnote *d*, Table I. [e] Unpurified product contaminated with phthalic acid. [f] Footnote *g*, Table I. [g] Products were carbon dioxide and tars. [h] Buffer B/moles of methyl group; B is 5.0 moles of $NaH_2PO_4 \cdot H_2O$. [i] Various ratios of sodium dichromate and buffers were used. [j] 3.0 moles of KH_2PO_4 and 2.0 moles of H_3PO_4. [k] 1,2-Naphthalic acid was obtained in 64% yield by oxidation of 1-hydroxymethyl-2-methylnaphthalene (0.25 mole) with sodium dichromate (0.54 mole, 30% excess) and water (250 ml.) and in 51% yield from 2-methyl-1-naphthoic acid (0.3 mole), sodium dichromate (0.4 mole, 25% excess), and water (250 ml.). Use of larger excesses of sodium dichromate decreased the yield.

p-*t*-Butyltoluene was oxidized in the presence of various buffers (Table III). The objectives were to evaluate the effects of buffers on the conversion, efficiency, degree of selectivity, and convenience in oxidation. Sodium hydroxide converts dichromate to chromate and this markedly retards oxidation. Magnesium sulfate is comparable in efficiency to excess dichromate as a buffer and does not alter the course of oxidation. Potassium alum, a strongly acidic buffer, increases the rate of oxidation but also results in destruction of some of the organic acids. With this buffer system the total conversions to acids are higher than in other systems, but the recovery of *p*-*t*-butyltoluene is less.

Table III

Effect of Buffers on Oxidation of *p*-*t*-Butyltoluene[a]

		Products	
Oxidizing mixture	Recovered *p*-*t*-butyltoluene, %	*p*-*t*-Butylbenzoic acid, %	Terephthalic acid, %
$K_2Cr_2O_7$ (0.21),[b] $MgSO_4$ (0.12)[b]	52	43	4
$K_2Cr_2O_7$ (0.21), K alum (0.07)	17[c]	56	6
$K_2Cr_2O_7$ (0.21), K alum (0.14)	0[d]	45	6
$K_2Cr_2O_7$ (0.21), NaOH (0.41)	97	2.7	. . .
$K_2Cr_2O_7$ (0.41; 100% excess)	52	43	4
$K_2Cr_2O_7$ (0.31; 50% excess)	52	43	4

[a] *p*-*t*-Butyltoluene (0.2 mole) and 150 ml. of water were used in each run; 10 hr., 250°. [b] Moles of reagents. [c] Some ring degradation occurred; carbon dioxide was evolved on opening bomb and on subsequent acidification of filtrates. [d] Extensive ring destruction resulted, no Cr^{+6} was left.

Oxidations of representative halo-, methoxy-, and nitrotoluenes and xylenes (Table II) were studied using various buffers in place of or in conjunction with excess alkali dichromate. Certain systems do not give selective oxidation to their aromatic acids; in general the most advantageous buffer is excess dichromate. *m*- and *p*-fluorotoluenes are oxidized to fluorobenzoic acids only in fair yields (35–55%); the extensive degradation can be partly controlled by use of the relatively acidic buffer, sodium dihydrogen phosphate–phosphoric acid. *o*-Fluorotoluene did not give *o*-fluorobenzoic acid under the conditions studied; conversion to carbon dioxide and tars occurred. *o*-, *m*-, and *p*-chlorotoluenes, chloro-*p*-xylene, *o*-bromotoluene, and bromo-*p*-xylene are oxidized in good yield by excess sodium dichromate; other buffer systems did not show any advantage. Oxidation of 1-bromo-2-methylnaph-

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[13] Upon completion of the present study, P. M. G. Bavin [*Can. J. Chem.*, **38**, 911 (1960)] and M. S. Newman and H. Boden [*J. Org. Chem.*, **26**, 1759 (1961)] have oxidized alkylarenes with sodium dichromate in this laboratory with advantage.

