3.21 (s, 1 H), 3.74 (t, 2 H), 3.85 (m, 1 H); lit.[9] ^{1}H NMR (CD_3OD) δ 1.17 (d), 2.60 (m), 3.66 (s), 4.74 (s); ^{13}C NMR ($CDCl_3$) δ 21.95, 35.22, 41.07, 61.03, 66.43.

2-Phenyl-1,4-oxathiane (14): ^{13}C NMR ($CDCl_3$) δ 26.32, 33.22, 69.80, 80.39; ^{13}C NMR ($CDCl_3$) δ 26.38, 33.23, 69.78, 80.39.[17]

2-Octyl-1,4-oxathiane (15): mp 4-5 °C; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, 3 H, J = 7 Hz, CH_3), 1.27 [br s, 10 H, $(CH_2)_5$], 2.30 (m, 2 H), 2.61 (m, 1 H), 2.87 (m, 1 H), 3.45-3.59 (br d, 1 H, OC*H* octyl), 1.30-1.50 [m, 4 H, $(CH_2)_2$], 3.73 (td, 1 H, J = 2.8, 12.0 Hz, C*H*O octyl), 4.22 (dt, 1 H, J = 2.8, 12.0 Hz, CHO octyl); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.61, 25.22, 26.55, 29.20, 29.46, 29.53, 31.37, 31.81, 36.40, 69.22, 78.15. Anal. Calcd for $C_{12}H_{24}OS$: C, 66.76; H, 11.11; S, 14.81. Found: C, 66.76; H, 11.16; S, 15.72.

***trans*-9-Methyl-1,4-oxathiadecalin (16)**: mp 7-8 °C; ^{1}H NMR ($CDCl_3$) δ 1.43, (s, 3 H, CH_3), 1.45-1.82 [m, 8 H, $(CH_2)_4$], 2.37 (dt, 1 H, J = 2.1, 13.3 Hz, C*H*S), 2.91-3.11 (m, 2 H, CH_2S), 3.82 (dq, 1 H, J = 1.9, 12.3 Hz, C*H*O), 4.04 (td, 1 H, J = 2.3, 12.3 Hz). Anal. Calcd for $C_9H_{16}OS$: C, 62.79, H, 9.30; S, 18.60. Found: C, 62.61; H, 9.30; S, 19.17.

***trans*-2-Methyl-2-hydroxycyclohexyl 2-hydroxyethyl sulfide (17)**: mp 34.5-36.0 °C; ^{1}H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CH_3), 1.25-1.58 (m, 4 H), 1.66-1.87 (m, 3 H, CH_2, SCH_2CHH_e), 2.0-2.08 (m, 1 H, SCH_2CHH_a), 2.61-2.87 (m, 3 H, $CHSCH_2CH_3$), 3.34 (br s, 1 H, O*H*), 3.60 (br s, 1 H, O*H*), 3.74-3.85 (m, 2 H, CH_2OH); ^{13}C NMR ($CDCl_3$) δ 21.58, 22.95, 25.88, 32.43, 35.17, 39.87, 56.94, 61.20, 72.64. Anal. Calcd for $C_9H_{18}O_2S$: C, 56.84, H, 9.47; S, 16.84. Found: C, 56.52; H, 9.54, S, 16.78.

2-Hydroxydecyl 2-hydroxyethyl sulfide (18): mp 26-27 °C; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, 3 H, J = 6.0 Hz, CH_3), 1.25 [m, 11 H, $(CH_2)_5CH$], 1.40-1.55 (br d, 3 H, $CHCH_2$), 2.70-2.82 (m, 3 H) 3.58-3.65 (br d, 1 H, C*H*OH), 3.72 (t, 2 H, J = 5.8 Hz, CH_2OH); ^{13}C NMR ($CDCl_3$) δ 13.96, 22.51, 25.60, 29.13, 29.41, 29.50, 31.72, 35.51, 36.23, 39.84, 61.12, 70.32. Anal. Calcd for $C_{12}H_{24}O_2S$: C, 61.54; H, 11.11; S, 13.68. Found: C, 61.45; H, 11.32; S, 13.57.

2-Phenyl-2-hydroxyethyl 2-hydroxyethyl sulfide (19): mp 43-45 °C; ^{1}H NMR ($CDCl_3$) δ 2.5-2.9 (m, 4 H, CH_2SCH_2), 3.57-3.70 (br d, 2 H), 3.80-3.92 (br d, 2 H), 3.97 (dd, 1 H, J = 5.7, 8.1 Hz, C_6H_5CHOH), 7.36 (m, 5 H, C_6H_5); ^{13}C NMR ($CDCl_3$) δ 35.56, 41.56, 61.26, 73.07, 125.85, 127.79, 128.83, 142.81. Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.61; H, 7.07; S, 16.16. Found: C, 60.13; H, 7.15; S, 16.17.

Acknowledgment is made to the Department of Energy for support of this research. We are also grateful to the American Chemical Society—Organic Division (sponsored by the Rohm & Haas Co.) for a fellowship to J.W.K. We thank Dr. J. C. Garcia Ruano for samples of *threo*- and *erythro*-**5** and NMR spectral data for *cis*- and *trans*-**4** and **14**. We are indebted to our colleagues E. L. Eliel and P. J. Kropp for their valuable assistance in this effort. Finally, a portion of this work was completed while S.A.E. was a National Research Council Senior Postdoctoral Fellow (Ford Foundation) and Fulbright Scholar at Universite Paul Sabatier, Toulouse, France.

(17) Personal communication from Professor J. L. Garcia-Ruano.

Syntheses and Chemistry of Some Dibenz[*c*,*e*]azepines

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5-Methyl-, 5,7-dimethyl-, and 5,7-diphenyl-substituted and unsubstituted 5*H*-dibenz[*c*,*e*]azepines were prepared by two general routes from [1,1'-biphenyl]-2,2'-dicarboxaldehyde. The unsubstituted dibenzazepine was converted into 1a,9b-dihydrophenanthro[9,10-*b*]azirine both by lithium diisopropylamide (LDA) and by UV irradiation. The disubstituted azepine derivatives failed, however, to undergo valence isomerization under such conditions. *N*-Benzylphenanthrene 9,10-imine was obtained directly from 2'-(bromomethyl)[1,1'-biphenyl]-2-carboxaldehyde and excess benzylamine. Aerial oxidation of 5,7-diphenyldibenz[*c*,*e*]azepine in the presence of 50% aqueous NaOH led, under phase-transfer conditions, to 5,7-diphenyldibenz[*c*,*e*]azepin-5-ol. Special structural features of this carbinol found by X-ray analysis are discussed.

