

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 recrystallized 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*: 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 acetate²² 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-benzanthracene¹² 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*: 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*: 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*: 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*: 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*: C, 82.0; H, 4.7.

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

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

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

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4-Bromo- and 4-Iodo-2,5,7-trinitrofluorenones as Complexing Agents¹

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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

(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).

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.

TABLE I
COMPLEXES OF 4-BROMO-2,5,7-TRINITROFLUORENONE

Aromatic component	Prepared in	Recrystallized from	Color	M.p., °C. ^a	Formula	—Bromine, %—	
						Calcd.	Found
1 Benzene	Benzene ^d	Same	Yellow	Dec.	C ₁₉ H ₁₀ BrN ₃ O ₇	17.0	17.1 ^e
2 Anthracene	Benzene-ethanol	Same	Dark violet	208–209	C ₂₇ H ₁₄ BrN ₃ O ₇	14.0	13.8
3 Fluoranthrene	Benzene-ethanol	Same	Orange	761–198	C ₂₉ H ₁₄ BrN ₃ O ₇	13.4	13.7
4 1-Cyclohexenyl-naphthalene ^e	Acetic acid	Same	Wine-red	135–136	C ₂₉ H ₁₈ BrN ₃ O ₇	13.3	13.3
5 Chrysene	Benzene	Same	Orange-red	263–265	C ₃₁ H ₁₆ BrN ₃ O ₇	12.9	12.8
6 Naphthacene ^f	Acetic acid	CCl ₄	Olive green	278–280	C ₃₁ H ₁₆ BrN ₃ O ₇	12.9	13.0
7 1-Methylbenzo[c]-phenanthrene ^g	Acetic acid	Acetic acid–CCl ₄	Red	163–164	C ₃₂ H ₁₈ BrN ₃ O ₇	12.6	12.7
8 1-Methoxybenzo[c]-phenanthrene ^h	Benzene	CCl ₄	Purple-violet	197–199	C ₃₂ H ₁₆ BrN ₃ O ₈	12.3	12.2
9 Benz[a]pyrene	Benzene	Same	Olive green	261–263	C ₃₃ H ₁₆ BrN ₃ O ₇	12.4	12.3
10 1-Acetylaminobenzo[c]-phenanthrene ⁱ	CCl ₄	Same	Cherry red	173–175	C ₃₃ H ₁₉ BrN ₄ O ₈	11.8	11.9
11 1,12-Dimethylbenzo[c]-phenanthrene ^j	Acetic acid	CCl ₄ –acetic acid	Red	144–145	C ₃₃ H ₂₀ BrN ₃ O ₇	12.3	12.4
12 Dibenz[a,h]anthracene	Benzene	Same	Purple	243–244	C ₃₅ H ₁₈ BrN ₃ O ₇	11.9	11.9

^a Most melting points occur with decomp., hence the rate of heating in general is rapid. ^b Analyses by Spang Laboratory, Ann Arbor, Mich. Correct values (within 0.3%) were also obtained for C, H, and N for each compound. ^c Analysis by A. Bernhardt, Mülheim, Germany. ^d Formed in and recrystallized from benzene; sample held at 1–2 mm. over paraffin wax for 1 day for analysis. ^e TNF complex has 2 moles of TNF; see Klemm ref. in footnote *e*, Table II. ^f Owing to insolubility of naphthacene, best results were obtained by using excess hydrocarbon in boiling acetic acid, followed by filtration while hot to remove excess naphthacene. ^g Does not form picrate; TNF derivative was formed in poor yield; see M. S. Newman and W. B. Wheatly, *J. Am. Chem. Soc.*, **70**, 1913 (1948). ^h Forms two 1:1 TNF derivatives; see ref. 3 in text. ⁱ No solid TNF derivative was obtained; see M. S. Newman and J. Blum, *J. Am. Chem. Soc.*, **86**, 1835 (1964). ^j M. S. Newman and M. Wolf, *ibid.*, **74**, 3225 (1952), report that neither picrate nor TNF derivative of this hydrocarbon could be prepared. Later, the TNF and TENF derivatives were prepared; see M. S. Newman and W. B. Lutz, *ibid.*, **78**, 2469 (1956).

The required bromo and iodo compounds I and II were prepared by nitration of 4-bromo- and 4-iodo-fluorenone, respectively. In order to prove that the nitro groups had the positions indicated, the bromine and iodine atoms were removed reductively by heating I and II with copper powder and benzoic acid.⁴ Isolation of 2,4,7-trinitrofluorenone² in each case proved that the structures of I and II are as stated.

On working with I and II it became obvious that these were excellent complexing agents. A number of complexes are listed in Tables I and II. Especially noteworthy is the fact that benzene forms stable 1:1 complexes with I and II. These complexes do not lose benzene on holding at 1–2 mm. pressure at room temperature for a day. However, the melting point cannot be taken since the benzene is lost on heating at temperatures below 100°. To our knowledge these represent the only known stable solid charge-transfer type of complex involving benzene and a polynitro compound. Benzene and toluene have been shown not to form complexes with TNF.⁵ The melting points of the few comparable complexes with 2,4,5,7-tetrinitrofluorenone⁶ are lower than those from BTNF or ITNF. All of the hydrocarbons we used form 1:1-complexes except prehnitene, which forms a 2:1-complex (see Table II).

