crystalline product separated upon cooling and when recrystallized from boiling water melted at 265–267°.[10] The toluidine salts of the other isomers were similarly prepared.

Potassium phenanthrene-3-sulfonate. The filtrate from which the sodium phenanthrene-1-sulfonate had been separated was heated to 90°, 800 ml. of a solution of potassium chloride, saturated at 25°, added, and the temperature allowed to drop to 60° where it was held for 30 min. The crystalline product was collected on a Buchner funnel and recrystallized from boiling water. The yield was 80–90 g. (27–30%). The toluidine salt melted at 218–219°.

Potassium phenanthrene-9-sulfonate. To the filtrate from which the potassium phenanthrene-3-sulfonate had been separated, there was added 400 ml. of a saturated solution of potassium chloride and the mixture refrigerated at 4° overnight. The precipitate was collected, dried, and digested first with 800 ml., and then with 400 ml. of boiling methanol. The combined methanol extracts were evaporated. The residue dissolved in 1 liter of boiling water was treated with 25 ml. of a 10% solution of barium chloride dihydrate. The mixture was held at the boiling temperature for 10 min. and then filtered on a preheated Buchner funnel. The precipitate which was a small amount of barium phenanthrene-2-sulfonate was retained. The filtrate was treated with 60 ml. of 5*M* sulfuric acid, digested at the boiling point for 10 min., and filtered to remove barium sulfate. To this filtrate there was added 150 ml. of a 20% solution of hydrated ferrous sulfate in 2% sulfuric acid. After this was allowed to stand in the cold overnight, the greenish crystals which formed were separated and recrystallized from boiling water to which was added a small amount of sulfuric acid and ferrous sulfate solution. The purified ferrous phenanthrene-9-sulfonate was suspended in 200 ml. of boiling water and treated with an equivalent amount of a 20% solution of potassium hydroxide. After digesting at the boiling point for 15 min. the mixture was filtered to remove iron hydroxide and the filtrate allowed to stand in the refrigerator overnight. The yield of recrystallized salt was 83–89 g. (28–30%). The toluidine salt melted at 230–232°.

Sodium phenanthrene-2-sulfonate. The alcohol-insoluble residue from which the 9-isomer had been extracted was dissolved in 1 liter of boiling water and 100 ml. of a 10% solution of barium chloride dihydrate was added. After digesting the mixture at the boiling point for 10 min., the barium phenanthrene-2-sulfonate was collected on a hot Buchner funnel and combined with the material obtained during the isolation of the potassium phenanthrene-9-sulfonate. The filtrate upon cooling deposited crystalline flakes of barium phenanthrene-3-sulfonate. The barium salts were separately converted to the free acids by treatment with 5% sulfuric acid. Subsequently the barium sulfate was removed and the respective solutions neutralized with a 25% solution of sodium hydroxide to yield crude sodium phenanthrene-2-sulfonate and with 25% solution of potassium hydroxide to yield 5–7 g. (*ca.* 2%) of the potassium phenanthrene-3-sulfonate. The latter was obtained in pure form. The 2-isomer, purified by recrystallization from boiling water was obtained in yields of 12–18 g. (4–6%). The toluidine salt melted at 283–285°.

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[10] All melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

Syntheses and Absorption Spectra of *cis*- and *trans*-9,10-Diaryl-9,10-dihydro-9,10-phenanthrenediols[1]

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AND WILLIAM F. O'CONNOR

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The syntheses and characterization of a series of *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols are described in which the 9,10-diaryl substituents vary in bulk (aryl = 4-methylphenyl, 2,4-dimethylphenyl, 2,4,6-trimethylphenyl, 2,3,5,6-tetramethylphenyl, and 1-naphthyl). Each *cis-trans* isomeric pair was configurationally related by oxidation to the same 2,2′-diaroylbiphenyl, and conversion to the same acid-catalyzed rearrangement product. Intramolecular hydrogen bonding measurements of the *cis*-diol series in the 3 micron region show $\Delta\nu$(OH) shifts of 38 cm.$^{-1}$ to 69 cm.$^{-1}$ In the *trans* series, only the *trans*-di(1-naphthyl) diol showed any hydrogen bonding [$\Delta\nu$(OH) = 36 cm.$^{-1}$]. These infrared measurements are interpreted in terms of the non-bonded steric effects of the aryl substituents upon the O—C—C angles at the 9,10-positions. A preferred conformation is suggested for the *trans*-di(1-naphthyl) diol. Interplanar angles of the biphenyl moiety calculated from ultraviolet absorption data show only a slight increase in both the *cis*- (32–36°) and *trans*-series (30–34°).

The molecule of 9,10-dihydrophenanthrene can be regarded as having a collinear biphenyl skeleton with a 2,2′-two-carbon-atom bridge. The two benzene rings are twisted at an angle of about 20° in order to accommodate the two methylene groups without appreciable distortion.[3]

As part of a study of *cis*- and *trans*-configurations about this two-carbon-atom bridge, we have prepared and characterized a series of *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols (II) in which the 9,10-diaryl substituents vary in bulk.

The general methods used in the synthesis and

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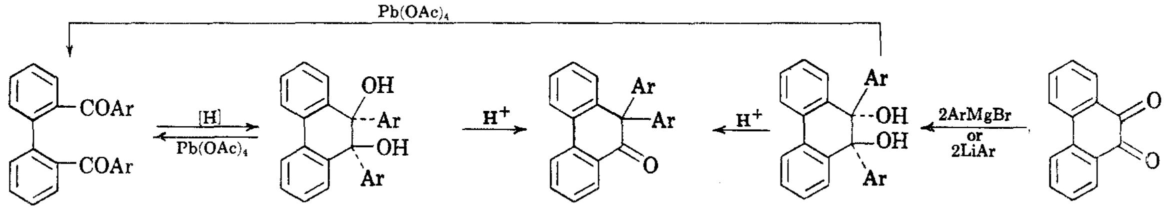
[1] Presented in part before the Organic Division of the Meeting-in-Miniature of the New York Section, AMERICAN CHEMICAL SOCIETY, February 15, 1957, and at the 132nd meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y., September, 1957.

[2] Ballistics Research Laboratory, Aberdeen Proving Ground, Md.

[3] G. H. Beaven, D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 854 (1952).

interconversion of these diol racemates are shown in the diagram.



