TABLE I

Run	Time, hr.	Extent of reaction, %	Yield, % II	III	VI	1,2-Dimethylcyclohexanol	6-Methyl-5-heptenol	IV	V
Formolysis of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate[a]									
a	0.1	80	7	30	5	...	4	23	30
b	0.25	96	5	13	10	...	..	21	28
c	1	99	5	9	37	...	..	19	24
d	5	100	1	2	78	Trace	..	5	7
e	10	100	0	Trace	91	Trace	..	1	2
Formolysis of 6-methyl-6-heptenyl *p*-nitrobenzenesulfonate									
f	1	96	4	10	37	(1-Methylcycloheptanol: trace)		19	24
g	6	98	0	Trace	95	(1-Methylcycloheptanol: trace)		..	..

[a] 0.02 *M* substrate and 0.04 *M* HCOONa in anhydrous HCOOH at 75°.

two hydrocarbons was approximately 45 and 55%, respectively. The absolute yields were determined on an SE-30 column at 70° by comparison of the peak areas produced from injections of the pentane solution and a standard (1.5×10^{-2} *M*) solution of *ca.* 45% 1-isopropylcyclopentene and *ca.* 55% isopropylidenecyclopentane. Thus 2-λ injections of the standard solution gave response for 165 units of area as compared with 186 units of area for the pentane solution. Therefore the combined concentration of the two hydrocarbons was 1.7×10^{-2} *M*, corresponding to an absolute yield of 53%, or 23% 1-isopropylcyclopentene and 30% isopropylidenecyclopentane.

Another formolysis experiment was carried out on a 0.626-g. scale. The procedure was identical with that described above except that ether was used for extraction of the entire formolysis reaction mixture, and the product was submitted to preparative vapor phase chromatography on a Carbowax 20M column at 130°. The alcoholic components, dimethylcyclopentylcarbinol and 2,2-dimethylcyclohexanol, were collected and their infrared spectra shown to be identical with those of the corresponding authentic materials. The isopropylidenecyclopentane fraction was also collected, and its identity was confirmed by infrared spectral comparison with an authentic sample and by preparation of its dibromo derivative, which was obtained from ethanol as colorless plates, m.p. 67–69°, undepressed on admixture with the authentic material described above.

2,2-Dimethylcyclohexanol.—A solution of 28 mg. of 2,2-dimethylcyclohexanol (purified as described above by preparative vapor phase chromatography), 44 mg. of *p*-nitrobenzenesulfonic acid (Eastman Kodak, practical grade), and 30 mg. of anhydrous sodium formate in 11 ml. of anhydrous formic acid was heated under an atmosphere of nitrogen at 75° for 20 hr. The reaction mixture was processed and the product was analyzed just as described above for run a of the formolysis of 6-methyl-5-heptenyl *p*-nitrobenzenesulfonate. The absolute yields of the alcoholic products were determined to be 76% of 2,2-dimethylcyclohexanol (retention time 11.4 min. on Craig succinate at 114°), *ca.* 1% of *trans*-1,2-dimethylcyclohexanol (7.8 min.), *ca.* 1% of *cis*-1,2-dimethylcyclohexanol (10.0 min.), and a trace of dimethylcyclopentylcarbinol (8.1 min.). The olefinic products consisted of *ca.* 1% of 1-isopropylcyclopentene (retention time 10 min. on SE-30 at 70°), *ca.* 0.5% of 2,3-dimethylcyclohexene (12.0 min.), and 2% of either pure isopropylidenecyclopentane (16.0 min.) or a mixture of isopropylidenecyclopentane and 1,2-dimethylcyclohexene (15.7 min.).

6-Methyl-6-heptenyl *p*-Nitrobenzenesulfonate.—An experiment with this substrate was conducted exactly as described above for runs c and d of the formolysis of the 6-methyl-5-heptenyl ester. The results of the analysis are summarized under run f, Table I.

Another experiment was performed exactly as described above for run a of the formolysis of the 6-methyl-5-heptenyl ester except that the reaction mixture was not divided and no analysis was made for hydrocarbons. The results are summarized under run g, Table I.

