trate. The solid weighed 1.57 g (35%), mp 193–195°. Two recrystallizations from methanol gave the analytical sample: mp 209–210.5°, with fine needles forming during heating; $[\alpha]^{24}D$ +87° (*c* 1.4, $CHCl_3$); uv max (CH_3OH) 261 mμ; nmr (DMSO-d_6) τ 1.82, 1.88 (both s, 1 proton each, H-2, H-8), 3.69 (s, 1, H-1′), 4.28 (s, 1, H-3′), 4.70 (s, 1, H-2′), 5.11 (m, 1, H-5′), 8.39 (d, 3, C-6′ CH_3), 8.56, 8.65 (both s, 6, *gem*-dimethyl); tlc in 9:1 ethyl acetate–methanol, R_f 0.41; paper chromatography on Whatman No. 1 paper, Rad 2.58. This compound rapidly decolorized solutions of bromine in carbon tetrachloride and potassium permanganate in aqueous ethanol.

Anal. Calcd for $C_{14}H_{17}N_5O_3$: C, 55.47; H, 5.65; N, 23.09. Found: C, 55.29; H, 5.58; N, 23.06.

Additional **6** can sometimes be obtained from the brown filtrates by chromatography on silicic acid[24] with 9:1 ethyl acetate–methanol. This chromatographic system worked well for the isolation of **6** in those cases where it would not crystallize easily from aqueous methanol.

Method B.—To a solution of 9 g (18.9 mmol) of **4** in 225 ml of *N*,*N*-dimethylformamide under a nitrogen atmosphere was added dropwise 225 ml of 1 *N* potassium *tert*-butoxide in *tert*-butyl alcohol and the mixture was heated at reflux for 22 hr. The dark brown residue obtained after evaporation of the solvents was partitioned between 150 ml each of chloroform and water. The water layer was extracted several more times with chloroform, and the extracts were combined, dried, and evaporated to dryness. Crystallization from methanol afforded 3.15 g (54%) of **6**. One recrystallization gave analytically pure material, mp 208.5–209.5°. This material was identical in every way to the crystals obtained from method A.

Anal. Found: C, 55.56; H, 5.76; N, 23.12.

9-(5,6-Dideoxy-α-L-*lyxo*-hex-5-enofuranosyl)adenine (7).—Compound **4** (4.5 g) was treated as described in method A for the preparation of **6**. The crude product was treated directly with 90% formic acid for 19 hr. The residue obtained after evaporation of the acid was dissolved in 30% aqueous methanol and chromatographed on a column of Bio-Rad AG1-X2 (OH, 200–400 mesh) using the same solvent system. Two uv-absorbing peaks were obtained, one of which was identified as **7** after crystallization from aqueous ethanol: yield 34 mg; mp 246–247° dec; $[\alpha]^{27}D$ −52.1° (*c* 0.305, 1 *N* HCl). The ir spectrum of **7** was identical with that of the D enantiomer prepared earlier.

Anal. Calcd for $C_{11}H_{13}N_5O_3$: C, 50.18; H, 4.98; N, 26.60. Found: C, 49.88; H, 5.04; N, 26.24.

9-(6-Deoxy-2,3-di-*O*-acetyl-5-*O*-*p*-toluenesulfonyl-α-L-mannofuranosyl)adenine (13).—A reaction mixture containing 13 g (38 mmol) of **1**, 22.4 ml of acetic anhydride, 224 ml of glacial acetic acid, and 12.5 ml of concentrated sulfuric acid was made up by a previously described procedure[3] and kept at room temperature for 48 hr. The mixture was poured on 500 g of ice, stirred until the ice melted, and extracted with chloroform (three 100-ml portions). The chloroform solution was washed with saturated aqueous sodium bicarbonate and sodium chloride (300 ml), and again with sodium chloride solution (250 ml). The organic layer was dried and evaporated, and traces of acetic acid were removed by evaporation of toluene, leaving 10 g (59%) of an oil (**12**).

The preparation of the nucleoside was carried out by previously described procedures. The oil was added to a reaction mixture consisting of 13.5 g of 6-benzamidochloromercuripurine, 13.5 g of Celite-545, 3.1 ml of titanium tetrachloride, and 1050 ml of 1,2-dichloroethane.[19] A hard syrup (11.1 g) was obtained which was dissolved in 100 ml of ethanol and treated at reflux with 56 ml of 10% ethanolic picric acid for 30 min.[7] Crystallization of the picrate of **13** ensued in the boiling solution at this point and was continued for several hours at room temperature, then in the refrigerator overnight. Recrystallization from acetone–ethanol gave 7.45 g (44%) of yellow crystals, mp 157–160°.

A solution containing 7.05 g of the picrate in 500 ml of 80% aqueous acetone was stirred for 3 hr with Bio-Rad AG1-X8 (CO_3^{-2}) resin.[8] The clear, colorless solution was filtered to remove the resin and evaporated, whereupon crystallization occurred. Recrystallization from acetone afforded 2.22 g of **13**: mp 179–181° to a viscous liquid which decomposed at about 200°; $[\alpha]^{26}D$ +36° (*c* 1.7, $CHCl_3$); ir (KBr) 3380 (NH), 1745 (C=O of acetate), 1678, 1608, 1572 (purine ring), 1170 (sulfonate) 1094, 1075 cm^{-1} (CO).

Anal. Calcd for $C_{22}H_{25}N_5O_8S$: C, 50.86; H, 4.85; N, 13.48. Found: C, 51.19; H, 4.82; N, 13.49.

Registry No.—**2**, 32658-92-7; **3**, 32658-93-8; **4**, 32658-94-9; **5**, 29847-42-5; **6**, 32658-96-1; **7**, 32658-97-2; **13**, 32658-98-3.

(24) Mallinckrodt, 100 mesh.