Ia: Ar = 4-methylphenyl
Ib: Ar = 2,4-dimethylphenyl
Ic: Ar = 2,4,6-trimethylphenyl
Id: Ar = 2,3,5,6-tetramethylphenyl
Ie: Ar = 1-naphthyl

cis-IIa: Ar = *p*-tolyl
cis-IIb: Ar = *m*-xylyl
cis-IIc: Ar = mesityl
cis-IId: Ar = duryl
cis-IIe: Ar = 1-naphthyl

IIIa: Ar = *p*-tolyl
IIIe: Ar = 1-naphthyl

trans-IIa: Ar = *p*-tolyl
trans-IIb: Ar = *m*-xylyl
trans-IIe: Ar = 1-naphthyl

The *cis*-diols were prepared by a Zn dust-KOH,[4,5] Mg-MgI$_2$[6-8] and/or Na-Hg[4,5] reduction of the appropriate 2,2′-diaroylbiphenyl (I) (Table I) which was obtained by a Friedel-Crafts aroylation with diphenoyl chloride (Table IV). The *trans*-diols were synthesized by a Grignard[5,9,10] or aryllithium reaction on phenanthrenequinone (Table I). These methods of syntheses are not unequivocal. For example in the preparation of the *cis*-di-(*p*-tolyl) diol (IIa) and the *cis*-di(1-naphthyl) diol (IIe), the Zn-dust-KOH technique gave a not unexpected separable mixture of both *cis* and *trans* isomers.[4,5] However, since four of the six *cis*-diol isomers listed in Table I were prepared by at least one alternate method of 2,2′-diaroylbiphenyl reduction, we believe that this method generally yields the *cis* isomer. Further metallo-organic reductions of phenanthrenequinone are known to yield *trans*-diols.[6,9-11] Many unsuccessful attempts were made to prepare the *trans*-dimesityl diol (IIc) and *trans*-diduryl diol (IId) by this latter technique. *cis*-9,10-Dihydro-9,10-phenanthrenediol was prepared by an OsO$_4$ hydroxylation of phenanthrene,[12] and a Na-Hg reduction of 2,2′-biphenyldialdehyde,[13] while the unsubstituted *trans*-diol was synthesized by a LiAlH$_4$ reduction of phenanthrenequinone.[14]

Where possible the *cis*- and *trans*-diols were configurationally related as follows. Each diol of a *cis-trans* isomeric pair gave the same oxidation product, the 2,2′-diaroylbiphenyl (I) on treatment with Pb(OAc)$_4$. Further, *cis*- and *trans*-9,10-dihydro-9-10-phenanthrenediols, and each diol of *cis-trans* pair IIa, IIb, and IIe was converted to an identical acid-catalyzed rearrangement product. The unsubstituted diols, IIa, and IIe gave the expected pinacol rearrangement product, respectively, 9,10-dihydro-9-phenanthrone, 10,10-di(*p*-tolyl)-9,10-dihydro-9-phenanthrone (IIIa), and 10,10-di-(1-naphthyl)-9,10-dihydro-9-phenanthrone (IIIe). The infrared spectra of phenanthrones IIIa and IIIe were quite similar. Both showed strong carbonyl absorption at 5.92 microns, and an intense carbonyl conjugated aryl band at 6.27 microns.[15] On the basis of combustion analyses, molecular weight determination, and infrared and ultraviolet absorption data, IIIb seems to be a dimeric rearrangement product formed by loss of one molecule of water from two molecules of the diol.[16]

All *cis*-diols with the exception of *cis*-diduryl diol (IId) gave a color change with potassium tetramethylosmate (Table V). This negative test for *cis*-IId is probably due to its insolubility in methanol. It was quantitatively recovered by filtration from the methanolic solution of potassium tetramethylosmate. *trans*-Diols gave no reaction. This color test is based on the formation of cyclic osmic esters and is specific for *cis*-diols in the 9,10-dihydrophenanthrene and 9,10-dihydropyrene series.[10,12] Color

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(4) W. E. Bachmann and E. J. Chu, *J. Am. Chem. Soc.*, **57**, 1095 (1935).

(5) W. E. Bachmann, *J. Am. Chem. Soc.*, **54**, 1969 (1932).

(6) R. F. Brown, *J. Am. Chem. Soc.*, **76**, 1279 (1954).

(7) R. C. Fuson and C. Hornberger, *J. Org. Chem.*, **16**, 637 (1951).

(8) R. C. Fuson and R. O. Kerr, *J. Org. Chem.*, **19**, 372 (1954).

(9) T. Zincke and W. Troppe, *Ann.*, **362**, 242 (1908).

(10) R. Criegee, E. Höger, G. Huber, P. Kruck, F. Marktscheffel, and H. Schellenberger, *Ann.*, **599**, 81 (1956).

(11) H. M. Crawford, M. Lumpkin, M. McDonald, *J. Am. Chem. Soc.*, **74**, 4087 (1952); R. C. Fuson and P. Tomboulian, *J. Am. Chem. Soc.*, **79**, 956 (1957).

(12) R. Criegee, B. Marchand, and H. Wannowius, *Ann.*, **550**, 99 (1942).

(13) Additional evidence for a *cis*-diol synthesis in a Na-Hg reduction.

(14) J. Booth, E. Boyland, and E. E. Turner, *J. Chem. Soc.*, 1188 (1950).

(15) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 61.

(16) Assignment and proof of structure of IIIb and the acid-catalyzed rearrangement products obtained from IIc and IId will be the subject of a separate communication. It is pertinent to this work only that the *cis*- and *trans*-IIb diols gave the same rearrangement product.