In a previous paper[1] we postulated that polycyclic arene imines are active metabolites of mutagenic and carcinogenic hydrocarbons. The aziridines were assumed to be formed in vivo by interaction of cellular nitrogen nucleophiles with arene oxides followed by enzymatic ring closure of the resulting amino alcohols. Support for this hypothesis has recently been found by biological tests which demonstrated unusually high mutagenic potencies of all polycyclic arene imines[2,3] as well as direct correlation between their activities and those of the corresponding epoxides.[2] Since the synthetic routes developed, so far, for aromatic imines[1,4-14] failed to be applicable to a considerable number of representative derivatives of carcinogenic polycycles,[15] we found it imperative to further investigate their preparation by new methods. It seemed that an attractive approach to these polycyclic aziridines could be the valence isomerization of diaryl[*c*,*e*]azepines. The syntheses of the latter compounds have, however, been

(1) Ittah, Y.; Shahak, I.; Blum, J. *J. Org. Chem.* **1978**, *43*, 397.
(2) (a) Glatt, H.; Yona, I.; Ben-Shoshan, S.; Jerushalmy, P.; Blum, J.; Oesch, F. In *Polynuclear Aromatic Hydrocarbons: Eight International Symposium on Mechanisms, Methods and Metabolism*; Cooke, M. W., Dennis, A. J., Eds.; Battelle Press, Columbus, Ohio, 1983; pp 485-496. (b) Glatt, H.; Ludewig, G.; Platt, K. L.; Waechter, F.; Yona, I.; Ben-Shoshan, S.; Jerushalmy, P.; Blum, J.; Oesch, F. *Cancer Res.* **1985**, *45*, 2600.
(3) Stark, A. A.; Zeiger, E.; Shtelzer, S.; Sheradsky, T.; Lifshitz, Y.; Blum, J. *Mutagenesis*, **1986**, *1*, 35.
(4) Markov, V. I.; Kremev, M. M.; Danilenko, D. A.; Baranovskaya, V. F. *Otkrystiya, Izobret., Prom. Obraztsy, Tovarnye Znaki* **1972**, *49*, 87; *Chem. Abstr.* **1972**, *77*, 88166g.
(5) Blum, J.; Ittah, Y.; Shahak, I. *Tetrahedron Lett.* **1975**, 4607.
(6) Shudo, K.; Okamoto, T. *Chem. Pharm. Bull.* **1976**, *24*, 1013.
(7) Ittah, Y.; Sasson, Y.; Shahak, I.; Tsaroom, S.; Blum, J. *J. Org. Chem.* **1978**, *43*, 4271.
(8) Denis, J. N.; Krief, A. *Tetrahedron* **1979**, *35*, 2901.
(9) Weitzberg, M.; Aizenshtat, Z.; Jerushalmy, P.; Blum, J. *J. Org. Chem.* **1980**, *45*, 4252.
(10) Weitzberg, M.; Aizenshtat, Z.; Blum, J. *J. Heterocyclic Chem.* **1981**, *18*, 1513.
(11) Shtelzer, S.; Weitzberg, M.; Jeries, J.; Sheradsky, T.; Aizenshtat, Z.; Blum, J. *J. Heterocyclic Chem.* **1984**, *21*, 1.
(12) Pochlauer, P.; Müller, E. P.; Peringer, P. *Helv. Chim. Acta* **1984**, *67*, 1238.
(13) Weitzberg, M.; Aizenshtat, Z.; Blum, J. *J. Heterocyclic Chem.* **1984**, *21*, 1597.
(14) Weitzberg, M.; Aizenshtat, Z.; Blum, J. *J. Heterocyclic Chem.* **1985**, *22*, 865.
(15) See, e.g.: (a) Blum, J.; Yona, I.; Tsaroom, S.; Sasson, Y. *J. Org. Chem.* **1979**, *44*, 4178. (b) Blum, J.; Ben-Shoshan, S. *J. Heterocyclic Chem.* **1983**, *20*, 1461.

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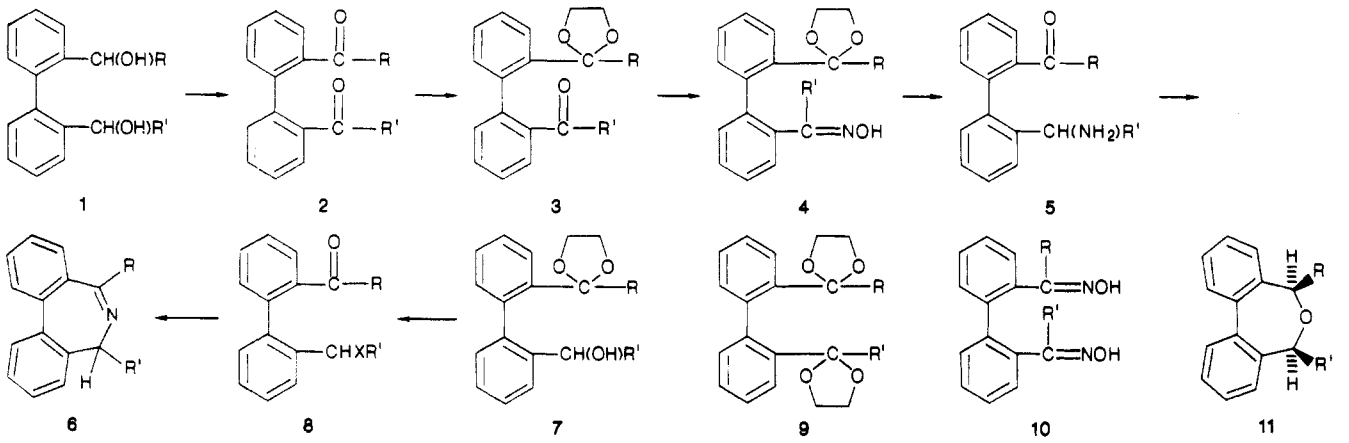


studied only to a limited extent[16-18] in spite of the observed pharmaceutical activity in some 5*H*-dibenz[*c*,*e*]azepines[17a] and, in particular, in their 6,7-dihydro derivatives.[19]

In this paper we wish to report two new synthese of dibenz[*c*,*e*]azepines and to describe the problems encountered with their transformation to phenanthrene 9,10-imines.

Results and Discussion

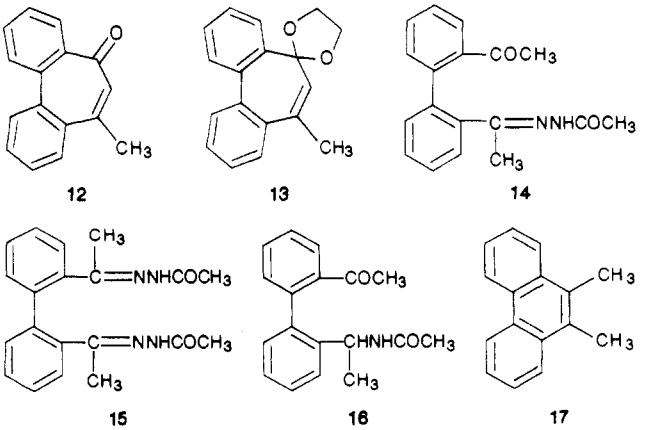
Syntheses of Dibenz[*c*,*e*]azepines. Two general routes, **2** → **3** → **4** → **5** → **6** and **7** → **8** → **6**, were followed in the syntheses of the 5*H*-dibenz[*c*,*e*]azepines. The unsubstituted parent compound **6** (R = R′ = H), was obtained in an overall yield of 42% from [1,1′-biphenyl]-2,2′-dicarboxaldehyde (**2**, R = R′ = H) by stepwise monoacetalization followed by oximation of **3** (R = R′ = H), $LiAlH_4$ reduction, and HCl-mediated cyclization of the resulting amino ketone **5** (R = R′ = H). The main difficulty in this synthesis was associated with the formation of some diacetal **9** (R = R′ = H), which proved difficult to separate from the monoacetal and from unreacted starting material. It could, however, be removed by column chromatography after treatment of the mixture with hydroxylamine.