[14] (a) A. H. Cook, J. Downer, and B. Hornung, *J. Chem. Soc.*, 505 (1941); (b) C. E. Adams, U. S. Patent 2,399,716 (1946); (c) J. J. Angyal, P. J. Morris, R. C. Rassack, and J. A. Waterer, *J. Chem. Soc.*, 2705 (1949); (d) oxidation of 1-(chloromethyl)-2-methylnaphthalene to 1,2-naphthalic acid was unsuccessful.

[15] R. Adams and L. O. Bender, *J. Am. Chem. Soc.*, **63**, 2773 (1941).

[16] (a) Isophthalic and phthalic acids, respectively, were also obtained in these experiments; the yields were not determined. (b) Private communication from M. E. D. Hillman. A study of synthesis of *o*-*t*-butylbenzoic acid will be reported in a separate publication.

[17] (a) K. B. Wiberg and R. S. Evans, *Tetrahedron*, **8**, 313 (1960). (b) R. H. Reitsema and N. L. Allphin [*J. Org. Chem.*, **27**, 27 (1962)] have reported that oxidation of ethylbenzene can be controlled to give phenylacetic acid. Our attempts to obtain phenylacetic acid from this system were unsuccessful.

thalene gave 1-bromo-2-naphthoic acid (55% yield, 34% conversion, poor quality) accompanied by extensive nuclear degradation; modifying the buffers or reaction temperatures did not result in significant improvement. Iodoterephthalic acid, however, is obtained in excellent yield and purity from iodo-*p*-xylene; the minimal attack on iodine is indeed striking.

Excellent yields of *m*- and *p*-nitrobenzoic acids are obtained from *m*- and *p*-nitrotoluenes. Use of a relatively acidic oxidizer system, sodium dichromate–potassium dihydrogen phosphate–phosphoric acid, was necessary; the sensitivity of nitro groups to alkaline reagents probably led to the failures under the usual conditions. *o*-Nitrobenzoic acid could not be obtained from *o*-nitrotoluene.

Methoxyl groups result in sensitivity of benzenoid nuclei; considerable destruction occurs in oxidation of anisole derivatives. Oxidations of *m*-methoxytoluene and 2-methoxy-*p*-xylene to *m*-methoxybenzoic and 2-methoxyterephthalic acids occur in fair yield in the presence of sodium dihydrogen phosphate. Conversion of phenyl *p*-tolyl ether and di-*p*-tolyl ether to *p*-phenoxybenzoic acid and diphenyl ether 4,4′-dicarboxylic acid is effected satisfactorily by sodium dichromate using normal techniques.[18]

A limited study of oxidation of simple heterocyclic derivatives by sodium dichromate was made. Nicotinic acid is obtained from 3-picoline in 80–85% yields.[19] 3-Methylthiophene gave 3-thiophenecarboxylic acid (80–85%); this is the most convenient method for preparing 3-thiophenecarboxylic acid. 2-Acetylthiophene, 2- and 4-picoline, lepidine, and 3-methyl-2-furoic acid did not give the corresponding acids; conditions for selective oxidation could not be found.

Experimental

Apparatus and Reagents.—Oxidations were effected in either: (1) a thermostatically controlled rocking autoclave (3.24-l. capacity), (2) a stainless steel gas cylinder (500-ml., Hoke Company) equipped with a thermocouple, pressure gauge, and rocking heating jacket, or (3) a similarly equipped autoclave (60-ml.) constructed from standard iron pipe. Corrosion of the equipment was insignificant and the system is not poisoned for subsequent use in hydrogenation. The autogenous pressure was 500–600 p.s.i.; no hazardous difficulties were experienced in the present study. If a compound is extensively oxidized (destruction of the nucleus, etc.), the pressure developed by the carbon dioxide at elevated temperatures may be greater than 600 p.s.i. Oxidation of compounds which may be largely destroyed should be effected in equipment with relatively greater safety factors.

Commercial inorganic reagents were used without further treatment. Sodium dichromate was preferred since it is more water-soluble than is potassium dichromate. Tap water was used throughout except for final washings of the oxidation product.