Ring Expansion of Hydroxyoxetanes to Dihydrofurans

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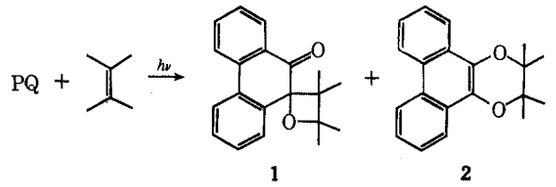
Reduction of the ketooxetanes **1** to the secondary alcohols **3** followed by treatment with acid led to rearrangement to the diols **4**, which, on dehydration, yielded the dihydrophenanthrofurans **5**. This reaction sequence and lanthanide-induced shift data were applied in elucidating the stereochemistry of **1**. The dehydration **4** → **5** proceeds either with retention or with inversion of the configuration depending on the nature of substituents.

α-Ketooxetanes can be prepared by the photoaddition of *o*-quinones or α diketones to olefins.[2] Most of these reactions have been carried out with phenanthrenequinone (PQ) which, in competing 1,2- and 1,4-cycloadditions, yields the ketooxetanes **1** and the dihydrophenanthrodioxins **2**, respectively.[3]



1 **2**

Oxetanes in general are known to undergo a number of acid catalyzed reactions, which may be used for different syntheses (for a review *cf.* ref 4). Rearrangement of oxetanes is, however, quite an unusual reaction.[4]

We have found that reduction of derivatives of **1** with $NaBH_4$ to the hydroxyoxetanes **3** and subsequent acid treatment led to rearrangement to the 1,4-diols **4**, which were readily dehydrated to the dihydrophenanthrofurans **5**.

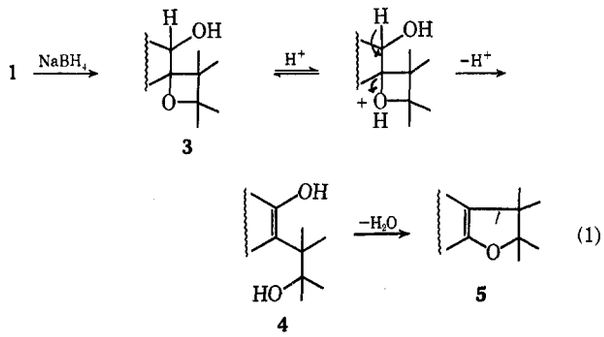
In this way, the compounds **5a–g** could be prepared from the corresponding oxetanes (**1a–g**). The struc-

(1) Research Laboratories, Eastman Kodak Company, Rochester, N. Y. 14650.

(2) S. Farid, D. Hess, and C. H. Krauch, *Chem. Ber.*, **100**, 3266 (1967).

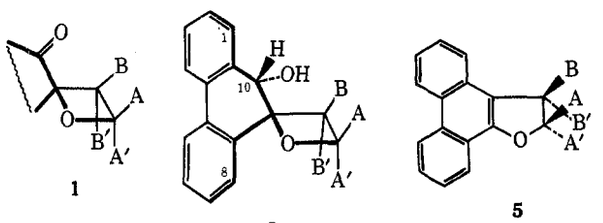
(3) S. Farid and D. Hess, *ibid.*, **102**, 3747 (1969).

(4) S. Searles, Jr., in "The Chemistry of Heterocyclic Compounds," Vol. 19, Part 2, A. Weissberger, Ed., Interscience, New York, N. Y., 1964, Chapter 9.

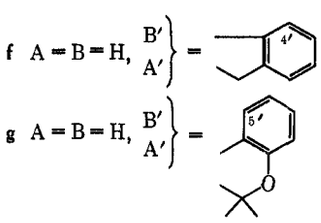


(1)

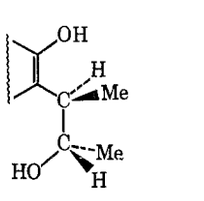
tural elucidation was based on spectroscopic data (see Experimental Section).



	A	A′	B	B′
a	H	Me	Me	H
b	H	Me	H	Me
c	H	H	Me	Me
d	H	Me	Me	Me
e	Me	Me	Me	Me (5e not prepared)



Since the dehydration is also an acid-catalyzed reaction, **3** could be directly transformed to the furans **5** without isolation of the diols **4**. Diol **4a** as derived from oxetane **1a** was isolated and its structure established by spectroscopic means (see Experimental Section).



The present reaction is, to our knowledge, the first oxetane ring-expanding rearrangement. The aromatization of the phenanthrene system in the rearrangement **3** → **4** is probably an important driving force for this reaction. Similar behavior is to be expected for related systems, *e.g.*, of the corresponding naphthalene derivatives. The reduced ketooxetanes derived from α diketones may, however, be more difficult to rearrange.

Stereochemistry of the Ketooxetanes 1.—The above reaction sequence has been applied in elucidating the stereochemistry of the ketooxetanes **1a**, **b**, and **d**. The photoaddition of PQ to either *cis*- or *trans*-2-butene yields two (**1a**, mp 99–101°, and **1b**, mp 123–126°) of the four possible oxetanes.[5] Reduction and acid treatment of **1a** and **1b** result in stereospecific formation of the furans **5a** and **5b**, respectively. According to the chemical shifts and coupling constants,[6] **5a** is assigned the trans and **5b** the cis structure. Hence one of the oxetanes **1a** or **1b** should have a cis, and the other a trans configuration.

The signals of the two methyl groups at the β-carbon atom in **1c–e** appear at τ 9.00 ± 0.07 and 9.25 ± 0.04. In the reduced derivatives **3c–e**, the corresponding signals are shifted slightly to lower ($\Delta\tau$ −0.04 ± 0.04) and to higher ($\Delta\tau$ +0.19 ± 0.04) field, respectively. Inspection of Dreiding models shows that the methyl group trans to the C=O or CHOH group (position B′) is in stronger shielding field of the neighboring benzene ring than the group at position B. Moreover, the slight change in the configuration of the six-membered ring on reduction of the keto group brings the B′ methyl protons more in the positive shielding envelope of the second benzene ring. Accordingly the lower field signals are assigned to the methyl group at position B, those at higher field to the methyl group at position B′. The methyl group at the β-carbon atom in **1a** shows its signals at τ 9.17, which is shifted to lower field ($\Delta\tau$ −0.06) in **3a**. The signals of the corresponding group in **1b** appear at τ 9.40, which is shifted to higher field ($\Delta\tau$ +0.25) on reduction to **3b**. This indicates that the methyl groups at the β-carbon atom in **1a** and **1b** are located cis and trans to the C=O group, respectively.