Alternatively, the unsubstituted 5*H*-dibenz[*c*,*e*]azepine was obtained by reduction of dialdehyde **2** (R = R′ = H) with $NaBH_4$ followed by transformation of the resulting diol **1** (R = R′ = H) into 2′-(bromomethyl)[1,1′-biphenyl]-2-carboxaldehyde (**8**, R = R′ = H, X = Br) via 5,7-dihydrodibenz[*c*,*e*]oxepin (**11**, R = H).[20,21] In contrast to the reaction of the latter compound with *aromatic amines*,[20] treatment with alcoholic ammonia solution led to neutral **6** (R = R′ = H) in almost quantitative yield.

Similarly, 5-methyl-5*H*-dibenz[*c*,*e*]azepine (**6**, R = H, R′ = CH_3) was prepared by ammonolysis of 2′-(1-bromoethyl)[1,1′-biphenyl]-2-carboxaldehyde (**8**, R = H, R′ = CH_3, X = Br) (obtained by interaction of **3** (R = H, R′ = CH_3) with methylmagnesium bromide followed by treatment of **7** (R = H, R′ = CH_3) with HBr).

It should be noted that the reaction of both bromo aldehydes **8**, R = R′ = H, X = Br, and **8**, R = H, R′ = CH_3, X = Br, with ammonia solution leads to *substitution* of the halogen atoms rather than to an attack on the carbonyl function. This was verified (i) by the fact that **5**, R = R′ = H, and **5**, R = H, R′ = CH_3 were the only amines formed upon addition of $Na(CN)BH_3$ to the reaction mixtures at the early stages of the ammonolyses and (ii) by the refractory behavior of the *chloro* aldehyde **8** (R = H, R′ = CH_3, X = Cl) toward NH_3.

5,7-Dimethyl-5*H*-dibenz[*c*,*e*]azepine (**6**, R = R′ = CH_3) was best obtained by the general route **1** → **2** → **3** → **4** → **5** → **6**. The product of [1,1′-biphenyl)-2,2′-dicarboxaldehyde and excess methylmagnesium bromide, **1** (R = R′ = CH_3), was oxidized by Jones reagent, followed by monoketalization, oximation, and $Na/C_5H_{11}OH$ reduction of the oxime **4** (R = R′ = CH_3). Upon acid hydrolysis of the ketal group, ring closure took place spontaneously to give the dibenzazepine derivatives in an overall yield of 35% (from [1,1′-biphenyl]-2,2′-dicarboxaldehyde). It is notable that the ketalization of **2** (R = R′ = CH_3) with ethylene glycol yields no diketal. The monoketal was, however, always accompanied by 7-methyldibenzo[*a*,*c*]-cyclohepten-5-one (**12**) and/or by its ethylene ketal **13**. The two byproducts are assumed to be formed by acid-catalyzed intramolecular condensation in **2** (R = R′ = CH_3). The relative yields of **3**, **12**, and **13** proved to depend



on the acid used in the process. For example, while a mixture of **2** (R = R′ = CH_3), ethylene glycol, and benzenesulfonic acid (molar ratio 1:1.2:0.03) afforded, after 6 h at reflux 72% of **3** (R = R′ = CH_3), 2% of **12**, and 6% of **13**, the mixture with 4-toluenesulfonic acid gave under the same conditions 39% of the ketal, 8% of **12** and 15% of **13**. Substitution of the sulfonic acids by sulfuric acid

(16) See e.g.: (a) Kreher, R.; Gerhardt, W. *Liebigs Ann. Chem.* **1981**, 240 and references cited therein. (b) Kreher, R.; Morgenstern, H. *Z. Chem.* **1982**, *22*, 258. (c) Kreher, R.; Moregenstern, H. *Chem.-Ztg.* **1983**, *107*, 70.

(17) (a) Gschwend, H. W.; Hamden, A. *J. Org. Chem.* **1982**, *47*, 3652. (b) Fitt, J. J.; Gschwend, H. W.; Hamden, A.; Boyer, S. K.; Haider, H. M. *J. Org. Chem.* **1982**, *47*, 3658; Gschwend, H. W. U.S. Patent 4315926, 1982; *Chem. Abst.* **1982**, *96*, 199554r.

(18) (a) Ruenitz, P. C.; McLennon, T. P.; Sternson, L. A. *Drug Metabol. Dispos.* **1979**, 7, 204. (b) Thomas, H. G.; Ruenitz, P. C. *J. Heterocyclic Chem.* **1984**, *21*, 1057.

(19) For example, azapetidine: *The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals*; 10th ed; Windholz, M., Ed., Merck: Rahway, NJ, 1983; p 130.

(20) Rieche, A.; Hoft, E.; Schulze, H. *Liebigs, Ann. Chem.* **1966**, *697*, 188.

(21) Wittig, G.; Davis, P.; Koenig, G. *Chem. Ber.* **1951**, *84*, 627.

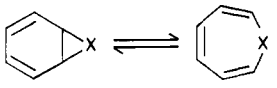
resulted in the formation of 91% of **12** free of **13** and only 1% of **3** (R = R′ = CH_3).

While the reduction of **4** (R = R′ = CH_3) by sodium in 1-pentanol proceeded smoothly, the oxime proved refractory towards $LiAlH_4$. Several other attempts to prepare the amino ketone **5** (R = R′ = CH_3) by reduction of monohydrazones (e.g., **14**) with Zn/AcOH in the presence of Ac_2O led only to low yields of **16** accompanied by considerable amounts of 9,10-dimethylphenanthrene (**17**).

For 5,7-diphenyl-5*H*-dibenz[*c*,*e*]azepine (**6**, R = R′ = C_6H_5) we followed the general route outlined above for the dimethyl compound. However, in contrast to the reaction of **2** (R = R′ = H) with methylmagnesium bromide, the reaction of the dialdehyde with either phenylmagnesium bromide or phenyllithium in *THF* (or THF–ether mixtures) gave 5,7-dihydro-5,7-diphenyldibenz[*c*,*e*]oxepin (**11**, R = C_6H_5) as the main product. In order to avoid the formation of the cyclic ether, the Grignard reaction had to be conducted in dry toluene in the presence of a relatively small amount of THF. 2,2′-Dibenzoyl-1,1′-biphenyl (**2**, R = R′ = C_6H_5) was formed by Jones oxidation of both **1** (R = R′ = C_6H_5) and **11** (R = C_6H_5). The reaction of the sparingly soluble oxepin derivative was, however, slow, as it required very high dilution.

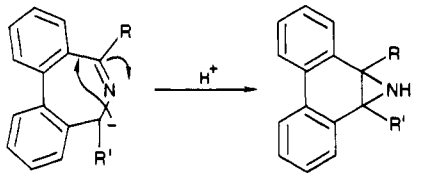
Owing to the steric hindrance implied by the phenyl groups, the ketalization of **2** (R = R′ = C_6H_5) gave mainly monoketal even when a large excess of ethylene glycol was employed. The oximation of **3** (R = R′ = C_6H_5) was accomplished by the special method for sterically hindered carbonyl compounds.[22,23] The reduction of the oxime **4** (R = R′ = C_6H_5) was best carried out with Zn and ammonia in the presence of ammonium acetate.