TABLE I

9,10-DIARYL-9,10-DIHYDRO-9,10-PHENANTHRENEDIOLS (II)

Reactant	Procedure	Diol	Yield, % *cis*	Yield, % *trans*	Diol, M.P., °C. *cis*	Diol, M.P., °C. *trans*	Phenanthrone, M.P., °C.
Phenanthrene	OsO_4	*cis*-9,10-Dihydro-9,10-phenanthrenediol	70		177–178[12]		147–149[b]
2,2′-Biphenyldialdehyde	Na-Hg	*cis*-9,10-Dihydro-9,10-phenanthrenediol	20		177–178		
Phenanthrenequinone	$LiAlH_4$	*trans*-9,10-Dihydro-9,10-phenanthrenediol		85		185–187[14]	
Ia	Zn-KOH	*cis*- and *trans*-Di(*p*-tolyl) diol (IIa)	50	20	212–213[5]	140–142[5]	162–163[c]
Ia	Na-Hg	*cis*-Di(*p*-tolyl) diol (IIa)	55		212–213		
Phenanthrenequinone	ArMgBr	*trans*-Di(*p*-tolyl) diol (IIa)		44		140–142	
Ib	Na-Hg	*cis*-Di(*m*-xylyl) diol (IIb)	40		147–148		104–105[d]
Ib	Mg-MgI_2	*cis*-Di(*m*-xylyl) diol (IIb)	14		147–148		
Phenanthrenequinone	LiAr	*trans*-Di(*m*-xylyl) diol (IIb)		0.7		130–131	
Ic	Mg-MgI_2	*cis*-Dimesityl diol (IIc)	24		200–201.5[8]		
Id	Mg-MgI_2	*cis*-Diduryl diol (IId)[a]	68[a]		231–232[a]		
Ie	Zn-KOH	*cis*- and *trans*-Di(1-naphthyl) diol (IIe)	20	38	205–206[4]	263–264[5,f]	286–287[e]
Ie	Na-Hg	*cis*-Di(1-naphthyl) diol (IIe)	25		205–206[4]		
Phenanthrenequinone	ArMgBr	*trans*-Di(1-naphthyl) diol (IIe)		64		263–264	

[a] This *cis*-diol was generously supplied by Prof. R. C. Fuson, Univ. of Illinois. Yield and m.p. data from Ref. 7. [b] 9,10-Dihydro-9-phenanthrone. [c] 10,10-Di(*p*-tolyl)-9,10-dihydro-9-phenanthrone (IIIa). [d] This rearrangement product (IIIb) is not a phenanthrone. See Ref. 16. [e] 10,10-Di(1-naphthyl)-9,10-dihydro-9-phenanthrone (IIIe); Bachmann and Chu[5] report a m.p. of 258.5–259°. However, their carbon analysis was 0.6% low. [f] Most recently, W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, 22, 881 (1957) report a melting point of 261°.

changes were also observed with potassium triacetylosmate for the *cis*-diols. The *trans*-diols gave various shades of the original blue color of the reagent. As expected from Criegee's work, the reaction was reversible only with the *trans*-diols. On addition of a solution of potassium acetate in acetic acid to the *trans*-diol osmic acid diester, the characteristic deep blue color of the reagent, triacetylosmate, was reformed. The diesters of the *cis*-diols did not react with potassium acetate.[10,12]

Infrared absorption spectra. Intramolecular hydrogen bonds. Using LiF optics to obtain high resolution, Kuhn[17] has found two hydroxyl absorption bands in the 3 micron region for a number of dihydroxy compounds, the higher frequency band due to unbonded OH and the lower frequency band due to intramolecularly bonded OH. The measurements were made at dilutions such that intermolecular bonding did not occur. The separation between these bands, $\Delta\nu$(OH), is a measure of the strength of the hydrogen bond and varies inversely with distance between the OH groups—the stronger the bond, the shorter is the distance between the two OH groups, and the greater is $\Delta\nu$.[18]

Our data are summarized in Table II. In the *cis* series of compounds, all of the compounds have an internal hydrogen bond. As the steric requirements of the aryl substituents in the 9 and 10 positions increase the OH groups are forced closer together. The hydrogen bonding observed for *cis*-IIc, *cis*-IId, and *cis*-IIe diols is the strongest yet reported for *cis*- or *trans*-1,2-diols.[17,19] In the *trans* series of compounds only the *trans*-di(1-naphthyl)diol (IIe) has a hydrogen bond. Thus in the *trans* compounds a

TABLE II

FREQUENCY OF HYDROXYL BANDS IN THE INFRARED (CM.$^{-1}$)

Compound	Free OH	Bonded OH	$\Delta\nu$(OH) *cis*	$\Delta\nu$(OH) *trans*
cis-9,10-Dihydro-9,10-phenanthrenediol[17]	3605	3547	38	
trans-9,10-Dihydro-9,10-phenanthrenediol[17]	3605			0
cis-Di(*p*-tolyl) diol (IIa)	3595	3548	47	
trans-Di(*p*-tolyl) diol (IIa)	3552			0
cis-Di(*m*-xylyl) diol (IIb)	3595	3539	56	
trans-Di(*m*-xylyl) diol (IIb)	3595			0[a]
cis-Dimesityl diol (IIc)	3594	3525	69	
cis-Diduryl diol (IId)	3594	3529	65	
cis-Di(1-naphthyl) diol (IIe)	3595	3532	63	
trans-Di(1-naphthyl) diol (IIe)	3596	3560		36

[a] This compound showed one broad band in contrast to the sharp bands obtained for all other compounds. We feel that this compound may have two-OH bands which are unresolved and hence appear as one broad band.

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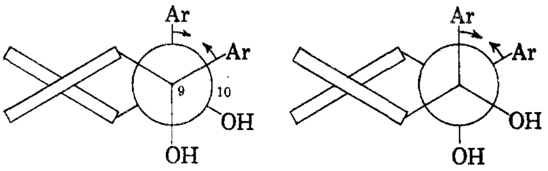
[17] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954).

[18] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937); R. M. Badger, *J. Chem. Phys.*, **8**, 288 (1940); W. Gordy, *J. Chem. Phys.*, **7**, 167 (1939); W. Gordy and S. C. Stamford, *J. Chem. Phys.*, **8**, 170 (1940).

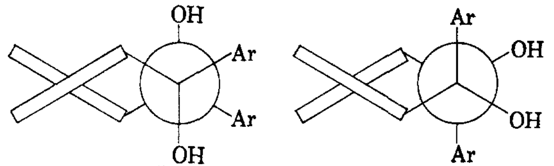
[19] (a) E. E. Eliel and C. Pillar, *J. Am. Chem. Soc.*, **77**, 3600 (1955). (*b*) A. R. H. Cole and P. R. Jeffries, *J. Chem. Soc.*, 4391 (1956).

hydrogen bond occurs only when the aryl substituents in the 9 and 10 positions are very large.

In the two possible low-energy skew conformations IV and V, for the *cis*-diols, one OH group is equatorial and the other is axial. These two OH groups are never more than 60° out of phase. There are two ways in which the OH groups can be brought closer together: (1) by rotation around the C—C bond between positions 9 and 10 as indicated by the arrows, and (2) by decreasing the O—C—C bond angles at the same positions.