The assignment of the trans structure to **1a** and the cis to **1b** followed from the chemical shifts of the protons on the oxetane ring. In **1a** (**3a**) these protons are shifted to higher field [τ 5.20 (5.25) and 7.28 (7.55)] than in **1b** (**3b**) [τ 4.72 (4.95) and 6.88 (6.69)] as a result of their being located cis to the methyl groups.[7]

A difference of 0.4 ppm in the chemical shift of the two methylene protons A and A′ is observed in the nmr spectrum of **3c** (τ 5.82 and 5.43), as well as in that of the corresponding compound in which the methyl groups are replaced by Cl atoms. Since similar τ values are obtained for the α proton in **1a** and **1d** (τ 5.25 and 5.18, respectively) both compounds should have the same stereochemistry at the α-carbon atom. Otherwise a τ value larger by about 0.4 ppm would have been observed for this proton in **1d** since a trans methyl group has only a small effect (0–0.1 ppm to lower field) on the chemical shift of a vicinal proton.[7]

The signals of the α and β protons in **1b**, **1f**, and **1g** undergo similar upfield (+0.2 ± 0.03 ppm) and downfield (−0.17 ± 0.02 ppm) shifts, respectively, on reduction to the corresponding alcohol. This points to similar stereochemistry of the oxetane ring in these compounds. Strong support for this view is obtained from the chemical shifts of the H-1 and H-8 protons in derivatives of **1** and **3**. These values were determined by

(5) S. Farid and K.-H. Scholz, *Chem. Commun.*, 412 (1968).

(6) **5a**: τ 5.27 (A), 6.48 (B′), 8.51 (A′), 8.51 (B) ($J_{AB'}$ = 4.2, $J_{AA'}$ = 6.4, $J_{BB'}$ = 7.0 Hz). **5b**: τ 4.88 (A), 6.26 (B), 8.36 (A′), 8.72 (B′) (J_{AB} = 8.1, $J_{AA'}$ = 6.8, $J_{BB'}$ = 7.2 Hz). These chemical shifts and coupling constants are in very good agreement with data for *trans*- and *cis*-2,3-dimethyl-2,3-dihydrobenzofurans, respectively [D. P. Brust, D. S. Tarbell, S. M. Hecht, E. C. Hayward, and L. D. Colebrook, *J. Org. Chem.*, **31**, 2192 (1966)].

(7) As found in an nmr study of several cyclobutane derivatives: J. Leitich, unpublished data, 1968; *cf.* also H. Weitkamp and F. Korte, *Tetrahedron, Suppl.*, **7**, 75 (1966).

using spin–spin decoupling, indor, and induced shift techniques. Both the H-1 and H-8 signals in **1a–d** appear at τ 2.06–2.18. In **1f** the H-1 proton signals appear at a slightly lower field (τ 1.93), whereas the H-8 signals are, in comparison, strongly shifted to higher field (τ 3.03). Also in the reduced derivatives the H-8 signals in **3a** and **3c** appear at τ 2.27 and 2.29, respectively, whereas the corresponding signals in **3f** appear at higher field (τ 3.05). This indicates that the H-8 proton in **1f** (**3f**) "lies" on the top of the benzene ring of the indene moiety; *i.e.*, the latter is trans to the C=O (CHOH) group.

The stereochemistry at the carbinol carbon in **3a**, **3c**, and **3f** was deduced from lanthanide-induced shift data. The shifts of the proton signals due to complex formation with tris(dipivalomethanato)europium(III) [Eu(DPM)$_3$][8] are given in Table I. The signals of the α-

TABLE I

Eu(DPM)$_3$-INDUCED SHIFTS[a] IN THE NMR SPECTRA OF **3a**, **3c**, AND **3f**

Proton		1	2	3	4	5	6	7
Induced shift	**3a**	3.6	1.9	1.9	3.1	2.2	0.5	−1.3
	3c	3.5	1.9	1.9	3.4	2.9	1.4	0.2
Proton		8	10	OH	A	A′	B	B′
Induced shift	**3a**	16.8	18.0	12.1	27.9	(9.5)	(9.8)	19.2
	3c	22.3	15.2	13.3	25.4	27.3	(10.3)	(11.9)
Proton		1	4	5	6	7	8	10
Induced shift	**3f**	2.6	2.5	1.9	0.9	0.4	17.1	12.5
Proton		OH	A	B	4′	5′	—CH$_2$—	
Induced shift	**3f**	9.6	20.4	11.1	6.1	1.9	10.0[b]	4.2[c]

[a] Determined from the slopes of the plots of shifts (in parts per million) *vs.* molar ratios of Eu(DPM)$_3$:**3**; concentration of **3** *ca.* 0.2 molar in CCl_4. Positive values indicate shifts to lower field and negative values to higher field. The induced shifts for methyl groups appear in parentheses. The shift of the OH signal is not taken in computation of the location of the lanthanide ion because of uncertainty in predicting the predominant position of this rotating hydrogen atom. [b] Trans to the proton at position A. [c] Cis to the proton at position A.

hydrogen atoms undergo larger shifts than that of the alcoholic α hydrogen and the latter is shifted more than the OH signal. This indicates that the ethereal oxygen and not the alcoholic oxygen associates with the lanthanide ion since, on complex formation with hydroxyl oxygens, the shift of the OH signal is three to five times that of the α hydrogen.[8]

We found[9] that the equilibrium constant for the complex formation between Eu(DPM)$_3$ and trimethylene oxide exceeds that for cyclohexanol only by a factor of *ca.* 2. We also found,[9] however, that steric hindrance suppresses the complex formation. The lack of significant complex formation with the hydroxyl oxygen indicates, therefore, that this group is sterically hindered, which is the case with the isomer, in which the OH is cis to the oxetane β-carbon atom (see formula). One would reach the same conclusion on the basis of the concept of steric approach control in hydride reduction of carbonyl compounds, which implies that the approach of the reagent to a sterically hindered carbonyl group will be from the least hindered side.[10]

A computer program[11] was used to determine the location of the Eu^{3+} ion in the complex with **3a**, **3c**, and **3f**, which maximizes the correlation between the induced shift and the geometric factor $[3(\cos^2\theta - 1)r^{-3}]$ of pseudocontact shift. These calculations were executed for planar and differently puckered oxetane conformers. The best agreement between measured and predicted shifts was obtained for the oxetane ring, which is puckered by about 40° in **3a** (Figure 1), by about 20° in **3c** (Figure 2), and planar ring for **3f** (Figure 3). It is interesting that this puckered conformer of **3a** has both methyl groups in equatorial positions, which is optimum for the most stable conformer. For both **3a** and **3c** such distortion of the oxetane ring leads to less sterically hindered conformers.