Chemical Transformations of Dibenz[*c*,*e*]azepines. The attempts to convert 5*H*-dibenz[*c*,*e*]azepines into phenanthrene imines were based on the observation that simple benzene imines, as well as their oxygen analogues, the benzene epoxides, exist as imine–azepine[24] and oxide–oxepin[25] equilibrium mixtures, respectively (eq 1).

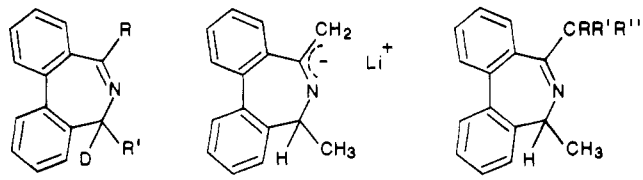


X = O, NR (1)

Unfortunately, numerous experiments to induce valence isomerization of **6** (R = R′ = H) under thermal conditions[26] were unsuccessful. We were, however, able to convert the dibenzazepine into phenanthrene 9,10-imine (**19**, R = R′ = H) both by photochemical and by deprotonation–protonation processes. Photolysis in CH_2Cl_2 with a 450-W medium-pressure mercury lamp gave 3% of the imine at 18% conversion. The low yield of the aziridine is, of course, due to secondary photochemical transformations that take place upon irradiation of substituted and unsubstituted phenanthrene imines.[28] The deprotonation of **6** (R = R′ = H) was accomplished by lithium diisopropylamide (LDA) at −78 °C. Heating of the reaction mixture at 50 °C for 48 h followed by reprotonation of the resulting anion **18** (R = R′ = H) gave 17% of **19** (R = R′ = H).



18 **19**



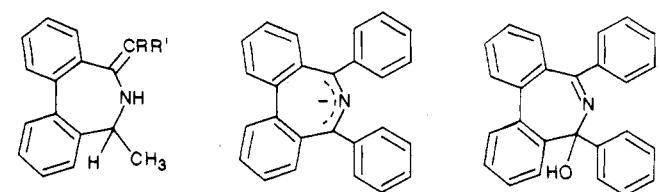
20 **21** **22**

Treatment of 5-methyl-5*H*-dibenz[*c*,*e*]azepine (**6**, R = H, R′ = CH_3) with LDA formed anion **18** (R = H, R′ = CH_3) that gave, however, after quenching with 99.99% D_2O, only **20** (R = H, R = CH_3) free of any methylated phenanthrene imine.

Reaction of the *di*methylated compound **6** (R = R′ = CH_3) with LDA yielded preferentially the azaallyl anion **21** in which C7 rather than C5 was involved. Consequently, quenching with D_2O gave **22** (R = R′ = H, R″ = D).

The sensitivity of the 7-methyl protons to H–D exchange was further demonstrated by the fast conversion of **6** (R = R′ = CH_3) into **22** (R = R′ = R″ = D) with cold 10% D_2SO_4 in D_2O and by the stepwise transformation of the unlabeled azepine derivative to mono-, di-, and trideuteriated compounds **22** (R = R′ = H, R″ = D, **22** (R = H, R′ = R″ = D), and **22** (R = R′ = R″ = D), respectively, during ^1H NMR measurements in CD_3NO_2 at 20 °C.

Realizing that, in contrast to the unsubstituted 5*H*-dibenz[*c*,*e*]azepine, the 5-methine proton in **6** (R = R′ = CH_3) is virtually unaffected by bases, we tried to attack this position through NBS bromination. We hoped that extrusion of halogen will result in the formation of a planar carbocation capable of rearrangement to **19**. In practice, however, also the bromination took place exclusively at the 7-methyl group. 5-Methyl-7-(monobromoethyl)-, 5-methyl-7-(dibromomethyl)-, and to a smaller extent, 5-methyl-7-(tribromomethyl)-5*H*-dibenz[*c*,*e*]azepine (**22**, R = R′ = H, R″ = Br; **22**, R = H, R′ = R″ = Br; and **22**, R = R′ = R″ = Br, respectively) were formed. This unexpected course of bromination is attributed to the existence of **6**, R = R′ = CH_3 (as well as the above mono- and dibromo compounds), as an equilibrium mixture with enamine **23**, R = R′ = H (or **23**, R = H, R′ = Br; **23**, R = R′ = Br).



23 **24** **25**

(22) Pearson, D. E.; Keaton, O. D. *J. Org. Chem.* **1963**, *28*, 1557.

(23) It should be noted, that unlike **3** (R = R′ = C_6H_5) the benzoyl compound **3** (R = H, R′ = C_6H_5) did not give any oxime even after prolonged treatment (2 months) with hydroxylamine under various conditions. For this reason we gave up our attempts to synthesize **6** (R = H, R′ = C_6H_5).

(24) See, e.g.: (a) Paquette, L. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 11. (b) Vogel, E.; Altenbach, H.-J.; Drossard, J.-M.; Schmickler, H.; Stegelmeier, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 1016.

(25) See, e.g.: Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 385.

(26) It was hoped that under thermal conditions **6** (R = R′ = H) can be transformed to the yet unknown, but theoretically stable, 6*H*-dibenz[*c*,*e*]azepine,[27] which in turn may be converted into **19** by the Cope rearrangement.

(27) Hess, B.A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron*, **1972**, *28*, 3657.

(28) Weitzberg, M.; Avnir, D.; Aizenshtat, Z.; Blum, J. *J. Heterocyclic Chem.* **1983**, *20*, 1019.

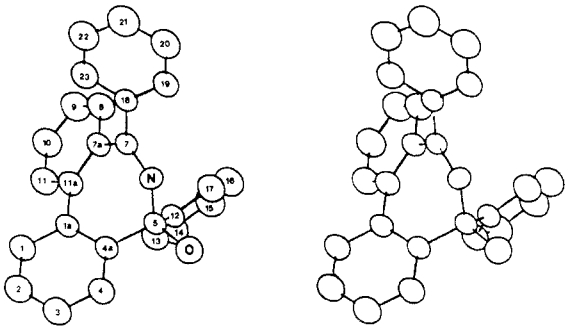


Figure 1. Stereoscopic view of compound **25**(i).

It was for these undesired reactions at the 7-methyl group of **6** (R = R′ = CH_3) that we synthesized the diphenyl derivative **6** (R = R′ = C_6H_5) in which the substituents have no transferable hydrogen atoms.

The reaction of **6** (R = R′ = C_6H_5) with LDA at −78 °C resulted in the formation of a dark violet coloring that did not fade as long as the mixture was kept below 0 °C. The color indicated the presence of **18** (R = R′ = C_6H_5) which gave the 5-deuterio compound **20** (R = R′ = C_6H_5) upon quenching with D_2O. It failed, however, to form any aziridine derivatives. A plausible explanation for this refractory behavior may be associated in part, with the existence of the anion as a stable π-allylic species **24**.