IV *cis*-DIOLS[a] V



VI VII

trans-DIOLS[a]

[a] These convenient conformational symbols for the two-carbon bridge system in the *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols are adapted from those originally reported by Professor Kurt Mislow for a four-carbon bridge system in lectures presented at the AAAS Symposium on Organic Reaction Mechanisms, December 1956, N. Y. Academy of Science, January 1957, and the N. Y. American Chemical Society Meeting-in-Miniature, February 1957, and from Professor Melvin S. Newman's projectional formulas, *J. Chem. Ed.*, **32**, 344 (1955).

Since in the rotation around the C–C bond, the biphenyl system approaches a planar (eclipsed) conformation in which the aryl groups are opposed,[20] increasing the size of the aryl groups would increase the distance between the OH groups. This is contrary to our experimental findings and we must therefore conclude that the OH groups are brought closer together by a decrease of the O—C—C bond angles. An examination of molecular models shows that there is considerable steric interference between the two aryl groups and between the aryl groups and the biphenyl moiety in the *cis* isomers of IIc, IId, and IIe. This steric interference can be relieved by increasing the Ar—C—C bond angles at positions 9 and 10 which at the same time decreases the O—C—C bond angles. This alteration of bond angles seems to be another example of the Thorpe-Ingold deformation theory which states that when one of the angles at a carbon atom is increased, the opposite angle is decreased.[21] The deformation suggested by this interpretation of the data involves bringing an equatorial OH bond and an axial OH bond closer together, and it is known that this type of deformation involves considerably less strain than bringing two equatorial bonds together.[19a] The ultraviolet data are in accord with this view since the increase in the Ar—C—C bond angle should be much more effective in bringing the hydrogen-bonded OH groups together than in forcing the two phenyl rings of the biphenyl system closer together (*i.e.*, less effective in increasing the interplanar angle).

The two skew conformations for the *trans*-diols show both OH groups as axial (VI) or equatorial (VII). A necessary but not sufficient condition for hydrogen bonding in these compounds is that the OH groups be in equatorial positions. Thus, for example, in *trans*-1,2-cyclohexanediol, the azimuthal angle formed by the two OH groups is 60°, and this compound has an internal hydrogen bond. In the 9,10-dihydro-9,10-phenanthrenediols, the biphenyl interplanar angle causes the azimuthal angle between C—O bonds to be much larger than 60°, and as a consequence, the distance between the OH groups is much larger than in *trans*-1,2-cyclohexanediol. In *trans*-9,10-dihydro-9,10-phenanthrenediol,[17] *trans*-9,10-dimethyl-9,10-dihydro-9,10-phenanthrenediol,[10] *trans*-IIa, and *trans*-IIb diols, there is no internal hydrogen bond, and there is no reason for the OH groups to exist in any preferred conformation. We must conclude therefore that the presence of the very large naphthyl groups forces *trans*-diol IIe into conformation VII. Further, a hydrogen bond is produced by enlarging the Ar—C—C angles with the consequent decrease in the O—C—C angles at position 9 and 10, thereby bringing the OH groups close enough together to form a hydrogen bond of approximately the same strength as that in *trans*-1,2-cyclohexanediol.

Ultraviolet absorption spectra. Interplanar angles. Many workers have pointed out that electronic spectra are a much more sensitive index of steric effects in a molecule in its equilibrium state than is optical resolvability.[22] Indeed, Braude[23a,b,c,d,e] and his students, and most recently Truce and Emrick[24] have used ultraviolet absorption data to calculate interplanar angles (θ) from ϵ values at λ_{max} of the biphenyl-type band (K-band). Table III summarizes similar results on the *cis*- and *trans*-diols IIa-IIe, *cis*- and *trans*-9,10-dihydro-9,10-phenanthrenediol, 9,10-dihydrophenanthrene, and the reference compound, fluorene. Both *cis*- and *trans*-diols re-

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[20] Conformational isomers IV and V are also enantiomers.

[21] J. W. Baker, *Tautomerism*, G. Rutledge and Sons, Ltd., London, 1934, p. 179.

[22] W. Klyne, *Progress in Stereochemistry*, Vol. I, Academic Press, Inc., New York, N. Y., 1954, Ch. 4.

[23] (a) E. A. Braude and C. F. Sondheimer, *J. Chem. Soc.*, 3754 (1955); (b) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 3766 (1955); (c) E. A. Braude and C. F. Sondheimer, *J. Chem. Soc.*, 3773 (1955); (d) E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 3776 (1955); (e) E. A. Braude, *Experientia*, Vol. XI, 457 (1955).

[24] W. E. Truce and D. D. Emrick, *J. Am. Chem. Soc.*, **78**, 6130 (1956).

TABLE III

ULTRAVIOLET ABSORPTION SPECTRA (BIPHENYL BANDS) AND INTERPLANAR ANGLES (θ)[a]

Compound	λ_{max} (mμ)		ϵ_{max}		$\epsilon/\epsilon^\circ = \cos^2\theta$		θ	
	cis	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*
Fluorene[b]	262		20,000		1.00		0	
9,10-Dihydrophenanthrene[c]	264		17,400		0.87		21°	
9,10-Dihydro-9,10-phenanthrenediol[d]	269	267	16,000	15,000	0.80	0.75	26°	30°
IIa	277	278	14,300	13,500	0.71	0.68	32°	34°
IIb	268	270	13,800	13,600	0.69	0.68	33°	34°
IIc	277		13,200		0.66		35°	
IId	276		13,000		0.65		36°	
IIe	278	278	28,000	26,900	1.40	1.34	—	—

[a] The data refers variously to absolute ethanol or cyclohexane solutions. Since measurements are solvent independent—our work and that reported by Beaven *et al.* (Ref. 3)—the comparison seems justified. [b] Our λ_{max} and ϵ_{max} data for the fluorene reference compound is in agreement with that reported by R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Organic Compounds*, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 311, but differs slightly from that reported by E. A. Braude and W. F. Forbes[23d] who obtained their data from W. V. Mayneord and E. M. F. Roe, *Proc. Roy. Soc.*, **A185**, 634 (1937). [c] Generously supplied by Prof. Donald D. Phillips, Cornell University. [d] Our values agree with those reported by R. N. Beale and E. Roe, *J. Chem. Soc.*, 2884 (1951).

vealed the expected bathochromic shift and decrease in ϵ which Braude[23e] has ascribed to partly forbidden transitions between the non-planar ground states and near-planar excited states enforced by the "locking" effect of the two-carbon-atom bridge. The insignificant increase in interplanar angles in going from the *cis*-di(*p*-tolyl) diol (IIa) to the *cis*-diduryl diol (IId) however, indicates that the increasing steric repulsions of the aryl substituents have a much greater effect on the hydroxyl groups than the biphenyl moiety. The bond angle distortion results almost wholly in an increase in H-bonding and only a negligible increase in interplanar angle.