Another experiment was conducted in a fashion identical with that of run g except on a larger scale (0.626 g. of the ester, m.p. 59.5–61°, 0.272 g. of sodium formate, and 100 ml. of formic acid). 2,2-Dimethylcyclohexanol was isolated by evaporative distillation in 60% yield. The infrared spectrum was identical with that of authentic material. The n.m.r. spectrum of the 2,2-dimethylcyclohexanol isolated from the formolysis exhibited absorption for 6 protons as a doublet centered at $\delta = 0.9$ p.p.m. (*gem*-dimethyl protons), 1 proton as a singlet at $\delta = 8.12$ p.p.m. (–OH proton), and 1 proton as a multiplet centered at $\delta = 3.25$ p.p.m. (proton α to –OH).

Relative Rates.—These experiments were carried out exactly as already described in detail.[2] The times required for disappearance of one-half of the alkenyl *p*-nitrobenzenesulfonates (0.02 *M* solution in anhydrous formic acid containing 0.04 *M* sodium formate) at 75° were: 5-methyl-5-hexenyl, 70 min.; 4-methyl-4-pentenyl, 30 min.; and 6-methyl-6-heptenyl, 4 min.

Acknowledgment.—Acknowledgment is made to the U. S. Public Health Service, the National Science Foundation, and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210]

A New Cyclization Reaction Leading to Epoxides of Aromatic Hydrocarbons[1,2]

BY MELVIN S. NEWMAN AND SHOSHANA BLUM

RECEIVED AUGUST 4, 1964

Treatment *o,o'*-diformylbiphenyl with trisdimethylaminophosphine yields 9,10-dihydro-9,10-epoxyphenanthrene (I) in high yield. Two other dialdehydes are cyclized to the epoxides II and III. These three epoxides represent the first epoxides of aromatic hydrocarbons that have been synthesized. On treatment with acid, the epoxides isomerize to phenolic compounds.

Although epoxy derivatives of aromatic hydrocarbons[2] have been postulated as intermediates in the metabolism of polycyclic aromatic hydrocarbons,[3] such compounds have as yet not been prepared.[4]

(1) This research was supported by Public Health Service Research Grant No. CA-05480-03.

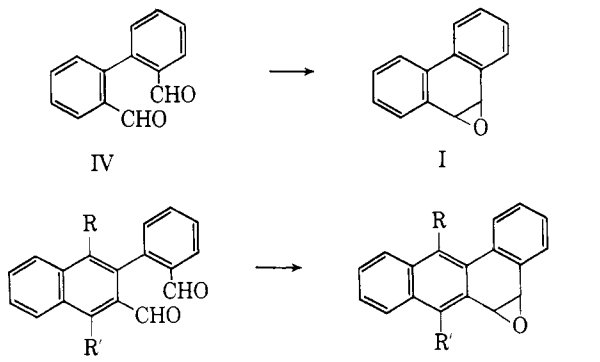
(2) The term epoxides of aromatic hydrocarbons means that if the oxygen atom is removed, an aromatic ring is produced from that ring which contains the two carbons to which the oxygen was attached.

(3) See E. Boyland and P. Sims, *Biochem. J.*, **84**, 571 (1962); **90**, 391 (1964), and earlier references therein.

(4) B. L. Van Duuren, I. Bekersky, and M. Lefar, *J. Org. Chem.*, **29**, 686 (1964), report that the 5,6-epoxide of dibenz[*a,h*]anthracene is present among

Herein we report the synthesis of three such epoxides: 9,10-dihydro-9,10-epoxyphenanthrene (I), 3,4-dihydro-3,4-epoxy-1,2-benzanthracene (II), and 3,4-dihydro-3,4-epoxy-10-methyl-1,2-benzanthracene[5] (III).