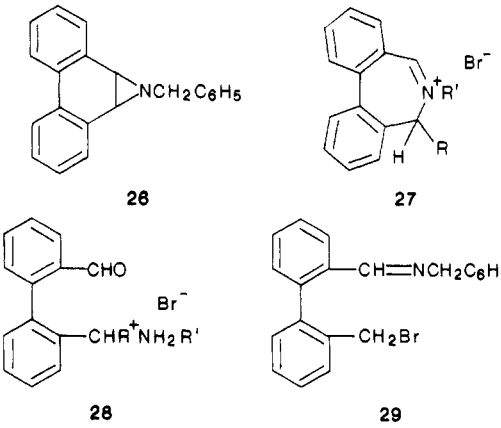
Other bases were found less effective in generation of **18**, but under phase-transfer conditions, (chlorobenzene-/water and tetrabutylammonium bromide), 50% NaOH converted the diphenyldibenzazepine, *in the presence of air* into 5,7-diphenyldibenz[*c*,*e*]azepin-5-ol (**25**) in 83% yield. The formation of the carbinol can be rationalized by aerial oxidation of **18** via a similar mechanism to that proposed for the transformation of fluorene to fluorenone.[29]

Since the structure of **25** could not be determined unequivocally by NMR spectroscopy, single-crystal X-ray analysis was performed. A stereoscopic drawing of the compound, for which the numerical data are given in Tables 1–10 as supplementary material, is shown in Figure 1. (See paragraph at the end of the paper about supplementary material).

The drawing indicates a substantial steric hindrance implied by the C5 phenyl group. It causes the hydroxyl oxygen to approach the aromatic H4 atom as near as 2.34 Å.[30] Owing to this steric effect, the resonance peaks of H4 appear at a very low field (8.338 ppm). The OH and the 7-phenyl moieties were found to be located in opposite directions, forming an angle of 178° in the plan.

By assuming the structure of **18** (R = R′ = C_6H_5) (which did not give crystals suitable for X-ray analysis) to resemble that of **25**, an alternative explanation for the inability of the anion to form an aziridine could be suggested. As one would expect the intramolecular cyclization to follow an S_N2 mechanism, the attacking carbon atom would have to possess an sp^3 configuration in the transition state,[32] forcing the pair of reacting electrons to the respective position of the C5 phenyl group in **25**. Consequently, the aromatic moiety would have to squeeze into the limited space which, in **25**, is hardly sufficient for the OH group.

Apart from the above transformations of **6** (R = R′ = H) to **19** (R = R′ = H), we were able to obtain the arene imine, 1-benzyl-1a,9b-dihydrophenanthro[9,10-*b*]azirine (**26**), in 9% yield, by treatment of 2′-(bromomethyl)-



26 **27**

28 **29**

[1,1′-biphenyl]-2-carboxaldehyde (**8**, R = R′ = H, X = Br) with excess of benzylamine. It appears, that in contrast to the reaction of the bromo aldehyde with aromatic amines [that form exclusively 6-aryl-5*H*-dibenz[*c*,*e*]azipinium bromides[20] (**27**, R′ = aryl) via aldehydo ammonium salts of type **28**], benzylamine gives a mixture of **28** (R = H, R′ = $CH_2C_6H_5$) *and* aldimine **29**. The latter then undergoes both cyclization and dehydrobromination to form the expected arene imine.

The ratio between **28** (R = H, R′ = $CH_2C_6H_5$) and **29** seems to be determined by kinetic factors. Therefore, the secondary bromide **8**, (R = H, R′ = CH_3, X = Br) that reacts with benzylamine much more slowly than the primary halide gives 6-benzyl-5-benzyldibenz[*c*,*e*]azepinium bromide **27** (R = CH_3, R′ = $CH_2C_6H_5$) (probably via **8**, R = CH_3, R′ = $CH_2C_6H_5$) as the only heterocyclic product.

Experimental Section

Acetalization of [1,1′-Biphenyl]-2,2′-dicarboxaldehyde. A mixture of 20 g (97 mmol) of [1,1-biphenyl]-2,2′-dicarboxaldehyde (**2**, R = R′ = H), 6.3 g (102 mmol) of dry ethylene glycol, 0.1 g of benzenesulfonic acid, and 500 mL of benzene was refluxed for 1 h. The water formed was continuously removed with the aid of a Dean–Stark device. Most of the solvent was removed under reduced pressure; the residue was extracted with ether and washed with 5% aqueous sodium hydrogen carbonate and water. The dried ether solution was treated with activated charcoal and concentrated. ^1H NMR analysis indicated the presence of 72% of 2-[2′-formyl-[1,1′-biphenyl]-2-yl]-1,3-dioxolane (**3**, R = R′ = H), 5% of 2,2′-[1,1′-biphenyl]-2,2′-diylbis(1,3-dioxolane) (**9**, R = R′ = H), and 23% of unreacted starting material. Flash chromatography on silica gel with CH_2Cl_2[33] afforded pure **3** (R = R′ = H); however complete separation of the monoacetal from **9** (R = R′ = H) required two further chromatographies and was associated with heavy losses.

Compound 3 (R = R′ = H): colorless oil; IR (neat) 1690 cm^{-1} (C=O); 60-MHz ^1H NMR ($CDCl_3$) δ 3.65–4.05 (m, 4, OCH_2CH_2O), 5.48 (s, 1, CH_2OCH), 7.20–8.22 (m, 8, aromatic), 10.30 (s, 1, HC=O); mass spectrum (70 eV, 25 °C), *m*/*z* (relative intensity) 210 [(M − CH_2CH_2O)$^{\cdot+}$ 7], 197 ($C_{13}H_9O_2^+$, 5), 194 [(M − OCH_2CH_2O)$^{\cdot+}$, 4], 181 ($C_{13}H_9O^+$, 100), 165 ($C_{13}H_9^+$, 20). Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.64; H, 5.51.

Compound 9 (R = R′ = H): colorless crystals, mp 52 °C (hexane); IR ($CHCl_3$) 1077 cm^{-1} (COC); 300-MHz ^1H NMR ($CDCl_3$) δ 3.778–4.073 (m, 8, OCH_2CH_2O), 5.494 (s, 2, CH_2OCH),

(29) For example: (a) Proskuryakov, V. A.; Chistyakov, A. N. *Khim. Tverd. Topl. (Moscow)* **1972**, 82. (b) Finger, C. Ger. Offen. 2704648, August 1978; *Chem. Abstr.* **1978**, *89*, 215121p.

(30) Taylor and Kennard[31] elaborated upon the crystal structures of 59 compounds in which O–H distances are shorter than 2.70 Å (i.e., shorter than the sum of the van der Waal's radii of O and H) and the X–H–O angles >90°. They attributed the short distances to electronic attractions between the oxygen and the hydrogen atoms. However, unlike our case, their examples did not suffer from any steric effects. In **25** a hydrogen bond between the oxygen atom and the nonpolarized aromatic H4 atom is not to be favored.

(31) Taylor, E.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.

(32) See, e.g.: Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Pergamon: Oxford, 1983.

(33) (a) Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *34*, 2923. (b) Jarvis, B. B.; Midiwo, J. O. *Aldrichimica Acta* **1980**, *13*, 42.

7.225–7.688 (m, 8, aromatic); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity) 298 ($M^{\bullet+}$, 13), 253 ($C_{16}H_{13}O_3^+$, 41), 225 ($C_{15}H_{13}O_2^+$, 39), 181 ($C_{13}H_9O^+$, 97), 152 ($C_{12}H_8^{\bullet+}$, 30), 73 ($C_3H_5O_2^+$, 100). Anal. Calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.09; H, 6.13.