We have available quantities of the complexes listed in Tables I and II if any person is interested in determining the crystalline structure.

Experimental

4-Bromo-2,5,7-trinitrofluorenone (BTNF, I).—In the best of several runs 2.54 g. of powdered 4-bromofluorenone⁷ was added

(4) This method is based on a comparable process for removal of aromatic chlorine in nitro compounds; see W. T. Smith, Jr., *J. Am. Chem. Soc.*, **71**, 2855 (1949).

(5) D. E. Laskowski and W. C. McCrone, *Anal. Chem.*, **26**, 1497 (1954).

(6) M. S. Newman and W. B. Lutz, *J. Am. Chem. Soc.*, **78**, 2469 (1956).

during 5 min. to a stirred mixture of 36 ml. of fuming nitric acid (*d.* 1.59–1.60), 25 ml. of 96% sulfuric acid, and 3 ml. of acetic acid at room temperature. The mixture was brought to reflux during 15 min. and held there for 60 min. The clear brown solution was cooled and poured on ice. The yellow precipitate was collected, washed with water, dried, and recrystallized twice from benzene to yield yellow crystals of the benzene complex (see Table I) of BTNF. After removing the benzene by heating to 70° under vacuum, a yellow powder remained. Recrystallization from ethanol afforded 3.08 g. (78%) of I as shiny yellow plates, m.p. 191–192°.

Anal. Calcd. for C₁₃H₄BrN₃O₇: C, 39.6; H, 1.0; Br, 20.3; N, 10.7. Found: C, 39.7; H, 1.1; Br, 20.5; N, 10.7.

4-Iodofluorenone.—Moist 4-aminofluorenone hydrogen sulfate, prepared from 49 g. of 4-aminofluorenone,⁷ was suspended in a solution at 0° of 85 ml. of concentrated sulfuric acid in 1.5 l. of water and diazotized with 18 g. of sodium nitrite. The mixture was stirred at 5° for 30 min., then filtered. The clear filtrate was treated with urea to remove excess nitrous acid and cooled to 0°. On adding slowly a solution of 60 g. of potassium iodide in 150 ml. of water a heavy red precipitate was formed. After a series of color changes on heating to 100° and holding at reflux for 30 min. the mixture was cooled and filtered. The solid was washed well with 10% potassium hydroxide to remove phenolic impurity and eventually was distilled at 1.5 mm. (b.p. 184–185°). Recrystallization from ethanol afforded 57 g. (74%) of bright yellow elongated prisms of 4-iodofluorenone, m.p. 121–122°.

Anal. Calcd. for C₁₃H₇IO: C, 51.0; H, 2.3; I, 41.5. Found: C, 51.1; H, 2.2; I, 41.4.

4-Iodo-2,5,7-trinitrofluorenone (ITNF, II).—As in the case of BTNF, 3.06 g. of 4-iodofluorenone was nitrated with 36 ml. of fuming nitric acid, 25 ml. of concentrated sulfuric acid, and 7 ml. of acetic acid. The reflux period was 45 min. The crude nitration products melted over a wide range, but one crystallization from benzene yielded the benzene complex (see Table II) in almost pure state. Recrystallization from ethanol afforded 2.10 g. (48%) of II as yellow fluffy crystals, m.p. 193–194°.

(7) 4-Bromofluorenone was prepared essentially as described by E. H. Huntress, K. Pfister, 3rd, and K. H. T. Pfister, *J. Am. Chem. Soc.*, **64**, 2845 (1942), but on a much larger scale. The yields were somewhat higher. In the last step, use of a 30% excess of cuprous bromide led to a 54% yield of pure 4-bromofluorenone, m.p. 127–128°.

TABLE II
 COMPLEXES OF 4-IODO-2,5,7-TRINITROFLUORENONE

Aromatic component	Prepared in	Recrystallized from	Color	M.p., °C. ^a	Formula	Iodine, ^b %	
						Calcd.	Found
1 Benzene	Benzene ^d	Same	Light orange	Dec.	C ₁₉ H ₁₀ IN ₃ O ₇	24.5	24.2 ^c
2 Toluene	Toluene ^d	Same	Light orange	Dec.	C ₂₀ H ₁₂ IN ₃ O ₇	23.8	23.9
3 2-Methylnaphthalene ^e	Acetic acid	Same	Orange	117-121	C ₂₄ H ₁₄ IN ₃ O ₇	21.8	21.9
4 Acenaphthene	Benzene-ethanol	CCl ₄	Red-brown	174-176	C ₂₈ H ₁₄ IN ₃ O ₇	21.4	21.4
5 Phenanthrene	Benzene-ethanol	Same	Orange	179-180	C ₂₇ H ₁₄ IN ₃ O ₇	20.5	20.6
6 Benz[a]anthracene	Benzene	Benzene-ethanol	Golden brown	247-248	C ₃₁ H ₁₆ IN ₃ O ₇	19.0	18.9
7 Benzo[c]phenanthrene	Benzene	Benzene-ethanol	Violet-black	185-186	C ₃₁ H ₁₆ IN ₃ O ₇	19.0	19.1
8 Triphenylene	Acetic acid	Benzene	Orange	259-260	C ₃₁ H ₁₆ IN ₃ O ₇	19.0	18.9
9 1-Methylbenz[a]-anthracene ^f	Benzene-ethanol	Same	Olive-brown	213-214	C ₃₂ O ₁₈ IN ₃ O ₇	18.6	18.4
10 1-Methoxybenzo[c]-phenanthrene	Benzene-ethanol	Same	Brown	190-192	C ₃₂ H ₁₈ IN ₃ O ₈	18.2	18.2
11 Prehnitene	Prehnitene ^d	Same	Orange	113-115	C ₃₃ H ₃₂ IN ₃ O ₇	17.9	18.1