It is unfortunate that the irrelevant extinction of *trans*-IIe diol with the suggested conformation VII, had a separate naphthalene absorption which overlapped the displaced K-band of biphenyl.

The total effect of the 9,10-bridgehead hydroxyl and aryl substituents on the interplanar angles is approximately equivalent to placing a methoxyl or methyl "handle" in the 4,5-position of 9,10-dihydrophenanthrene.[2,22,23e] Since Wittig and Zimmerman[25] have demonstrated indirectly that the molecule 4,5-dimethyl-9,10-dihydrophenanthrene is dissymmetric, it may not be presumptuous here to note the intriguing possibility of similar optical behavior in the substituted two-carbon-atom bridged biphenyls reported herein.[26]

EXPERIMENTAL[27]

Hydroxyl absorption measurements were made by Dr. Lester P. Kuhn at the Ballistics Research Laboratory, Aberdeen Proving Ground, Md. with a Perkin-Elmer Model 12B Spectrometer equipped with a LiF prism. See Ref. 17 for details of sample preparation. The ultraviolet spectra were run in a Beckmann Quartz Spectrophotometer Model DU using 1 cm. quartz cells. The reported ϵ values are the average of three to six measurements at diol concentrations ranging from 0.005 g./liter to 0.015 g./liter in either ethanol or cyclohexane.

2,2'-Diaroylbiphenoyl (I). The appropriate diketones were obtained directly by a Friedel-Crafts aroylation with 2,2'-diphenoylchloride (Table IV). Nightingale, Heiner, and French[28] used this procedure to prepare 2,2'-di(4-methylbenzoyl)biphenyl (Ia) and 2,2'-di(2,4-dimethylbenzoyl)-biphenyl (Ib) in unreported yields. We have extended their technique to the preparation of 2,2'-di(2,4,6-trimethylbenzoyl)biphenyl (Ic), 2,2'-di(2,3,5,6-tetramethylbenzoyl)-biphenyl (Id), and 2,2'-di(1-naphthoyl)biphenyl (Ie). Thus, 8.0 g. anhydrous $AlCl_3$ (0.06 mole) were added to a stirred mixture of 100 ml. tetrachloroethane, 5.6 g. (0.02 mole) diphenoyl chloride, and 6.71 g. (0.05 mole) durene. After complete addition of the $AlCl_3$ (20 min.), the mixture was refluxed for 15 min. and then stirred at room temperature for 10 hr. The resulting dark brown mixture was hydrolyzed with 200 g. ice and 15 ml. concd. HCl. The solid which separated was filtered and air dried. The tetrachloride layer of the two phase system was separated and dried over anhydrous $CaSO_4$. Filtration, followed by evaporation of the solvent to dryness gave a dark colored solid. The combined solids (5.51 g., 58%) were recrystallized from toluene (charcoal) and finally from propanol to give 2.8 g. (26%) of Id, m.p. 253–255°. The structures of Ia, Ib, Ic, Id, and Ie have previously been established by unequivocal syntheses which culminated with a chromic acid oxidation of either the appropriate 9,10-diarylphenanthrene[7] or the 9,10-diaryl-

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(25) G. Wittig and H. Zimmerman, *Ber.*, **86**, 629 (1953).

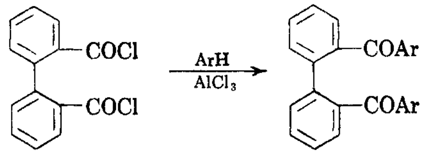
(26)[11] If the biphenyl system is rigidly twisted, six stereomeric forms are possible in theory: (±)-*cis*, (±)-*trans* A, and (±)-*trans* B; if on the other hand the biphenyl system readily passes through a planar (or equivalent) conformation, only three stereomeric forms will be isolable, *cis*, and (±)-*trans*.[11] The first reported evidence for this concept has been the result of the elegant work of Prof. Kurt Mislow and his students, New York University, who have observed racemization of the *cis*-diastereomer of 1,2,3,4-dibenzo-1,3-cyclooctadiene and mutarotation of one of the two possible *trans*-forms [*Trans. N. Y. Academy of Science*, **19**, 298 (1957)]. Although Prof. Mislow's compound contains a four-carbon-atom bridge, the theoretical arguments for this concept can be applied with no modification to compounds with only a two-carbon-atom bridge.

(27) All melting points are uncorrected. The microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(28) D. Nightingale, H. E. Heiner, and H. E. French, *J. Am. Chem. Soc.*, **72**, 1875 (1950).

TABLE IV

2,2′-DIAROYLBIPHENYLS



2,2′-Diaroylbiphenyl	Mole Ratio	Reaction			2,2-Diaroylbiphenyl		
	ArH/Diphenoylchloride/AlCl$_3$	Solvent	Time, Hrs.	Yield,[a] %	M.P., °C.	Recrystallizing Solvent	Lit. M.P., °C.
Ia	27.9/1.0/2.7	Toluene	8–12[b]	70	136–137	EtOH	136.5–137[4,28]
Ib	23.5/1.0/3.0	*m*-Xylene	3[b]	61	129–131	EtOH	126.5–127[28]
Ic	20.0/1.0/3.0	Mesitylene	5[b]	59	226–228[d]	EtOH	219–220[28]; 226–228[7]
Id	2.5/1.0/3.0	Tetrachloroethane	10[b]	26	253–255[e]	C_6H_6	255–256[8]
Ie	2.5/1.0/3.0	CS$_2$	5[c]	12	198–200	HOAc	200[4]

[a] All yield figures are the average of at least two runs. [b] Reactions run at room temperature. [c] Reaction run at 0–5°C. [d] Our melting point agrees with that reported by R. C. Fuson and C. Hornberger,[7] and differs from that reported by D. Nightingale, H. Heiner, and H. E. French.[28] [e] For purposes of comparison, a sample of 2,2′-diduroylbiphenyl was generously provided by Prof. R. C. Fuson, University of Illinois. His method of preparation is found in Ref. 8.