In each case the synthesis involved a new cyclization reaction of a dialdehyde on treatment with trisdimethylaminophosphine.[6] The dialdehyde IV was prepared by ozonization of phenanthrene[7] and the new dialdehydes V and VI were prepared essentially as described for a similar dialdehyde.[8,9] The cyclizations of these dialdehydes by use of trisdimethylaminophosphine in benzene proceeded readily in high yields. However, attempts to cyclize VII failed, presumably because of the extra steric effect provided by the added methyl group at position R in VII.[10]



IV I

V, R = R′ = H
VI, R = H, R′ = CH_3
VII, R = R′ = CH_3

II, R = R′ = H
III, R = H, R′ = CH_3

In the hope that epoxides of benzocyclobutenes might result, *o*-phthalaldehyde and 2,3-diformylnaphthalene were treated with Mark's reagent. However, only the intermolecular condensation products 1,2-di-(*o*-formylphenyl)ethylene oxide and 1,2-di(3-formyl-2-naphthyl)ethylene oxide were obtained (in about 30–40% yields).[11] The remainder consisted of dark phosphorus-containing oils. The cyclization reaction failed to give any phosphorus-free compounds when attempted with 1,8-diformylnaphthalene and homophthalaldehyde. The fact that these two aldehydes do not exist in the free aldehyde forms is undoubtedly the reason why the hoped-for cyclized epoxides were not obtained.

The epoxides I, II, and III are sensitive to acid treatment. They rearrange easily and in high yields to 9-phenanthrol, 3-hydroxy-1,2-benzanthracene,[12] and 10-methyl-3-hydroxy-1,2-benzanthracene,[12] respectively. We cannot say that none of the corresponding 4-hydroxy-1,2-benzanthracenes[13] is formed but certainly very little is produced.

Attempts were made to isomerize I into a dibenzoxepin.[14] However, on heating compound I was converted into 9-phenanthrol in high yield. In a similar way, II was converted into 3-hydroxy-1,2-benzanthracene in 65% yield.

Experimental[15]

9,10-Dihydro-9,10-epoxyphenanthrene (I).—When 1.0 g. of trisdimethylaminophosphine[6] was added to 1.00 g. of finely divided 2,2′-dialdehydobiphenyl[7] an exothermic reaction occurred. After a few minutes the phosphorus compounds were removed by trituration with a small amount of cold ether and the epoxide was crystallized from cyclohexane. Recrystallization afforded 0.82 g. (89%) of I as colorless crystals, m.p. 104–105° uncor.[16] The n.m.r. spectrum showed a multiplet equivalent to eight hydrogens in the 1.9–2.8 τ range and a peak at 5.6 τ equivalent to two hydrogens. The infrared spectrum showed a strong band at 11.22 μ, which may be attributed to the oxirane structure.[17]

Anal.[18] Calcd. for $C_{14}H_{10}O$: C, 86.6: H, 5.2. Found[s]: C, 86.8; H, 5.4.

In the best of several runs a similar result (81% yield) was obtained on holding a benzene solution of the dialdehyde and phosphine at reflux for 1 hr. Purification of the final product is easier in the cases of reactions run in benzene.

After heating at reflux a stirred reaction mixture of 250 mg. of I in 20 ml. of benzene and 15 ml. of 10% hydrochloric acid under nitrogen for 30 min., the potassium hydroxide-soluble portion of the products afforded 194 mg. (77%) of light tan 9-phenanthrol, m.p. 151–152°, no depression on mixing with an authentic sample prepared from 9,10-phenanthraquinone.[19]

In another experiment, the epoxide was heated slowly up to 120°. A sample removed at this time proved to be unchanged epoxide by infrared analysis. On heating to 150° at 1 mm., some colorless material sublimed onto the wall of the tube. This was identified as 9-phenanthrol by m.p. and infrared spectrum. The liquid remaining was essentially pure epoxide. By the time that a temperature of 200° was reached (about 15 min. from the time when 120° was attained) almost all of the material had sublimed and proved to be pure 9-phenanthrol.