^a Most melting points occur with decomposition; hence the rates of heating in the cases cited are rapid. ^b Analyses by Spang Laboratory, Ann Arbor, Mich. Correct values (within 0.3%) were also obtained for C, H, and N for each compound. ^c Analysis by A. Bernhardt, Mülheim, Germany. ^d Formed in and recrystallized from hydrocarbon component; samples held at 1-2 mm. over para fin wax for 1 day for analysis. ^e According to M. Orchin, L. Reggel, and E. O. Woolfolk, *J. Am. Chem. Soc.*, **69**, 1225 (1947), the TNF complex has 2 moles of TNF. See, however, L. H. Klemm and J. W. Sprague, *J. Org. Chem.*, **19**, 1464 (1954). ^f Forms only a dipicrate; see M. Orchin, *ibid.*, **16**, 1165 (1951). For TNF derivative see K. H. Takemura, H. D. Cameron, and M. S. Newman, *J. Am. Chem. Soc.*, **75**, 3280 (1953).

 TABLE III
 ULTRAVIOLET SPECTRA OF 4-BROMO-2,5,7-TRINITROFLUORENONE (I)
 AND 4-IODO-2,5,7-TRINITROFLUORENONE (II)^a

I in chloroform, 18.6 mg./l.	λ_{\max} , m μ	244.0	249.5	255.5	261.5	283.0	334.0	353 ^b	376 ^b
	log ϵ	4.34	4.36	4.37	4.32	4.45	3.98	3.68	3.51
I in 95% ethanol, 14.0 mg./l.	λ_{\max} , m μ	243.0	248.5	254.5	261.0	283.0	333.5	352 ^b	376 ^b
	log ϵ	4.29	4.27	4.25	4.24	4.42	3.97	3.83	3.60
I in benzene, 36.4 mg./l.	λ_{\max} , m μ					272.0	282.0		385 ^b
	log ϵ					4.30	4.31		3.62
II in chloroform, 18.0 mg./l.	λ_{\max} , m μ	239.0	244.0	249.5	255.5	261.5	286.5	347.5	390 ^b
	log ϵ	4.45	4.48	4.53	4.54	4.47	4.39	3.98	3.66
II in 95% ethanol, 14.8 mg./l.	λ_{\max} , m μ	226.5	243.0	248.5	254.5	261.0	284.5	346.0	390 ^b
	log ϵ	4.46	4.40	4.39	4.38	4.35	4.35	3.99	3.73
II in benzene, 36.0 mg./l.	λ_{\max} , m μ					272.5	281.5		396 ^b
	log ϵ					4.26	4.26		3.54

^a Spectra taken on a Cary 14 spectrophotometer. ^b Inflection point (approx.).

Anal. Calcd. for C₁₈H₄IN₃O₇: C, 35.4; H, 0.9; I, 28.8; N, 9.5. Found: C, 35.5; H, 1.0; I, 29.1; N, 9.8.

Proof of Structure of I and II.—In the best of several trials a mixture of 0.5 g. of II and 0.80 g. of benzoic acid was heated in a test tube to about 170° (internal thermometer). On addition of 0.5 g. of copper powder⁸ during 5 min. an exothermic reaction caused the temperature to rise to 180°. After cooling, the unused reaction mixture was extracted with sodium bicarbonate solution. Chromatography of the neutral product over Florisil⁹ using benzene as eluent yielded a first fraction which, on recrystalliza-

tion from benzene, afforded 0.28 g. (78%) of 2,4,7-trinitrofluorenone.² Comparison with an authentic sample was by m.p. and infrared spectra. The temperature range of the reaction, 170-180°, is crucial if a good yield of TNF is to be obtained.

In the case of the debromination of I by a similar process, the best yield of TNF obtained was 22%, since higher melting mixtures and tars were obtained. We feel certain that no other trinitrofluorenones were present, and, hence, the structure of I is established.

The ultraviolet spectra of I and II are given in Table III. Since the spectra in benzene are so different from the spectra in chloroform and in ethanol, we believe that the spectra in benzene represent the spectra of the benzene complexes.

(8) "Extra Fine Copper" No. 5143, O. Hommel Co., Pittsburgh, Pa., was used. Venus Copper 44F led to poor results.

(9) A magnesia-silica gel catalyst, Floridin Co.