9,10-dihydro-9,10-phenanthrenediol,[4,5,8] or by an Ullman reaction on the aryl-2-bromophenyl ketone.[4,5,8,28]

2,2′-Biphenyldialdehyde. Pale yellow needles from 70% ethanol, m.p. 61–62°.[29]

Phenanthrenequinone. Orange needles from ethanol, m.p. 208–210°.[30]

cis-9,10-Dihydro-9,10-phenanthrenediol was obtained in 70% yield from phenanthrene, OsO_4 and pyridine[12] as white, fine silk needles from toluene, m.p. 177–178°. Alternatively this compound was prepared by treatment of 2,2-biphenyldialdehyde with Na-Hg.[4,5] Thus 0.5 g. (0.0024 mole) 2,2′-biphenyldialdehyde was shaken for 1 week with 11.5 g. of 5% Na-Hg (0.025 g. atom Na) in 50 ml. absolute ether. Hydrolysis of this mixture with dilute acetic acid (1:10), separation of the two resulting layers, and evaporation of the ether layer gave a yellow oil. Careful agitation of this oil with several ml. of cold 95% ethanol dissolved the oil and left crystalline plates, m.p. 135–138° which were immediately filtered. Several recrystallizations from *n*-propyl alcohol (charcoal) raised the m.p. to 177–178° which was not depressed on admixture with a sample prepared by the osmylation technique. The yield of pure diol was 0.1 g. (20%).

trans-9,10-Dihydro-9,10-phenanthrenediol was obtained in 85% yield from the $LiAlH_4$ reduction of phenanthrenequinone,[14] as white, fine silk needles from cyclohexane, m.p. 185–187°.

cis-9,10-Di(p-tolyl)-9,10-dihydro-9,10-phenanthrenediol (*cis*-IIa). Bachmann's[4,5] procedures were generally followed: 3.0 g. of Ia (0.0077 mole) was dissolved in 120 ml. of 95% ethanol. Nine g. of Zn dust, and 15 ml. of 40% KOH solution were then added and the mixture was refluxed (stirring) for 8 hr. After filtration, the Zn-dust residue was extracted twice with 25 ml. portions of hot ethanol and the combined filtrates poured into ice HCl-mixture. The precipitated solid was filtered, washed with water, and thoroughly air-dried before recrystallization from propanol. The first fraction was separated and after several recrystallizations from propanol (charcoal), yielded 1.5 g. (0.0038 mole, 50%) of *cis*-IIa, m.p. 212–213°. The solubilities of *cis*-IIa and *trans*-IIa are reversed in acetone. Therefore, the combined filtrates of these recrystallizations were evaporated to dryness, and recrystallized from acetone to yield 0.6 g. (0.0015 mole, 20%) of *trans*-IIa, m.p. 140–142°.

Alternatively, the Na-Hg reduction of Ia gave *cis*-IIa, m.p. 212–213° in 55% yield, undepressed on admixture with *cis*-IIa diol prepared by the Zn-dust reduction.

trans-9,10-Di(p-tolyl)-9,10-dihydro-9,10-phenanthrenediol (*trans*-IIa). The Grignard reagent was prepared in the usual manner: 50 ml. of anhydrous ether, 5.5 g. of Mg turnings, 8 ml. of bromotoluene, and a crystal of I_2 were stirred and gently heated until the Grignard reaction had commenced. Three portions of 8 ml. each of bromotoluene (total 0.24 mole) were then added alternately with three portions of 10 ml. each of anhydrous ether. The mixture was refluxed for 15 min. and then cooled. Fifty ml. of dry benzene was added to the prepared Grignard reagent, and with cooling, 17 g. (0.079 mole) of phenanthrenequinone was added (stirring) in 4 portions sufficient to maintain a vigorous reflux, after which the solution was refluxed for 5 hr. After cooling, the complex was hydrolyzed by pouring it into a mixture of 200 g. ice and 300 ml. concd. HCl. The water layer was separated and the solid material at the two-layer interface was filtered. The benzene-ether layer was dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The oil residue was digested with a few ml. of cold ethanol to remove the oily impurity. The solid residue was combined with the solid material from the interface and the whole was twice recrystallized from ethanol (charcoal) to yield 13.5 g. (44%) of *trans*-IIa, m.p. 140–142°. The mother liquor contains 4,4′-dimethylbiphenyl as a very soluble by-product. It was obtained by slow evaporation of the solvent ethanol to dryness in an evaporating dish. The center portion of the solid residue in the dish was again dissolved in ethanol and the process repeated several times to give 1.0 g. (0.0055 mole, 4.5% conversion based on bromotoluene) of 4,4′-dimethylbiphenyl, m.p. 120–121° (lit. m.p. 121–122°).[31]

With benzene as a recrystallizing solvent, a low melting benzene-diol adduct, m.p. 103–104°, was formed. Combustion analyses gave consistently and reproducibly high carbon and hydrogen analyses. All attempts to remove the benzene were unsuccessful. The adduct was ultimately identified as such by its infrared spectrum which was virtually superimposable upon that of *trans*-diol IIa with a single exception of strong benzene band at 14.82 microns.[32]

cis-9,10-Di(m-xylyl)-9,10-dihydro-9,10-phenanthrenediol (*cis*-IIb). The procedure of Fuson and Hornberger[7] was followed. Thus, 2.02 g. of I_2 was added under a nitrogen

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(29) W. J. Schmitt, E. J. Moriconi, and W. F. O'Connor, *J. Am. Chem. Soc.*, **77**, 5640 (1955).

(30) R. Wendland and J. LaLonde, *Org. Syntheses*, **34**, 76 (1954).

(31) F. Ullman and G. M. Meyer, *Ann.*, **332**, 44 (1904).