General Procedure.—The reactants were charged into the autoclave and heated and shaken (60 c.p.m.) for 18 hr. If a stirred autoclave or Magne-Dash is used the reaction time can be shortened to 3–5 hr. The vessel was cooled to 60–80° and opened; the contents were discharged. The autoclave was then washed with sufficient warm water to remove all products. The washings were combined and filtered with suction to separate the chromic oxide. The chromic oxide was washed with warm water until acidification of aliquots of the filtrates gave no precipitate of the organic acid.

The clear alkaline filtrates and the wash liquors were combined, extracted with ether when necessary to remove any entrained starting materials, and acidified with hydrochloric acid (1:1). The precipitated product was collected by suction filtration after the mixture had been cooled to room temperature or lower. The product was then washed with water until the washings were colorless. Except in special cases, no attempt was made to increase the yield of product by extracting or further working up the acidified filtrates.

Attempted Oxidation of Phenanthrene.—Phenanthrene (45.0 g., 0.25 mole; m.p. 97–98°), sodium dichromate (155.0 g., 0.52 mole), and water (250 ml.) were charged into a 500-ml. reactor and heated and shaken at 250° for 18 hr. Upon opening the reaction vessel the aqueous sodium dichromate was removed and the phenanthrene which had crusted on the reactor wall was washed with water, dissolved in hot ethanol, filtered to remove dirt, and poured into water. The phenanthrene recovered weighed 43 g. (96%), m.p. 97–98°.

Benzo[c]phenanthrene, biphenyl, chrysene, fluoranthene, picene, triphenylene, naphthalene, and *o*-, *m*-, and *p*-terphenyls were treated similarly to phenanthrene. There was no evidence of oxidation.

Oxidation of Fluorene to Fluorenone.—Fluorene (50 g., 0.30 mole), sodium dichromate (100 g., 0.34 mole; 70% excess), and water (250 ml.) were heated in a shaking autoclave (500-ml.) for 18 hr. at 250°. The mixture of fluorene and chromic oxide (green) was filtered with suction and washed well with water (pH of filtrate $\sim$13). The dried filter cake was extracted with hot isopropyl alcohol. The bright yellow extracts were filtered to remove suspended particles, concentrated, and diluted while hot with water to incipient turbidity. On cooling, fluorenone (50 g., 91% yield) was obtained, m.p. 82–83°, no depression by an authentic sample. Dilution of the mother liquors with water gave additional fluorenone (4.4 g., 8%, m.p. 82–83°); the total yield was 99%.

4H-Cyclopenta[*d,e,f*]phenanthren-4-one.—4H-Cyclopenta[*d,e,f*]phenanthrene (1.90 g., 0.01 mole), sodium dichromate (3 g., 0.01 mole), and water (25 ml.) were heated for 18 hr. at 250°. The mixture was worked up as described in the preceding experiment to give yellow 4H-cyclopenta[*d,e,f*]phenanthrene-4-one (1.91 g., 0.0094 mole, 94%), m.p. 169–170°, lit.[20] m.p. 170°. The mixture melting point with an authentic sample was undepressed.

2-Naphthoic Acid.—2-Methylnaphthalene (320 g., 2.25 moles), sodium dichromate (1050 g., 3.50 moles, 50% excess), and water (1.8 l.) were shaken in an autoclave (3.25-l.) for 18 hr. at 250°. The reactor was emptied at 60° and the content was filtered to remove chromic oxide. The filter residue was washed with warm water (7 l.) until all of the sodium 2-naphthoate was removed. The aqueous solution was acidified with hydrochloric acid (1:1). After the mixture had cooled overnight, the precipitate which had formed was filtered, washed well with water, and air dried. White 2-naphthoic acid (360 g., 2.09 moles) was obtained in 93% yield, m.p. 184–185°, no depression by an authentic sample.