Kinetics and Mechanisms.—The kinetics of the conversions **3** → **4** → **5** were studied by uv spectroscopy. Compounds **4** and **5** show the first absorption band (^1L_b) in the range 26–30 × 10^3 cm^{-1}, with a vibrational structure ($\Delta\nu \approx 1400$ cm^{-1}) similar to that of the dihydrophenanthrodioxins **2** (*cf.* ref 12). The O–O′ transition of this band in the spectrum of **5** (at 26.9 ± 0.3 × 10^3 cm^{-1}, $\epsilon \approx 2100$ in benzene) is shifted (*ca.* 500 cm^{-1}) to a lower wavenumber than that of **4**. Because of this difference in the spectra of **4** and **5** the rate of formation of these compounds could be measured.

Depending on the compound and the reaction conditions the ratio of k_1/k_2 varies considerably.[13] At 40°

$$3 + H^+ \xrightarrow{k_1} 4$$

$$4 + H^+ \xrightarrow{k_2} 5$$

with 10^{-3} *M* hydrogen chloride in benzene, **3a** was transformed almost quantitatively to **4a** ($k_1 \approx 1$ l. mol^{-1} sec^{-1}). Compound **5a** was not formed in appreciable amounts under these conditions ($k_1 \gg k_2$).[14] On the other hand, **3b** reacted detectably only at much higher acid concentrations. For example, at 40° with 4 × 10^{-2} *M* hydrogen chloride in benzene, k_1 has the value ~ 2 × 10^{-4} l. mol^{-1} sec^{-1}. In this reaction the characteristic uv maxima of the diol could be detected only in the early phases of the reaction ($k_1 \ll k_2$).[14] In the reaction of **3a** with 10^{-1} *M* CF_3COOH in benzene, both **4a** and **5a** were detected in comparable amounts over a relatively long reaction period ($k_1 \sim k_2$).

For the hydrolysis of trimethylene oxide, Pritchard, *et al.*,[15] have shown that a preliminary equilibrium proton transfer giving an oxonium ion precedes an SN1 sub-

(8) C. C. Hinckley, M. R. Klotz, and F. Patil, *J. Amer. Chem. Soc.*, **93**, 2417 (1971); J. K. M. Sanders and D. H. Williams, *ibid.*, **93**, 641 (1971); P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *ibid.*, **92**, 5734 (1970).

(9) S. Farid and C. Schnuell, unpublished results.

(10) *Cf.* S.-I. Yamada and K. Koga in "Selective Organic Transformations," Vol. 1, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, N. Y., 1970.

(11) S. Farid, A. Ateya, and M. Maggio, *Chem. Commun.*, 1285 (1971).

(12) C. H. Krauch, S. Farid, and G. O. Schenck, *Chem. Ber.*, **98**, 3102 (1965).

(13) The observed reaction constant k_1 is given by $k_1 = K \cdot k$, where K is the equilibrium constant for the formation of the conjugate acid of **4** and k the constant of the rate-determining elimination reaction

$$H^+ + 4 \overset{K}{\rightleftharpoons} (4 - H^+) \overset{k}{\rightarrow} 5$$

The same applies for k_2, where the rate-determining step is a nucleophilic displacement.

(14) The kinetics of the reaction **3** → **4** can be easily studied if $k_1 \gg k_2$ or $k_1 \ll k_2$ (in the later case $d[4]/dt \approx 0$). The rate of disappearance of **3** can be derived from plots of the absorption at the O–O′ transition of **4** or **5** *vs.* time, respectively.

(15) F. A. Long, J. G. Pritchard, and F. E. Stafford, *J. Amer. Chem. Soc.*, **79**, 2362 (1957); J. G. Pritchard and F. A. Long, *ibid.*, **80**, 4162 (1958).

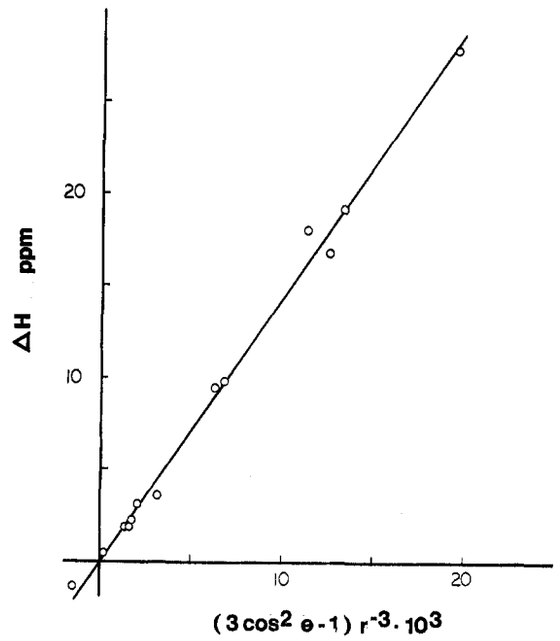


Figure 1.—Plot of the Eu(DPM)$_3$-induced shift in **3a** *vs.* the pseudocontact geometric factor for the computer-determined location of the lanthanide ion (Eu–O distance, 2.8 Å).