2-Phenylnaphthalene-3,2′-dicarboxaldehyde (V).—A solution of 9.9 g. of sodium metaperiodate in 150 ml. of water and 800 ml. of methanol was added to a solution of 3.0 g. of 3,4-dihydro-3,4-dihydroxy-1,2-benzanthracene[8] in 3 l. of methanol and 600 ml. of water. After 48 hr. at room temperature the methanol was removed under reduced pressure. The cream-colored solid was collected and purified by chromatography over Florisil[20] with benzene–1% acetone. The first fraction of eluate was recrystallized from ether–Skellysolve F[21] at −70° to yield 1.7 g. (57%) of pure dialdehyde V, m.p. 81.0–81.5°.

Anal. Calcd. for $C_{18}H_{12}O_2$: C, 83.1; H, 4.6. Found[s]: C, 83.0; H, 4.7.

---

the products of treatment of the hydrocarbon with perbenzoic acid to the extent of 0.04%, but this compound was not isolated.

(5) The synthesis of III was undertaken at the suggestion of Dr. J. A. Miller, McArdle Memorial Laboratory, University of Wisconsin, who called our attention to the method of Mark (ref. 6) as a possible route to III. Studies on the biological activity of I, II, and III are under way by Dr. Miller.

(6) V. Mark, *J. Am. Chem. Soc.*, **85**, 1884 (1963). For other examples of condensation reactions effected by phosphorus compounds see F. Ramirez, N. Ramanathan, and N. B. Desai, *ibid.*, **85**, 3465 (1963), and references therein.

(7) P. S. Bailey and R. E. Erickson, *Org. Syn.*, **41**, 41 (1961).

(8) J. W. Cook and R. Schoenthal, *J. Chem. Soc.*, 172 (1948).

(9) H. I. Hadler and A. C. Kryger, *J. Org. Chem.*, **25**, 1896 (1960).

(10) See ref. 6 for a possible mechanism involved in the condensation of two molecules of benzaldehyde to form stilbene oxide. If this mechanism is correct, the reason for the failure to obtain an epoxide from VII is that the ylide formed from the aldehyde group on the phenyl ring of VII cannot be oriented properly to allow for the second stage of the reaction to proceed because the methyl group at R prohibits correct orientation for cyclization.

(11) We do not know if the epoxides have the *cis* or *trans* structure as only one isomer of each was isolated. Mark, ref. 6, obtained mainly *trans*-stilbene oxide.

(12) We thank Prof. L. F. Fieser of Harvard University for supplying authentic samples of the hydroxybenzanthracenes.

(13) 4-Hydroxy-1,2-benzanthracene has not been reported. The references to it: *Chem. Abstr.*, **39**, 2126[2] (1945); *Chem. Zentr.*, 550 (1944-I), are incorrect as the 4′-hydroxy compound was involved in the original reference; *Tumori*, [2] **14**, (26) 273 (1940).

(14) The fact that the dibenzoxepin and I are isomeric was pointed out by Prof. H. Shechter. The first synthesis of an oxepin has been announced: E. Vogel, R. Schubart, and W. A. Bull, *Angew. Chem.*, **76**, 535 (1964).

(15) All experiments involving an epoxy compound were carried out in *dry* solvents under dry nitrogen.

(16) All melting points were taken in a stirred liquid bath with a calibrated thermometer.

(17) In L. J. Bellamy, "Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 102 ff the various bands that have been assigned to oxiranes are discussed. In our cases, the band occurred in the 11.22–11.35 μ region.

(18) Microanalyses marked[s] by the Spang Laboratory, Ann Arbor, Mich.; marked[s] by Galbraith Laboratories, Knoxville, Tenn.

(19) F. R Tapp and A. Findlay, *J. Chem. Soc.*, 3141 (1929).

(20) A magnesia–silica gel catalyst, Floridin Co.

(21) Petroleum ether, b.p. *ca.* 40°.