2-(2′-Formyl-[1,1′-biphenyl]-2-yl)-1,3-dioxolane Oxime (4, R = R′ = H) and [1,1′-Biphenyl]-2,2′-dicarboxaldehyde Dioxime (10, R = R′ = H). To a solution of 10 g of the above reaction mixture of **2** (R = R′ = H) and ethylene glycol in 100 mL of ethanol was added a solution of 14 g of hydroxylamine hydrochloride, 22 g of anhydrous sodium acetate, and 1 g of sodium hydroxide in 100 mL of the same solvent. After 15 min at reflux, water was added and the oily precipitate extracted with ether. The concentrated solution was flash chromatographed on silica gel with dichloromethane to give 5.7 g (69%) of **4** (R = R′ = H) and 0.5 g (21%) of **10** (R = R′ = H).

Compound 4 (R = R′ = H): viscous oil; IR ($CHCl_3$) 3588 cm^{-1} (OH); 300-MHz ^1H NMR ($CDCl_3$) δ 3.681–3.993 (m, 4, OCH_2CH_2O), 5.488 (s, 1, CH_2OCH), 7.854 (s, 1, NOH), 7.110–7.891 (m, 8, aromatic), 9.221 (br s, 1, OH); mass spectrum (70 eV, 150 °C), *m/z* (relative intensity) 269 ($M^{\bullet+}$, 1.5), 196 [$(M-C_3H_5O_2)^+$, 100], 180 ($C_{13}H_8O^{\bullet+}$, 19), 178 ($C_{13}H_8N^+$, 18), 165 ($C_{13}H_9^+$, 10). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.33; H, 5.42; N, 5.21.

Compound 10 (R = R′ = H): mp 185 °C (lit.[34] 186–187 °C); IR ($CHCl_3$) 3675, 3587 cm^{-1} (OH); 300-MHz ^1H NMR ($CDCl_3$) δ 7.304 (s, 2, NOH), 7.265–7.815 (m, 8, aromatic).

5*H*-Dibenz[*c*,*e*]azepine (6, R = R′ = H). A. A solution of 888 mg (3.3 mmol) of **4** (R = R′ = H) in 50 mL of anhydrous ether was added dropwise at 0 °C under argon to a stirred suspension of 700 mg (18 mmol) of $LiAlH_4$ in 150 mL of the same solvent. After stirring the mixture for 24 h at 25 °C there was added in the following order 0.7 mL of water, 0.7 mL of 15% aqueous sodium hydroxide and 2.1 mL of water. The slurry was filtered and the filtrate extracted repeatedly with ether. The organic solution was washed with water, dried, and concentrated to yield yellow oily **5** (R = R′ = H) which was treated, without purification, with 2 mL of concentrated hydrochloric acid. After being stirred for 20 h, the mixture was neutralized with 5% aqueous NaOH and extracted with ether. The resulting yellow oil was flash chromatographed on silica gel with a mixture of ether and hexane (1:9). Sublimation of the semisolid, so obtained, at 0.01 mm gave 543 mg (85%) of **6** (R = R′ = H) as colorless crystals; mp 84–85 °C (lit.[16] 84–85 °C).

B. A solution of 1.00 g (3.6 mmol) of 2′-(bromomethyl)[1,1′-biphenyl]-2-carboxaldehyde (**8**, R = R′ = H, X = Br) (prepared according to Rieche et al[20] from 5,7-dihydrodibenz[*c*,*e*]oxepin (**11**, R = R′ = H) and 20 mL of 25% aqueous ammonia in 100 mL of ethanol was refluxed for 5 h. The mixture was cooled and stirred for 15 min with 20 mL of 10% aqueous NaOH solution. The organic material was extracted with methylene chloride and worked up as above to give 667 mg (95%) of pure **6** (R = R′ = H).

Transformation of 6 (R = R′ = H) into 1a,9b-Dihydro-1*H*-phenanthro[9,10-*b*]azirine (19, R = R′ = H). A. Into a solution of 1.88 g (29.5 mmol) of n-butyllithium in 19 mL of hexane and 6 mL of THF was injected under argon at −78 °C, 3.5 mL of diisopropylamine. After the mixture had been stirred at this temperature for 30 min, 1 g (5.2 mmol) of the azepine **6** (R = R′ = H) was added. The dark violet solution was stirred, first at −78 °C for 3 h, and then for 48 h at 50 °C. Water was added and the organic material extracted into CH_2Cl_2. The water washed organic solution was dried ($MgSO_4$) and the solvent removed under reduced pressure. The resulting mixture was triturated with ether and *n*-pentane to give 170 mg (17%) of **19** (R = R′ = H) of mp 163–164 °C that was identical with an authentic sample.[14]

B. A solution of 193 mg (1 mmol) of **7** (R = R′ = H) in 400 mL of spectroscopical grade degassed CH_2Cl_2 was placed in a quartz tube, purged with argon, and irradiated at room temperature with a 450-W medium-pressure mercury lamp. After 2.5 h the reaction mixture was analyzed on a 5% Altech R.P.-18 HPLC column and found to contain 82% of unchanged starting material and 3% of the phenanthreneimine **19** (R = R′ = H).

(34) Hannon, J.; Kenner, J. *J. Chem. Soc.* **1934**, 138.

1-[2′-([1,3-Dioxolan]-2-yl)-[1,1′-biphenyl]-2-yl]ethanol (7, R = H, R′ = CH_3). To a Grignard solution of 170 mmol of methylmagnesium bromide in 250 mL of ether was added dropwise a solution of 14.4 g (56.8 mmol) of **3** (R = R′ = H) in 40 mL of dry THF. The mixture was refluxed with stirring for 16 h. The mixture was cooled (0 °C) and decomposed with ice cold saturated ammonium chloride solution. Extraction (2×) with ether and removal of the dried solvent afforded **7** (R = H, R′ = CH_3) as a pale yellow viscous oil: IR (neat) 3400 (OH) 1077 cm^{-1} (COC); 300-MHz ^1H NMR ($CDCl_3$) δ 1.354 (d, 3, *J* = 5.9 Hz, CH_3), 1.660 (br s, 1, OH), 3.610–4.120 (m, 4, OCH_2CH_2O), 4.610 (q, 1, *J* = 5.9 Hz, $CHCH_3$), 5.461 (s,1, CH_2OCH), 7.256–7.910 (m, 8, aromatic); mass spectrum (70 eV, 90 °C), *m/z* (relative intensity) 270 ($M^{\bullet+}$, 2), 253 ($C_{17}H_{17}O_2^+$, 28), 252 ($C_{17}H_{13}^+$, 31), 192 ($C_{15}H_{12}^{\bullet+}$, 45), 181 ($C_{14}H_{13}^+$, 100), 180 ($C_{14}H_{12}^{\bullet+}$, 63), 165 ($C_{13}H_9^+$, 100). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.28; H, 6.62.

2′-(1-Chloroethyl)[1,1′-biphenyl]-2-carboxaldehyde (8, R = H, R′ = CH_3, X = Cl). A mixture of 5.0 g (18.5 mmol) of **7** (R = H, R′ = CH_3), 150 mL of CH_2Cl_2, and 20 mL of concentrated hydrochloric acid was refluxed for 16 h. The layers were separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic solutions were neutralized ($NaHCO_3$), concentrated, and chromatographed on silica gel (mixtures of 20 to 50% of ether in hexane served as eluent) to give 3.5 g (77%) of the expected chloride; colorless oil; (IR (neat) 1680 cm^{-1} (C=O); 300-MHz ^1H NMR ($CDCl_3$) δ 1.710 (d, 3, *J* = 4 Hz, CH_3), 4.851 (q, 1, *J* = 4 Hz, $CHCH_3$), 7.184–8.086 (m, 8, aromatic), 9.753 (s, 1, CHO). Anal. Calcd for $C_{15}H_{13}ClO$: C, 73.62; H, 5.35; Cl, 14.49. Found: C, 73.76; H, 5.68; Cl, 14.91.