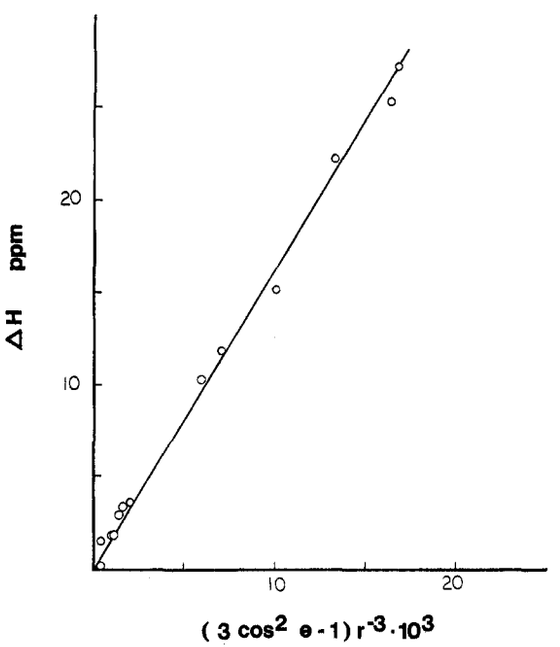


Figure 2.—Plot of the Eu(DPM)$_3$-induced shift in **3b** *vs.* the pseudocontact geometric factor for the computer-determined location of the lanthanide ion (Eu–O distance, 3.1 Å).

stitution. It is reasonable to assume also that in the rearrangement **3** → **4** a fast equilibrium between **3** and its conjugate acid (eq 1) precedes the kinetically controlling E1 or E2 elimination step. This reaction would be expected to proceed with retention of configuration regardless of the reaction order of the elimination. We obtained **5a** from **3a** and **5b** from **3b** on carrying out the reaction in either water-free benzene with hydrogen chloride or CF_3COOH, in aqueous dioxane with hydrochloric acid or in 90% acetic acid (**3b** did not react under the latter conditions). Since **5a** and **5b** have the same configuration as the starting oxetanes **3a** and **3b**, the dehydration to the furans in these cases

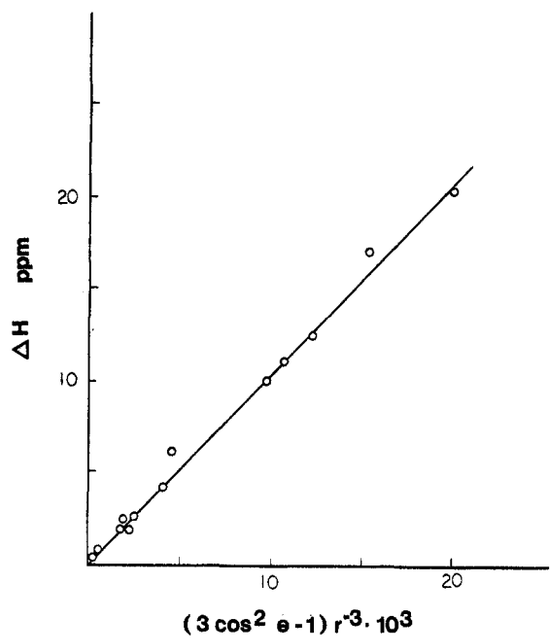
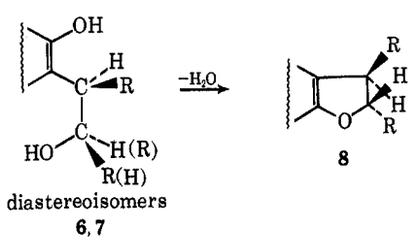


Figure 3.—Plot of the Eu(DPM)$_3$-induced shift in **3f** *vs.* the pseudocontact geometric factor for the computer-determined location of the lanthanide ion (Eu–O distance, 2.9 Å).

should have occurred *without* inversion.[16] On the other hand, both diastereoisomers[17] of the di-*tert*-butyl-substituted diols **6** and **7** yield on dehydration the same trans furan derivative[18] **8**. Thus, in one of these reactions inversion should have occurred. This dehydration clearly proceeds according to another mechanism (SN2 with inversion or SN1) owing to steric factors.



diastereoisomers **6**, **7** → **8**

R = *tert*-butyl

The kinetics of the dehydration of **4a** with CF_3COOH (7.1×10^{-2} *M*) in benzene were studied also by uv spectroscopy. Reaction constants of 4.6, 5.8, 7.6, and 8.9×10^{-3} l. mol^{-1} sec^{-1} were measured at 29.6, 34.8, 39.5, and 43.8°, respectively. This corresponds to an activation energy and an entropy of activation of 9.3 ± 0.3 kcal mol^{-1} and −38 ± 3 cal mol^{-1} °C^{-1}, respectively.

The dihydrofuran **5h** could also be prepared from the corresponding hydroxyoxetane **3h** having an acetal structure. This, however, followed another reaction route in which the other C–O bond of the oxetane ring is cleaved. On mild acid treatment, **3h** gave the tetra-

(16) The exact nature of this stereochemically unexpected reaction needs further investigation.

(17) These compounds are synthesized *via* photoaddition of PQ to 1,2-di-*tert*-butylethylene, which will be described in a separate publication.

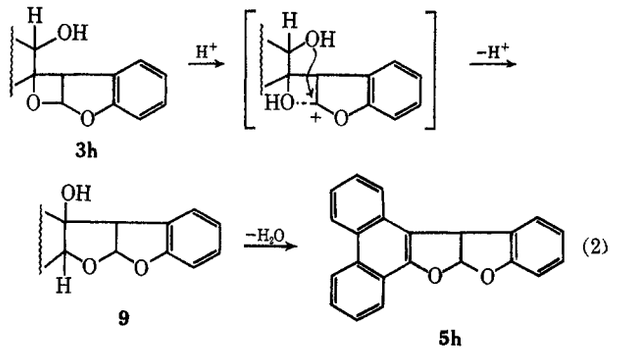
(18) As indicated by a distinctly smaller coupling constant of 1.8 Hz between the C-2 and C-3 protons in **8** compared with the normal value of 4.2 Hz in **5a**, the five-membered ring in **8** is apparently so distorted, owing to steric interference of the two *tert*-butyl groups, that the dihedral angle Φ between the H–C–C–H planes is considerably less than 120°.[19]

(19) H. Conroy, *Advan. Org. Chem.*, **2**, 265 (1960).