When larger excesses of sodium dichromate (55–64%) were employed, the yields were 90–92% and more carbon dioxide was formed

1,2-Naphthalic Acid (from 1,2-Dimethylnaphthalene).—1,2-Dimethylnaphthalene (32 g., 0.204 mole), sodium dichromate (180 g., 0.60 mole, 47% excess), and water (275 ml.) were heated at 250° for 18 hr.[21] The filtrates (pH 12), on acidification, liberated carbon dioxide and precipitated 1,2-naphthalic acid (36.5 g., 0.169 mole, 83% yield), m.p. 170–174°, lit.[22] m.p. 175°, contaminated with a small amount of nonmelting material. Distillation of the product, b.p. 190–200° (3 mm.), gave white 1,2-naphthalic anhydride (30.4 g., 0.153 mole, 75%), m.p. 167–168°, lit.[22] m.p. 168°, and left greyish white naphthalene-1,6-dicarboxylic acid (3.2 g., 0.0148 mole, 10%), m.p. 300°. The naphthalene-1,6-dicarboxylic acid is derived from 1,6-dimethylnaphthalene in commercial 1,2-dimethylnaphthalene and was identified by esterification with methanol and sulfuric acid to dimethyl 1,6-naphthalenedicarboxylate, m.p. 97–98°, lit.[22] m.p. 98°.

Thiophene-3-carboxylic Acid.—3-Methylthiophene (30.0 g., 0.306 mole), sodium dichromate (110 g., 0.37 mole, 21% excess), and water were heated at 250° for 16 hr. No starting material

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[18] The authors wish to acknowledge the assistance of Mr. Julian Hamerski, Worthington Junior College, Worthington, Minn., in these experiments.

[19] See also ref. 8e.

[20] H. Medenwald, *Chem. Ber.*, **86**, 287 (1953).

[21] When the oxidation was carried out at 235° for 18 hr., approximately 15% of the initial dimethylnaphthalene was recovered.

[22] E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1739 (1936).

could be recovered. Acidification of the strongly alkaline filtrates (pH 13) gave carbon dioxide, hydrogen sulfide, and thiophene-3-carboxylic acid (25 g.), m.p. 137–138°, lit.[23] m.p. 138.4°. The ether extracts of the acinified filtrates gave additional thiophene-3-carboxylic acid (7 g.), m.p. 137–138°, for a total yield of 82% (32 g., 0.25 mole). The melting point of the acid was undepressed when mixed with an authentic sample. The oxidation results were independent of the excess sodium dichromate employed (0–64% excess).

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(23) E. Campaigne and W. LeSeur, *J. Am. Chem. Soc.*, **70**, 1555 (1948).

The Alkali Metal Catalyzed Reactions of ω-Phenyl-1-alkenes. The Novel Cyclizations of 6-Phenyl-1-hexene and 7-Phenyl-1-heptene[1,2]

HERMAN PINES,[3] NORMAN C. SIH,[4] AND EDWARD LEWICKI

The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois

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The catalytic conversion of 6-phenyl-1-hexene and 7-phenyl-1-heptene in the presence of alkali metal–organoalkali metal catalysts has been investigated. The potassium- and cesium-catalyzed reactions afforded a substantial amount of intramolecular cyclization; sodium caused primarily double-bond migrations, while butyllithium exerted no catalytic effect. In potassium- and cesium-catalyzed reactions, 6-phenyl-1-hexene produced mainly *cis*- and *trans*-1-methyl-2-phenylcyclopentane and 1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene. 7-Phenyl-1-heptene yielded mostly *cis*- and *trans*-1-methyl-2-phenylcyclohexane and 1,2,3,4,4a,9a-hexahydrofluorene.

The sodium- and potassium-catalyzed side-chain alkylation, alkenylation, and aralkylation by olefins of alkyl aromatic hydrocarbons having a benzylic hydrogen have been the subject of extensive study in our laboratory.[1,5] For example, when toluene was used as an alkyl aromatic, its alkylation by ethylene gave mainly *n*-propylbenzene and 3-phenylpentane,[6] its alkenylation by isoprene yielded both 1-phenyl-3-methylpentene and 1-phenyl-4-methylpentene,[7] and its aralkylation by styrene produced 1,3-diphenylpropane.[8] The formation of the majority of products from these base-catalyzed reactions is explained *via* a carbanion mechanism.[5]

In order to further the understanding of the base-catalyzed reactions, the present investigation has been extended to include ω-phenyl-1-alkenes which contain both intrinsic acidic benzylic hydrogens and double bonds.