2′-(1-Bromoethyl)[1,1′-biphenyl]-2-carboxaldehyde (8, R = H, R′ = CH_3, X = Br) was obtained in 75% yield by treatment of 3.0 g (11.1 mmol) of **7**, (R = H, R′ = CH_3) in 150 mL of CH_2Cl_2 with 20 mL of concentrated hydrobromic acid for 16 h at reflux. Chromatography on silica gel (20–50% ether in hexane served as eluent) yielded 2.4 g (75%) of the expected bromide as a pale yellow oil; IR (neat) 1685 cm^{-1} (C=O); 200-MHz ^1H NMR ($CDCl_3$) δ 1.871 (d, 3, *J* = 7 Hz, CH_3), 4.892 (q, 1, *J* = 7 Hz, $CHCH_3$), 7.210–8.121 (m, 8, aromatic), 9.562 (s, 1, CHO); mass spectrum (68 eV, 55 °C), *m/z* (relative intensity) 290, 288 ($M^{\bullet+}$, 3, 3), 211 ($C_{15}H_{15}O^+$, 79), 210 ($C_{15}H_{14}O^{\bullet+}$, 92), 196 ($C_{14}H_{12}O^{\bullet+}$, 71), 182 ($C_{13}H_{10}O^{\bullet+}$, 100), 181 ($C_{14}H_{13}^+$ and $C_{13}H_9O^+$, 66), 180 ($C_{14}H_{12}^{\bullet+}$, 80), 179 ($C_{14}H_{11}^+$, 78), 152 ($C_{12}H_8^{\bullet+}$, 65). Anal. Calcd for $C_{15}H_{13}BrO$: C, 62.29; H, 4.53; Br, 27.63. Found: C, 62.77; H, 4.64; Br, 27.65.

5-Methyl-5*H*-dibenz[*c*,*e*]azepine (6, R = H, R′ = CH_3). A mixture of 2 g (6.9 mmol) of **8** (R = H, R′ = CH_3, X = Br), 20 mL of 25% aqueous ammonia, and 75 mL of ethanol was stirred at 80 °C for 20 h. After the mixture had been cooled to room temperature, 20 mL of 10% aqueous NaOH was added and the mixture stirred for 15 min. The organic material was extracted with CH_2Cl_2, washed with water, and chromatographed on silica gel (40 to 90% ether–hexane mixtures served as eluent). The final fraction afforded 1.29 g (90%) of **6** (R = H, R′ = CH_3) as a viscous oil; 200-MHz ^1H NMR ($CDCl_3$) δ 1.851 (d, 3, *J* = 6 Hz, CH_3), 3.832 (q, 1, *J* = 6 Hz, $CHCH_3$), 9.240–7.762 (m, 8, aromatic), 8.385 (d, 1, CH=N); mass spectrum (70 eV, 60 °C), *m/z* (relative intensity) 208 [$(M + H)^+$, 95], 207 ($M^{\bullet+}$, 92), 192 ($C_{14}H_{10}N^+$, 92), 181 ($C_{14}H_{13}^+$, 75), 179 ($C_{14}H_{11}^+$, 97), 166 ($C_{13}H_{10}^{\bullet+}$, 70), 165 ($C_{13}H_9^+$, 100), 153 ($C_{12}H_9^+$, 13), 152 ($C_{12}H_8^{\bullet+}$, 50). Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.93; H, 6.60; N, 6.61.

When a solution of 500 mg of the azepine derivative in 7 mL of dry THF was treated for 3 h at −78 °C with excess LDA followed by quenching of the violet solution with D_2O, 5-deuterio-5-methyldibenz[*c*,*e*]azepine (**20**, R = H, R′ = CH_3) was obtained (only the ^1H signal at 3.832 disappeared).

1,1′-[1,1′-Biphenyl]-2,2′-diylbis(ethanone) (2, R = R′ = CH_3). To a stirred Grignard solution prepared from 8 g (0.33 mol) of Mg, excess CH_3Br, and 450 mL of ether was added 20 g (0.095 mol) of **2** (R = R′ = H) in 100 mL of anhydrous THF. The mixture was refluxed for 20 h, cooled, and treated with HCl and water. The aqueous phase was extracted several times with ether which was then washed with 5% aqueous $NaHCO_3$, dried on $MgSO_4$, and treated with decolorizing carbon. Removal of the solvents under reduced pressure and recrystallization of the residue from ether afforded 19.98 g (86%) of **1,1′-[1,1′-biphenyl]-2,2-diylbis(ethanol)** (**1**, R = R′ = CH_3) of mp 143–146

°C as a 1:1 mixture of *dl* and *meso* isomers;[35] 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.334 and 1.354 (d, 6, $J_a = J_b$ = 5.9 Hz, CH_3), 1.661 and 1.602 (br s, 2, OH), 4.547 and 4.762 (q, 2, $J_a = J_b$ = 5.9 Hz, CH(OH)CH_3), 7.050 and 7.145 (d, 2, $J_a = J_b$ = 7.4 Hz; H6, H6′), 7.256–7.455 (m, 4, H4, H4′, H5, H5′), 7.558 and 7.649 (d, 2, J_a = 7.8 Hz, J_b = 7.4 Hz, H3, H3′).

To a stirred solution of 8 g (33 mmol) of the mixture of isomeric diols in 300 mL of acetone was added during 90 min at 0 °C a solution of 8 g (80 mmol) of CrO_3. The mixture was allowed to warm up to room temperature and left for 6 h. Extraction with ether and neutralization of the organic layer with 5% aqueous $NaHCO_3$ gave after partial removal of the solvent 7.32 g (93%) of **2**, R = R′ = CH_3 as colorless prisms; mp 94–95 °C (lit.[36] 93–94 °C); 300-MHz ^{1}H NMR ($CDCl_3$) δ 2.255 (s, 6, CH_3), 7.166 (dd, 2, $J_{4,6}$ = 1.6 Hz, $J_{5,6}$ = 7.0 Hz, H6, H6′), 7.437 and 7.479 (ABXY pattern, 4, J_{AB} = 7.5 Hz, $J_{3,4}$ = 7.4 Hz, $J_{5,6}$ = 7.0 Hz, H4, H4′, H5, H5′), 7.731 (dd, 2, $J_{3,4}$ = 7.4 Hz, $J_{3,5}$ = 2.0 Hz, H3, H3′).

Mono- and diacetylhydrazones of **2** (R = R′ = CH_3) were obtained by refluxing a solution of 3.25 g (13.5 mmol) of the diketone, 0.8 g (10.8 mmol) of acethydrazide in 40 mL of absolute EtOH and 30 mL of glacial acetic acid for 20 h. The solvents were removed under reduced pressure, and the residue was dissolved in 50 mL of boiling CH_2Cl_2. After 24 h at 5 °C, 300 mg of the dihydrazone **15** separated. The filtered solution was concentrated and flash chromatographed on silica gel. After washing the column with pure hexane and with a 1:1 mixture of ether and hexane, there was eluted 1.4 g (43%) of unreacted starting material. A 9:1 mixture of ether and ethyl acetate afforded then 720 mg (18%) of **14**. The final fraction of 474 mg of **15** was extracted from the column with a 6:1 mixture of the latter solvents. The total yield of **15** was 16%.