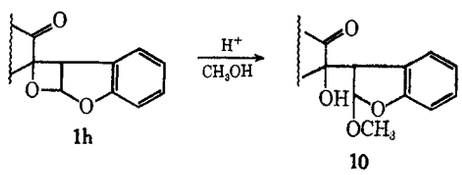
TABLE II

Compd	Recryst from	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
3a	Ethanol	192–194	$C_{18}H_{18}O_2$	81.17	6.81	80.92	6.77
3b	Petroleum ether	168–173	$C_{18}H_{18}O_2$	81.17	6.81	80.97	6.75
3c	Ethanol	135–136	$C_{18}H_{18}O_2$	81.17	6.81	81.22	6.80
3d	Benzene	177–179	$C_{19}H_{20}O_2$	81.40	7.19	81.40	7.08
3e	Nmr spectroscopically detected, not isolated						
3f	Petroleum ether	182–185	$C_{23}H_{18}O_2$	84.64	5.56	84.48	5.60
3g	Ethanol	201–204	$C_{25}H_{22}O_3$	81.06	5.99	80.94	6.00

hydrohydroxyfuran **9**, a reaction which can be explained in terms of an intramolecular nucleophilic displacement (*cf.* eq 2); **5h** was obtained on dehydration of **9** with P_2O_5.



Treatment with strong acid (0.2 *M* CF_3COOH, in benzene) cleaved **3h** (as indicated by uv) to 9,10-dihydroxyphenanthrene, which was oxidized readily with atmospheric oxygen to PQ. Similarly, the ketooxetane **1h** reopened to PQ and benzofuran on reacting with H_2SO_4 in aqueous dioxane.[12] When the reaction was carried out in methanol/HCl, however, ketol **10** was obtained. This intermolecular displacement points to a C–O bond cleavage analogous to that in eq 2.



Experimental Section

The nmr spectra were taken on Varian A-60A and A-56/60 spectrometers using TMS as internal standard. Infrared spectra were recorded in KBr or in CCl_4 on a grating spectrophotometer MH-2 SEM Brückl, Munich. The uv spectra were determined on a modified Bausch and Lomb 505 spectrophotometer. The uv measurements for the kinetic studies were carried out on a Beckman DK2 spectrophotometer using 1-cm water-jacketed cells (accuracy ±0.1°). Mass spectra were obtained with an Atlas CH-4 mass spectrometer (70 eV). Melting points were determined on a Kofler hot stage and are uncorrected. The petroleum ether used has a boiling range of 50 to 70°. Florisil (60–100 mesh, Fluka) was used for column chromatography and silica gel H (Merck) for preparative layer chromatography.

Reduction of 1[20] to 3.—To 100 mg of **1** in 5 ml of dioxane, a solution of *ca.* 30 mg of $NaBH_4$ and 5 mg of NaOH in 5 ml of 80% methanol was added dropwise. The mixture was stirred for 30 min. After distillation of the solvents at reduced pressure, the residue was diluted with water and twice extracted with ether to give **3** (in colorless crystalline form) in 80–90% yield. Analytical samples were obtained by recrystallization as given in Table II. All derivatives of **3** showed in uv (dioxane) a shoulder at *ca.* 33.2 × 10^3 cm^{-1} ($\epsilon \approx 3500$) and a maximum at *ca.* 36.8 × 10^3 cm^{-1} ($\epsilon \approx 12{,}000$); in ir (KBr) ν_{OH} ranging between 3330 and 3390 cm^{-1} (broad, intermolecular hydrogen bonding). In the nmr spectra ($CDCl_3$) of **3a–g** the CH–OH signal was observed between τ 4.78 and 5.03 (as singlet after shaking the solution with D_2O). The signals of the methyl groups at the α-carbon atom of the oxetane ring appeared at τ 8.53 (**3a**), 8.64 (**3b**), 8.72 (**3d**), 8.47 and 8.57 (**3e**); of those at the β-carbon atom at 9.11 (**3a**), 9.65 (**3b**), 8.93, 9.35 (**3c**), 9.02, 9.51 (**3d**), 8.98 and 9.52 (**3e**). The CH–CH_3 coupling constants were $J_{AA'}$ = 6.3 (**3a**), 6.8 (**3b**), 6.5 (**3d**) Hz; $J_{BB'}$ = 7.5 (**3a**), 7.9 (**3b**) Hz. The CH–CH coupling constants were $J_{AB'}$ = 7.9 (**3a**) and J_{AB} = 8.6 (**3b**) Hz. The H-C-H coupling constant, $|J_{AA'}|$, in **3c** was 5.0 Hz. Other nmr data are given in the text. Nmr ($CDCl_3$) data: of **3f**, τ 3.96 (broad d, J = 7.0 Hz, 1, H-4′ of the indene moiety), 4.37 (m, 1, –OCH<), 5.66 (d, J = 6.0 Hz, 1, –CH<), 6.65 (m, 2, $>CH_2$); **3g**, τ 4.19 (broad d, J = 7.5 Hz, 1, H-5′), 5.05 (d, J = 7.8 Hz, 1, –OCH<), 5.82 (d, J = 7.8 Hz, 1, –CH<), 8.35 and 9.07 [two s, each 3, $>C(CH_3)_2$].

10-(3-Hydroxy-2-butyl)-9-phenanthrol (4a).—A solution of 270 mg of **3a** in 20 ml of 60% acetic acid was heated for 0.5 hr at 50–60°, neutralized with $NaHCO_3$, and extracted with ether. After distillation of the ether, 10 ml of benzene was added to the residue; 45 mg of colorless crystals of **4a** remained insoluble. Compound **5a** (105 mg) was obtained by preparative layer chromatography of the mother liquor. In another experiment, 50 mg of **3a** was treated for 2 hr at 40° with 20 ml of 10^{-3} *M* hydrogen chloride in benzene. The solution was concentrated at reduced pressure to provide on cooling 38 mg of **4a**: mp 235–238° (from benzene); ir (KBr) 3340 (hydroxyl), 1595, 753, 722 cm^{-1} (aromatic); nmr (acetone-d_6) τ 5.47 (d of q, J = 3.7 and 6.4 Hz, 1, >CH–OH), 6.04 (d of q, J = 3.7 and 7.4 Hz, 1, >CH–), 8.50 (d, J = 7.4 Hz, 3, $>CHCH_3$), 8.84 [d, J = 6.4 Hz, 3, $-CH(OH)CH_3$]; mass spectrum *m/e* (rel intensity) 266 (69) (M^+), 248 (38) ($M - H_2O^+$), 233 (40) ($M - H_2O - CH_3^+$), 221 (100) ($M - CH(CH_3) - OH^+$), 202 (20), 193 (19) [$M - CH(CH_3) - CH(CH_3) - OH^+$], 178 (31), 165 (21).