(32) We are indebted to Dr. R. L. Wagner, Chas. Pfizer and Co., Inc. for the infrared (CS_2) and ultraviolet (cyclohexane) solution spectra of these compounds.

atmosphere over a 15-min. period to a well stirred, initially heated mixture of 19.0 ml. of dry *n*-butyl ether, 23.0 ml. of dry toluene, and 2.12 g. Mg filings. The solution gradually became colorless as the reaction proceeded. After 15 min., a solution of 2.2 g. (0.00525 mole) of 2,2′-di(2,4-dimethylbenzoyl)biphenyl (Ib) in 19.0 ml. toluene was added over a period of 1/2 hr. Color changes of solution were: yellow after one-half of Ib had been added, violet after 3 hr. reflux and light brown to gray after 4 hr. reflux. Refluxing and stirring was continued overnight (15-hr. total) after which the solution appeared faintly yellow. The reaction product was decanted from the Mg and the solution poured into 20 g. ice and 25 ml. concd. HCl. The Mg residue was extracted with 30 ml. dry ethyl ether and the solution added to the ice–HCl mixture. The organic layer was extracted three times with water, dried over $CaSO_4$, and after filtration, evaporated to dryness. The residual oil was digested with anhydrous methanol and evaporated until crystallization occurred to yield 0.50 g. of crude *cis*-diol IIb. Recrystallization from ethyl alcohol (4 wk.) or n-hexane (15 min.) (charcoal) gave 0.30 g. (14%) of *cis*-IIb, m.p. 147–148°. Alternatively, *cis*-IIb was prepared in 40% yield, m.p. 147–148° from a Na-Hg reduction of Ib. A mixed melting point of the diols prepared by the alternate methods showed no depression.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.70; H, 6.71. Found: C, 85.76; H, 6.67.

trans-9,10-Di(m-xylyl)-9,10-dihydro-9,10-phenanthrenediol (*trans*-IIb). The *m*-xylyllithium was prepared under a nitrogen atmosphere in the usual manner.[33] To a solution of 1.6 g. of freshly prepared 1-bromo-2,4-dimethylbenzene[34] in 25 ml. anhydrous ether was added 1.4 g. (0.20 g.-atom) of lithium wire. The remainder of the bromoxylene (13.4 g.; total 0.088 mole) dissolved in 50 ml. of dry ether was added dropwise as soon as the initially vigorous reaction had subsided (1 hr.). Several runs were made at ice-bath temperatures, but the reaction proceeded most conveniently at room temperature. The *m*-xylyllithium was then filtered through an L-shaped tube loosely plugged with glass wool into a dry 250-ml. three-neck flask, also under a nitrogen atmosphere. To the almost clear solution, cooled to 0° with an ice-salt bath was added (stirring) 4.3 g. (0.021 mole) of phenanthrenequinone suspended in 50 ml. of benzene. The mixture was stirred overnight at room temperature. Hydrolysis of the complex intermediate was accomplished by adding the suspension to 100 g. ice and 5 ml. dilute HCl. The benzene-ether layer was then separated, dried, and evaporated to dryness. The resulting oil contained large amounts of phenanthrenequinone which remained undissolved after digesting the oil with several ml. of ether. Filtration of the insoluble phenanthrenequinone, and subsequent evaporation of the ether solution left an oil. This oil was treated with 40 ml. of dry petroleum ether (30–60°) and then 5–10 ml. of dry ether until all of the oil had dissolved leaving the crude white diol. This was filtered and recrystallized (charcoal) three times to yield 58 mg. (0.7%) of *trans*-diol (IIb) white needles, m.p. 130–131°.

Anal. Calcd. for $C_{30}H_{28}O_2$: C, 85.70; H, 6.71. Found: C, 85.58; H, 6.62.

All attempts to prepare this compound by the normal Grignard reaction using a wide variety of concentrations, temperatures, and isolation procedures led to no identifiable diol.

cis-9,10-Dimesityl-9,10-dihydro-9,10-phenanthrenediol (*cis*-IIc). Fuson's directions[8] for preparing *cis*-IIc were followed using a nitrogen atmosphere throughout. It was obtained in 24% yield, m.p. 200–201° from methanol.

cis-9,10-Diduryl-9,10-dihydro-9,10-phenanthrenediol (*cis*-IId). This compound, m.p. 231–232° was generously supplied by Prof. R. C. Fuson and was used directly in all measurements and reactions.

cis-9,10-Di(1-naphthyl)-9,10-dihydro-9,10-phenanthrenediol (*cis*-IIe). This compound, m.p. 205–206°,[4] from propanol, was prepared in the same manner as *cis*-IIa *via* Zn-dust–KOH reduction (20% yield) and Na-Hg reduction (25%) of 2,2′-di(1-naphthoyl)biphenyl (Ie). In the former reduction, a 38% yield of the *trans*-isomer was also obtained.

trans-9,10-Di(1-naphthyl)-9,10-dihydro-9,10-phenanthrenediol (*trans*-IIe). This compound, m.p. 263–264°, from isopropyl alcohol, was prepared in 64% yield by a Grignard reaction on phenanthrenequinone,[4] in the same manner as in the preparation of *trans*-Ia. A mixed melting point of the *trans* isomer prepared in this manner and by the Zn-dust–KOH reduction of Ie showed no depression.

Color tests with Criegee's Reagents.[10,12] Potassium tetramethylosmate ($0.001M$) and potassium triacetylosmate ($0.001M$) solutions were prepared, respectively, in absolute methanol and glacial acetic acid as directed.[12] The color tests were conveniently run with 0.5 ml. of the reagent and approximately 10^{-6} mole of the diol. Results are summarized in Table V.

TABLE V

COLOR CHANGES WITH CRIEGEE'S REAGENTS[a]

	Potassium Tetramethylosmate		Potassium Triacetylosmate	
Compound	*cis*	*trans*	*cis*[b]	*trans*[b]
9,10-Dihydro-9,10-phenanthrenediol	Pale green	Green	Pale violet	Deep blue
IIa	Yellow	No reaction	Yellow	Deep blue
IIb	Yellow	No reaction	Deep violet	Deep blue
IIc	Deep blue		Deep violet	
IId	No reaction[c]		Pale violet	
IIe	Yellow-green	No reaction	Deep violet	Deep blue

[a] The colors reported are those which appeared after the solutions of reagent and diol were in contact 30 min. [b] To show the reversibility of this reaction on treatment of the reagent-diol solution with potassium acetate in acetic acid, the recorded color is that which appears after the potassium acetate in acetic acid has been added. [c] *cis*-Diol (IId) is insoluble in MeOH solvent used for reagent preparation.

Diol oxidation with lead tetraacetate. The 2,2′-diaroylbiphenyls, respectively, Ia, Ib, and Ie were obtained from each of *cis-trans* isomeric diol pairs by warming a benzene or acetic acid solution of excess lead tetraacetate and each diol (25–50 mg.) of the series, IIa, IIb, and IIe, for 15–30 min. in a steam bath. Similarly, *cis*-IIc and *cis*-IId, gave, respectively, Ic and Id.