3,4-Dihydro-3,4-epoxy-1,2-benzanthracene (II).—In the best of several experiments a solution of 540 mg. (3.3 mmoles) of trisdimethylaminophosphine in 15 ml. of benzene was added dropwise to a stirred solution of 800 mg. (3.1 mmoles) of V in 15 ml. of benzene at 55°. After 2 hr. at 55° the benzene was removed under vacuum. The residue was triturated quickly with 10 ml. of cold dry ether to remove phosphorus compounds and then recrystalli ed from dry ether to yield 555 mg. (74%) of II as colorless crystals, m.p. 119–120° dec. when heated at the rate of 6° per min. The crystals turn yellow near 100° (see below); II shows a band at 11.30 μ and two doublets at 5.50 and 5.59 τ, J 4.5 c.p.s. for each.

Anal. Calcd. for $C_{18}H_{12}O$: C, 88.5; H, 4.9. Found[g]: C, 88.2; H, 5.0.

When the above reaction was run at the reflux temperature of benzene, the yield of II dropped to 32%. When II was treated with hydrochloric acid, as in the case of I, a 43% yield of 3-hydroxy-1,2-benzanthracene,[4] m.p. 196–205° dec., was obtained. The acetate[22] melted at 128–129°. The infrared spectra of our 3-hydroxy-1,2-benzanthracene and of Prof. Fieser's were identical. When the material in the mother liquor of the above acid treatment was subjected to a similar treatment a further quantity of 3-hydroxy-1,2-benzanthracene was obtained. Other tests with acidic reagents appeared less promising. We did not pursue this reaction as the II at hand was needed for biological experiments.

When 105 mg. of pure II was heated at 1 mm. the crystals turned yellow at about 100°. A violent reaction occurred near 120° and the solid liquefied. At about 160° (bath temperature) the oil solidified. After heating at 160° for 5 min., the tube was cooled and the pale yellow-orange solid melted at 172–180°. The infrared spectra of this material and of authentic 3-hydroxy-1,2-benzanthracene[12] were almost identical. After two recrystallizations from toluene, 68 mg. (65%) of pure 3-hydroxy-1,2-benzanthracene, m.p. 201–203° dec., was obtained.

3,4-Dihydro-3,4-dihydroxy-10-methyl-1,2-benzanthracene.—By a procedure similar to that described,[9] 3.3 g. of pure 10-methyl-1,2-benzanthracene was oxidized to the dihydroxy compound, m.p. 194–195°, in 64% yield.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.6; H, 5.8. Found[g]: C, 82.5; H, 5.9.

1-Methyl-3-phenylnaphthalene-2,2′-dicarboxaldehyde (VI).—The oxidation of the above diol to VI, m.p. 100.0–100.5°, was accomplished in 76% yield as described.[8]

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.2; H, 5.1. Found[g]: C, 83.0; H, 5.0.

3,4-Dihydro-3,4-epoxy-10-methyl-1,2-benzanthracene (III).—In the best of several experiments a solution of 1.0 g. of trisdimethylaminophosphine in 10 ml. of benzene was added to a solution of 1.35 g. of VI in 25 ml. of benzene. After stirring at reflux for 2 hr. the mixture was worked up as described for II to yield 0.83 g. of colorless III, m.p. 117–120° when heated at the rate of 8° per min. There is darkening on heating when a temperature of 108° is reached and the actual melting range depends on the rate of heating. The pure compound shows a band at 11.35 μ (epoxide) and on n.m.r. analysis shows doublets (oxirane hydrogens) at 5.25 and 5.75 τ, J 4.5 c.p.s. for each. The methyl hydrogens give a single peak at 7.30 τ.

Anal. Calcd. for $C_{19}H_{14}O$: C, 88.4; H, 5.4. Found[g]: C, 88.3; H, 5.5.

In experiments at 60°, the dialdehyde was recovered unchanged. On chromatography of III over Florisil using benzene–cyclohexane, rearrangement of III to 3-hydroxy-10-methyl-1,2-benzanthracene,[23] m.p. 192–193°, occurred. The same hydroxy compound was obtained on acid treatment as in the case of II. The hydroxy compound was converted into 3-methoxy-10-methyl-1,2-benzanthracene, m.p. 182–183°, and the picrate of this compared with a sample of picrate supplied.[12] Our picrate, m.p. 141–142°, was the brown polymorph.[23] The infrared spectra of this and of Fieser's picrate in KBr were identical.