Anal. Calcd for $C_{18}H_{18}O_2$ (266.3): C, 81.17; H, 6.81; active H(2), 0.75. Found: C, 81.00; H, 7.07; active H, 0.68.

Acetylation of Diol 4a.—A mixture of 35 mg of **4a**, 5 ml of acetic anhydride, and 0.5 ml of pyridine was refluxed for 2 hr. Decomposition with ice, neutralization with $NaHCO_3$, and extraction with ether provided 30 mg of the diacetate of **4a**: mp 100–102°; ir (CCl_4) $\nu_{C=O}$ 1735 cm^{-1} (aliphatic acetate),[22] 1772 cm^{-1} (vinyl acetate);[22] nmr ($CDCl_3$) τ 4.36 (d of q, J = 9.8 and 6.3 Hz, 1, >CH–OAc), 6.07 (d of q, J = 9.8 and 7.7 Hz, 1, >CH–), 7.47 (s, 3, phenanthryl $OCOCH_3$), 8.39 (s, 3, aliphatic $OCOCH_3$),[23] 8.51 (d, J = 7.7 Hz, 3, $>CHCH_3$), 8.55 [d, J = 6.3 Hz, 3, $-CH(OAc)CH_3$]; mass spectrum *m/e* (rel intensity) 350 (26) (M^+), 308 (42) (M – ketene$^+$) pointing to the vinyl acetate,[24] 248 (100) (308 – acetic acid$^+$) pointing to the aliphatic acetate,[24] 233 (49), 221 (28).

Anal. Calcd for $C_{22}H_{22}O_4$ (350.4): C, 75.41; H, 6.33. Found: C, 75.62; H, 6.28.

Methyl-Substituted 2,3-Dihydrophenanthro[9,10-*b*]furans (5a–d).—A solution of 100 mg of **3a–d** in 5 ml of dioxane was treated with 5 ml of 10% hydrochloric acid and heated at 70–80° for 3 hr. The solution was neutralized with $NaHCO_3$, concentrated under reduced pressure, and extracted with ether. The

(20) The formation of **1a–e** is briefly mentioned in ref 5 and ref 21; the experimental details will be described in a separate publication. Compounds **1f** and **1g** are described in ref 12.

(21) S. Farid, *Chem. Commun.*, 1268 (1967).

(22) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 1959, pp 179–182.

(23) This unusual high-field shift is interpreted in terms of the acetyl group being located predominantly above the phenanthrene moiety.

(24) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, pp 468–471.

TABLE III

Compd	Substituents	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
5a	*trans*-2,3-Dimethyl	73–76	$C_{18}H_{16}O$	87.06	6.50	86.89	6.57
5b	*cis*-2,3-Dimethyl	78–82	$C_{18}H_{16}O$	87.06	6.50	86.81	6.43
5c	3,3-Dimethyl	123–125	$C_{18}H_{16}O$	87.06	6.50	87.13	6.68
5d	2,3,3-Trimethyl	147–149	$C_{19}H_{18}O$	86.98	6.91	86.85	6.86

residue after distillation of ether was purified by layer chromatography (silica gel H, developed with benzene, R_f ~0.7, detected by its violet fluorescence, extracted with ether), yield 60–70%. Analytical samples were obtained by sublimation (distillation) and recrystallization from methanol. In the ir (KBr) the enol ether C=C stretching vibration at *ca.* 1640 cm^{-1} was much weaker than the corresponding band[12] in **2**. The nmr data ($CDCl_3$) of **5a** and **5b** are given in footnote 6; **5c**, τ 5.48 (s, 2, $-OCH_2-$), 8.32 [s, 6, $>C(CH_3)_2$]; **5d**, τ 5.46 (q, J = 6.7 Hz, 1, $-OCH<$), 8.45 (d, J = 6.7 Hz, 3, $-OCHCH_3$), 8.41 and 8.69 [two s, each 3, $C(CH_3)_2$]. The signals of protons at the carbon atom directly attached to the phenanthrene moiety were broadened by 0.4–0.6 Hz owing to long-range coupling with aromatic protons. Melting points and analytical data are given in Table III.

Compound **5a** was also formed on heating 30 mg of **3a** with 30 ml of 90% acetic acid for 10 hr as indicated by nmr of the residue remaining after distillation of the solvents.

Compound **3a** (50 mg) was treated with 20 ml of 0.5 *M* hydrogen chloride in absolute benzene for 2 hr at room temperature. On evaporation of the the solution under reduced pressure **5a** was obtained as a colorless oil in almost quantitative yield (identification by nmr, ir, and uv). Repeating the last reaction with 3×10^{-2} *M* CF_3COOH instead of hydrogen chloride and recrystallizing the residue from benzene yielded 9 mg of **4a** (identified by melting point and nmr). The mother liquor contained mainly **5a** and traces of **4a** (as shown by nmr); no other compounds could be detected.

Similar treatment of **3b** with 10^{-1} *M* CF_3COOH or 5×10^{-2} *M* hydrogen chloride in benzene for 4 hr at 30–35° afforded **5b** (as shown by nmr). In another experiment, 2 drops of CF_3COOH were added to 20 mg of **3b** in 1 ml of $CDCl_3$ in an nmr tube; after a few minutes the spectrum indicated complete transformation to **5b**.

Dehydration of 4a to 5a.—Diol **4a** (100 mg) was heated at 70–80° with 8% hydrochloric acid (10 ml) in dioxane (10 ml) for 3 hr. Working up as described for the corresponding experiments mentioned above yielded 78 mg of **5a** (uv, nmr). Refluxing a benzene solution of **4a** (30 mg) with ~200 mg of P_2O_5 for 1 hr, washing with water, and purifying by layer chromatography provided 17 mg of **5a** (nmr, ir, and uv).