Acid-catalyzed rearrangements. Each diol of the *cis-trans* isomeric pairs 9,10-dihydro-9,10-phenanthrenediol, IIa, IIb, and IIe, was dissolved in the minimum volume of hot glacial acetic acid to which was added 2–3 drops of concd.

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(33) *Organic Reactions*, Vol. VII, p. 286 (1954).

(34) Preparation identical to that for bromomesitylene, L. I. Smith, *Org. Syntheses*, **Vol. II**, p. 95 (1943).

sulfuric acid. The solution was heated on a steam bath for 15–30 min. In all cases, the *cis*-diols reacted visibly more rapidly than the *trans*-diols. A few drops of water were sufficient to precipitate the rearrangement product if this had not occurred at the end of 30 min. The product was filtered, washed with water, and recrystallized. In this manner, the following four rearrangement products were obtained:

9,10-Dihydro-9-phenanthrone, m.p. 147–149° (lit. m.p., 152°)[35] from ethanol, was obtained from both *cis*- and *trans*-9,10-dihydro-9,10-phenanthrendiol. It is unstable on standing in air or in solution and changes color from pale yellow to pink to red in a relatively short time. After rapid filtration, a single pale yellow crystal was quickly selected for melting point determination. The time interval between commencement of the rearrangement process and the melting point determination approximated 20 min.

10,10-Di(p-tolyl)-9,10-dihydro-9-phenanthrone (IIIa), m.p. 163–164.5° from absolute ethanol was obtained in 90% yield from *cis*-IIa and in 80% yield from *trans*-IIa.

Anal. Calcd. for $C_{28}H_{22}O$: C, 89.80; H, 5.92. Found: C, 89.69; H, 5.88.

Bachmann[4] prepared IIIa, m.p. 158–159° by a similar pinacol rearrangement using iodine and glacial acetic acid.

10,10-Di(1-naphthyl)-9,10-dihydro-9-phenanthrone (IIIe), m.p. 286–287°[36] from absolute ethanol was obtained in 90% yield from *cis*-IIe and in 35% yield from *trans*-IIe.

Anal. Calcd. for $C_{34}H_{22}O$: C, 91.46; H, 4.97. Found: C, 91.45; H, 5.33.

The infrared spectra of phenanthrones IIIa and IIIe are quite similar and show identical absorption bands, attributed to aromatic ketones at 5.92, 6.27, and 7.90 microns, and to aromatic substituents at 6.90, 7.18, 12.62, 13.03, 13.26, 13.66, and 14.40 microns.[37]

Rearrangement Product (IIIb), m.p. 104–105° from ethanol was obtained in 95% yield from *cis*-IIb and in 90% yield from *trans*-IIb.

Anal. Calcd. for $C_{60}H_{54}O_3$: C, 87.55; H, 6.61; Mol. wt., 823. Found: C, 87.56; H, 6.71; Mol. wt., 881 ± 10% (Signer-Barger).

The infrared spectrum of IIIb showed a weak band at 2.95μ (OH), moderate bands at 6.23μ, 6.92μ, 8.13, 9.25, and 10.57μ (aryl substituents), and strong bands at 6.01μ and 13.65μ; λ_{max} 253 mμ, ϵ_{max} 68,200.

Acknowledgment. The authors take pleasure in thanking the Research Corp. for grants initiating and supporting this work. Special thanks are due to William J. Schmitt, S. J., Woodstock College, Woodstock, Md. whose serendipity led us to this investigation.

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(35) F. R. Japp and A. Findlay, *J. Chem. Soc.*, 1121 (1897).

(36) See Table I, Ref. (e).

(37) We are indebted to Mr. Daniel McCarthy for the infrared spectra (KBr) disk for these compounds.

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA]

gem-Dinitro Esters. I. Preparation and Some Reactions of α-Hydroxy-β,β-dinitropropionic and -butyric Acids

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The preparation of α-hydroxy-β,β-dinitro-propionic and -butyric acids by the condensation of dinitromethane and 1,1-dinitroethane, respectively, with glyoxylic acid, their esterification and acylation, and some of their physical properties are described.

As part of a study of the chemistry and properties of *gem*-dinitro esters, .several α-hydroxy-β,β-dinitro acids and esters were prepared by the condensation of 1,1-dinitroparaffins with glyoxylic acid derivatives.

The condensation of nitroparaffins with carbonyl compounds to form nitro alcohols was first reported by Henry[2] in 1895. Subsequent studies of this reaction, primarily using mononitroparaffins, were reviewed by Hass and Riley.[3] Chattaway and Witherington[4] successfully used the hydrate of a carbonyl compound in this same condensation to obtain nitro alcohols. Shechter and Conrad[5] prepared α-hydroxy-β-nitropropionic acid by the condensation of nitromethane with glyoxylic acid in aqueous solution.

In the present investigation α-hydroxy-β,β-dinitrobutyric acid (I) was prepared by the acid-catalyzed condensation of 1,1-dinitroethane with glyoxylic acid hydrate. It was also obtained, although in lower yield, in the attempted preparation of 2,2,5,5-tetranitro-3,4-hexanediol by the reaction of 1,1-dinitroethane with a commercial grade of glyoxal.[6] The α-hydroxy acid was stable in acidic or neutral media but it rapidly reacted with two moles of base to form glyoxylate and dinitroethane anions. Esterification with ethanol or methanol in the presence of sulfuric acid was normal in contrast

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(1) Present address: Stanford Research Institute, Menlo Park, Calif.

(2) L. Henry, *Compt. rend.*, 120, 1265 (1895).

(3) H. B. Hass and E. F. Riley, *Chem. Revs.*, 32, 406 (1943).

(4) F. D. Chattaway and P. Witherington, *J. Chem. Soc.*, 1178 (1935).

(5) H. Shechter and F. Conrad, *J. Am. Chem. Soc.*, 75, 5612 (1953).

(6) α-Hydroxy-β,β-dinitrobutyric acid could arise in one of several ways, for instance, by oxidation of an intermediate condensation product as α-hydroxy-β,β-dinitrobutyraldehyde or by preliminary oxidation of the glyoxal to glyoxylic acid, followed by normal condensation. The mechanism of this reaction, however, was not investigated.