The reactions of 6-phenyl-1-hexene and 7-phenyl-1-heptene will be discussed in the present paper. Their intramolecular alkylations (cyclization) seem to be plausible owing to the close proximity of the benzylic carbon to the terminal double bond. The success of this type of cyclization depends largely on the relative rate of intramolecular alkylation against those of the competing reactions, such as isomerization of the double bond, hydride addition, intermolecular alkylation, etc. Cyclization which necessitates a special molecular orientation is usually attended by a negative entropy of activation, and therefore generally is a less favorable reaction.

The next paper of this series will describe the reactions of 4-phenyl-1-butene and 5-phenyl-1-pentene which were investigated to determine what products would be obtained in a system where ring formation was unfavored.

Alkali metals *per se* are not the catalysts and it is necessary to use a chain initiator, such as anthracene, *o*-chlorotoluene, etc., for the reaction to occur. These initiators usually react readily with alkali metals to give organoalkali metal compounds which initiate the reaction. The relative behaviors of the alkali metals as alkylation (or alkenylation or aralkylation) catalysts[9] have been compared in only a few instances.[5,10,11] Therefore the effect of lithium, sodium, potassium, and cesium upon the reaction was also investigated.

Discussion of Results

The reactions of ω-phenyl-1-alkenes, initiated by *o*-chlorotoluene,[12] were carried out at the refluxing temperature (about 185°) of an inert solvent, such as *n*-butylcyclohexane or *sec*-butylcyclohexane, in the presence of an alkali metal–organoalkali metal catalyst under the experimental conditions give in Table I.

The rate of conversion of ω-phenyl-1-alkenes was found to be dependent largely on how the catalyst was prepared. In various runs using the same metal as catalyst, the required reaction times differed, but, nevertheless, the product distributions remained nearly the same. Therefore the product distribution may be considered as a measure of the catalytic character of different alkali metals.

I. 6-Phenyl-1-hexene.—The composition of products obtained from this reaction is summarized in Table II (see Scheme I). Hydride addition and double bond migration are the two most common reactions of olefins brought about by alkali metal catalysis.[5] In the present study, the production of *n*-hexylbenzene (**2**) either from the parent olefin **1** or from its isomers (**3**,

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(1) Paper XXIX of the series, "Base-Catalyzed Reactions." Paper XXVIII: H. Pines and N. C. Sih, *J. Org. Chem.*, **30**, 280 (1965).

(2) This work was supported in part by a National Science Foundation Grant NSF-G 14503.

(3) To whom inquiries should be made.

(4) Taken in part from the Ph.D. Thesis of N. C. Sih, Northwestern University, June 1964.

(5) For literature references, see H. Pines and L. Schaap, *Advan. Catalysis*, **12**, 116 (1960).

(6) H. Pines, J. A. Vesely, and V. N. Ipatieff, *J. Am. Chem. Soc.*, **77**, 554 (1955).

(7) See ref. 1, paper XXVIII of this series.

(8) H. Pines and D. Wunderlich, *J. Am. Chem. Soc.*, **80**, 6001 (1958).

(9) The actual catalyst is alkali metal–organoalkali metal. The term, "base" or "alkali metal," is used throughout this paper as catalyst for simplicity.

(10) L. Schaap and H. Pines, *J. Am. Chem. Soc.*, **79**, 4967 (1957).

(11) The "size effect" of alkali metal ions was related to the product distribution of monoadducts in pentylation of arenes. See paper XXVIII of this series (ref. 1).

(12) H. Gilman and H. A. Pacevitz, *J. Am. Chem. Soc.*, **62**, 673 (1940).