Dialdehyde VII was prepared as described,[9] but all attempts to cyclize it to an epoxide failed. When treated in benzene at 60° as above, VII was recovered unchanged. At higher temperature phosphorus-containing materials were obtained.

1,2-Di(*o*-formylphenyl)ethylene Oxide.—A solution of 1.00 g. of trisdimethylaminophosphine in 15 ml. of benzene was added during 30 min. to a solution of 0.70 g. of pure *o*-phthalaldehyde,[24] m.p. 55–56°, in 20 ml. of benzene. After refluxing for 2 hr. the product was isolated as in previously described cases. Crystallization from ether afforded 0.37 g. (37%) of the named compound, m.p. 149–150°; infrared bands at 5.95 (formyl group) and at 11.35 μ (oxirane); oxirane hydrogen peak (n.m.r.) at 5.34 (unsplit), aldehydic hydrogen at −0.10 τ.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found[g]: C, 76.2; H, 4.9.

In several other attempts, including a fairly high dilution experiment, the yield was about the same.

1,2-Di-(3-formyl-2-naphthyl)ethylene Oxide.—In reactions similar to those described immediately above, except that 2,3-diformylnaphthalene,[24] m.p. 133–135°, was used, the named compound was isolated in 43% yield as colorless elongated prisms, m.p. 218–219°, from benzene; infrared bands at 5.95 (formyl group) and 11.35 μ (oxirane); oxirane hydrogen peak (n.m.r.) at 5.20 (unsplit), aldehydic hydrogen at −0.27 τ.

Anal. Calcd. for $C_{24}H_{16}O_3$: C, 81.8; H, 4.5. Found[g]: C, 82.0; H, 4.7.

(22) L. F. Fieser and E. M. Dietz, *J. Am. Chem. Soc.*, **51**, 3141 (1929).

(23) L. F. Fieser and E. B. Hershberg, *ibid.*, **59**, 1028 (1937).

(24) Obtained from the Aldrich Co., Milwaukee, Wis.

[CONTRIBUTION FROM THE EVANS CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210]

4-Bromo- and 4-Iodo-2,5,7-trinitrofluorenones as Complexing Agents[1]

BY MELVIN S. NEWMAN AND JOCHANAN BLUM

RECEIVED AUGUST 5, 1964

The two reagents of the title have been prepared as reagents of use in forming charge-transfer type complexes suitable for X-ray analysis. The syntheses are described and many complexes listed in Tables I and II.

The present work was stimulated by the fact that 1-methoxybenzo[*c*]phenanthrene forms two 1:1-complexes with 2,4,7-trinitrofluorenone (TNF).[2] One complex, m.p. 212°, is black and the other, m.p. 157°, is brown-red.[3] The thought arose that the structure of these two complexes might be determined by X-ray analysis of the crystals. However, X-ray crystal analysis of a substance which does not have a heavy atom, such as bromine or iodine, is considerably more difficult and time-consuming than would be the case if such an atom were present. Accordingly, we have synthesized 4-bromo-2,5,7-trinitrofluorenone (BTNF, I) and 4-iodo-2,5,7-trinitrofluorenone (ITNF, II) in the hope that two different complexes, suitable for X-ray analysis, might be obtained with 1-methoxybenzo[*c*]phenanthrene. However, only one complex was formed with BTNF and ITNF.

We have prepared complexes of BTNF and ITNF (see Table I) with a number of substances with three objects in mind: 1, to test the ability of these reagents to form complexes; 2, to see if two different 1:1-complexes might be obtained; and 3, to make complexes available for X-ray crystallographic studies.

(1) This work was supported by Grant No. CA-05480-03 from the U. S. Public Health Service.

(2) M. Orchin and O. Woolfolk, *J. Am. Chem. Soc.*, **68**, 1727 (1946).

(3) M. S. Newman and J. Blum, *ibid.*, **86**, 503 (1964).