9a,14b-Dihydro-10*H*-indeno[2,1-*b*]phenanthro[9,10-*d*]furan (5f).—A solution of 250 mg of **3f** in 10 ml of dioxane was heated 3 hr at 70° with 10 ml of 10% hydrochloric acid. After a few minutes, colorless needles of **5f** began to precipitate (150 mg). Another 70 mg of **5f** was obtained by concentrating the solution, mp 238–239° (from ethanol). A sublimed sample gave the same melting point; nmr ($CDCl_3$) τ 4.15 (m, 1, $-OCH<$), 4.66 (d, J = 7.8 Hz, 1, $>CH-$). The mass spectrum showed a parent peak at m/e 308.

Anal. Calcd for $C_{23}H_{16}O$: C, 89.58; H, 5.23. Found: C, 89.40; H, 5.28.

9a,15b-Dihydro-10,10-dimethyl-10*H*-[1]benzopyrano[3,4-*b*]-phenanthro[9,10-*d*]furan (5g).—Compound **3g** (140 mg) was treated with hydrochloric acid as described for **5f** to provide 120 mg of **5g**: mp 247° (sublimed sample); nmr ($CDCl_3$) τ 5.07 (s, 2, $-OCH_aCH_b<$), 8.17 and 8.55 [two s, each 3, $>C(CH_3)_2$] [J_{ab} = 7.5 Hz (measured from spectrum in C_6D_6)]; mass spectrum parent peak at m/e 352.

Anal. Calcd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 84.90; H, 5.77.

2,3-Di-*tert*-butyl-2,3-dihydrophenanthro[9,10-*b*]furan (8).—A solution containing 50 mg of either **6** (mp 193–195°) or **7** (mp 153–156°) in 10 ml of benzene was refluxed for 3 hr with ~200 mg of P_2O_5. The solution was washed with water and evaporated, and the residue was purified by layer chromatography, yielding 20–30 mg of **8** and a few milligrams of the starting compounds. Recrystallization from ethanol afforded colorless crystals of **8**: mp 129–130°; nmr ($CDCl_3$) τ 5.43 (d, J = 1.8 Hz, 1, $-OCH<$), 6.58 (d, J = 1.8 Hz, 1, $>CH-$), 9.01 and 9.12 [two s, each 9, two $C(CH_3)_3$]; mass spectrum parent peak at m/e 332.

Anal. Calcd for $C_{24}H_{28}O$: C, 86.70; H, 8.49. Found: C, 86.39; H, 8.41.

8b,9a,14b,14c-Tetrahydro-14c-hydroxybenzofuro[2,3-*b*]phenanthro[9,10-*d*]furan (9).—A solution of 650 mg of **3h**[12] in 10 ml of dioxane was heated at 50° with 10 ml of 50% acetic acid. After 1 hr the solution was neutralized, concentrated under reduced pressure, and extracted with ether to give 450 mg of **9** (in crystalline form): mp 212–214° (acetone–petroleum ether); ν_{OH} (KBr) 3510 cm^{-1}; uv (dioxane) ν_{max} at 36.7×10^3 cm^{-1} (ϵ 20,600); nmr ($CDCl_3$) τ 3.97 (d, J = 6.0 Hz, 1, $-OCHO-$), 5.15 (s, 1, $>CHO-$), 5.53 (d, J = 6.0 Hz, 1, $>CH-$); mass spectrum parent peak at m/e 328.

Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.34; H, 4.89.

9a,14b-Dihydrobenzofuro[2,3-*b*]phenanthro[9,10-*d*]furan (5h).—A solution of **9** (220 mg) in benzene (15 ml) was refluxed for 4 hr with ~0.5 g of P_2O_5. After filtration, washing with water, and distillation of the solvent, the residue was fractionally sublimed at 200° (0.1 Torr) to provide colorless crystals of **5h** (~10% yield): mp 249–250° (the melting point did not change after recrystallization from acetone); nmr ($CDCl_3$) τ 4.48 (d, J = 7.4 Hz, $>CH-$) [the signals of the $-OCHO-$ proton fall together with the aromatic signals (τ <3)]; mass spectrum parent peak at m/e 310.

Anal. Calcd for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.05; H, 4.65.

10-(2,3-Dihydro-2-methoxy-3-benzofuryl)-10-hydroxy-9(10*H*)-phenanthrone (10).—Concentrated hydrochloric acid (0.2 ml) was added to 100 mg of **1h** in 10 ml of methanol. The solution was warmed to 30–40° for 30 min. After concentration of the solution at reduced pressure and cooling, colorless crystals of **10** (75 mg) precipitated out: mp 128–132° (recrystallized from methanol); ir (KBr) ν_{OH} 3480 cm^{-1}, $\nu_{C=O}$ 1680 cm^{-1}; uv (dioxane) ν_{max} 30.5 (ϵ 3100), 35.6 (9000), 41.0 $\times 10^3$ cm^{-1} (26,000); nmr ($CDCl_3$) τ 4.63 (d, J = 1.7 Hz, 1, $-OCHO-$), 5.86 (s, 1, $-OH$), 6.52 (m, long range coupling with the aromatic protons[12] in addition to the vicinal coupling, 1, $>CH-$), 6.67 (s, 3, $-OCH_3$); mass spectrum m/e 358 (M^+), main peaks at m/e 326 (M − methanol$^+$), 209 (phenanthrene semiquinone$^+$), 210 (phenanthrenehydroquinone$^+$), 149 (M − 209$^+$).

Anal. Calcd for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found: C, 77.29; H, 5.02.

Registry No.—**3a**, 32528-65-7; **3b**, 32528-66-8; **3c**, 32528-67-9; **3d**, 32528-68-0; **3e**, 32528-69-1; **3f**, 32528-70-4; **3g**, 32528-71-5; **4a**, 32528-72-6; **4a** diacetate, 32528-73-7; **5a**, 32528-74-8; **5b**, 32528-75-9; **5c**, 32528-76-0; **5d**, 32528-77-1; **5f**, 32528-78-2; **5g**, 32528-79-3; **5h**, 32528-80-6; **8**, 32528-81-7; **9**, 32528-82-8; **10**, 32528-83-9; Eu(DPM)$_3$, 15522-71-1.

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