Monohydrazone 14: mp 157–158 °C (from ether); IR (Nujol) 3175 (NH), 1685 (C=O), 1665 cm^{-1} (NC=O); 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.851 (s, 3, N=CCH_3), 1.910 (s, 3, NHCOCH_3), 2.089 (s, 3, CCOCH_3), 7.222–7.649 (m, 8, aromatic), 8.594 (s, 1, NH); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity) 251 [(M − $COCH_3$)$^+$, 100], 192 ($C_{14}H_{10}N^+$, 69), 179 ($C_{13}H_{10}N^+$), 165 ($C_{13}H_9^+$, 21). Anal. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.26; H, 6.33; N, 9.43.

Dihydrazone 15: mp 252–254 °C (from CH_2Cl_2); IR (Nujol) 3190 (NH) 1665 cm^{-1} (C=O); 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.692 (s, 6, N=CCH_3), 2014 (s, 6, NHCOCH_3), 7.287–7.481 (m, 8, aromatic), 8.547 (s, 2, NH); mass spectrum (70 eV, 80 °C), *m/z* (relative intensity) 324 [(M − CN)$^+$, 37], 277 [(M − NH=NCOCH_3)$^+$, 100], 251 ($C_{16}H_{15}N_2O^+$, 92), 192 ($C_{14}H_{10}N^+$, 60). Anal. Calcd for $C_{20}H_{22}N_4O_2$: C, 68.55; H, 6.33; N, 15.99. Found: C, 68.81; H, 6.35; N, 15.74.

Reduction of 1,1′-[1,1′-Biphenyl]-2,2′-diylbis(ethanone) Monoacetylhydrazone (14). Typically, a mixture of 800 mg (2.72 mmol) of **10**, 2.5 g of Zn powder, 10 mL of acetic acid, and 10 mL of acetic anhydride was heated with agitation at 60 °C for 20 h. Water and chloroform were added, and the organic layer was washed with water and 5% aqueous $NaHCO_3$. The resulting material was flash chromatographed on silica gel with a 2:3 mixture of ether–hexane to yield 62 mg (11%) of 9,10-dimethylphenanthrene (**17**); mp 143–144 °C (lit.[37] 143–144 °C) and 504 mg (66%) of **1-[2′-(1-*N*-acetamidoethyl)-[1,1′-biphenyl]-2-yl]ethanone (16)**; mp 151–152 °C (from ether–pentane); IR ($CHCl_3$) 3200 (NH) 1670 (C=O), 1620 cm^{-1} (NHC=O); 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.215 (s, 3, NHCOCH_3), 1.455 (m, 3, CHCH_3), 1.616 (s, 3, COCH_3), 6.053 (m, 1, CHCH$_3$), 6.750–7.828 (m, 8, aromatic), 7.720 (br s, 1 NH, affected by D_2O); mass spectrum (70 eV, 90 °C), *m/z* (relative intensity) 281 ($M^{\cdot+}$, 0.9), 238 [(M − $COCH_3$)$^+$, 100], 223 ($C_{16}H_{15}O^+$, 51), 208 ($C_{15}H_{12}O^{\cdot+}$, 31), 194 ($C_{14}H_{10}O^{\cdot+}$, 13), 179 ($C_{14}H_{11}^+$, 43), 165 ($C_{13}H_9^+$, 22). Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 77.14; H, 6.43.

Reaction of 2 (R = R′ = CH_3) with Ethylene Glycol. In a typical experiment, a mixture of 5.16 g (21.5 mmol) of **2** (R = R′ = CH_3), 1.55 g (26 mmol) of ethylene glycol, 0.1 g of benzenesulfonic acid, and 150 mL of benzene was refluxed for 6 h. The water formed was removed continuously with the aid of a Dean–Stark device. The resulting yellow oil was flash chromatographed on silica gel (a 3:7 mixture of ether and hexane as eluent) to yield 0.34 g (6%) of **2-(7-methyl-5*H*-dibenzo[*a*,*c*]cyclohepten-5-yl)-1,3-dioxolane (13)** as the first fraction, 94 mg (2%) of the free ketone **12** as the second fraction, 4.36 g (72%) of **3**, R = R′ = CH_3 as the third fraction, and finally 0.92 g (18%) of unreacted starting diketone.

1-[2′-[(2-Methyl-1,3-dioxolan)-2-yl][1,1′-biphenyl]-2-yl]ethanone (3, R = R′ = CH_3): colorless prisms, mp 93–94 °C (from ether/hexane); IR ($CHCl_3$) 1685 cm^{-1} (C=O); 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.387 (s, 3, COCH_3), 2.156 (s, 3, OCCH_3), 3.524–3.912 (m, 4, OCH_2CH_2O), 7.131 (dd, 1, $J_{4,6}$ = 2.2 Hz, $J_{5,6}$ = 6.6 Hz, H6), 7.232–7.492 (m, 5, H3, H4, H4′, H5, H5′), 7.666 (dd, 1, $J_{4',6'}$ = 2.2 Hz, $J_{5',6'}$ = 7.0 Hz, H6′) 7.788 (dd, 1, $J_{3',4'}$ = 7.4 Hz, $J_{3',5'}$ = 1.8 Hz, H3′); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity) 267 [(M − CH_3)$^+$, 19], 209 ($C_{15}H_{13}O^+$, 4), 195 ($C_{14}H_{11}O^+$, 100), 181 ($C_{13}H_9O^+$, 65), 165 ($C_{13}H_9^+$, 30), 152 ($C_{12}H_8^{\cdot+}$, 43). Anal. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.68; H, 6.34.

7-Methyl-5*H*-dibenzo[*a*,*c*]cyclohepten-5-one (12): colorless prisms; mp 125–127 °C (from ether–hexane mixture); IR (neat) 1700 cm^{-1} (C=O); 300-MHz ^{1}H NMR ($CDCl_3$) δ 2.359 (d, 3, *J* = 1.2 Hz, CH=CCH_3), 6.537 (q, 1, *J* = 1.2 Hz, CH=CCH$_3$), 7.381–7.373 (m, 8, aromatic); mass spectrum (70 eV, 70 °C), *m/z* (relative intensity) 220 ($M^{\cdot+}$, 22), 192 [(M − CO)$^+$, 100], 176 ($C_{14}H_8^{\cdot+}$, 6), 165 ($C_{13}H_9^+$, 13). Anal. Calcd for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.42; H, 5.76.

Ketal 13: colorless oil; 300-MHz ^{1}H NMR ($CDCl_3$) δ 2.158 (d, 3, *J* = 1.5 Hz, CH=CCH_3), 3.485 (m, 1, CH_2CHH), 3.732 (m, 1, CH_2CH*H*), 4.037 (m, 2, CH_2CH_2), 6.196 (q, 1, *J* = 1.5 Hz, C*H*=CCH$_3$), 7.374–7.409 and 7.578–7.729 (two m, 8, aromatic); mass spectrum (70 eV, 70 °C), *m/z* (relative intensity) 264 ($M^{\cdot+}$, 5), 249 [(M − CH_3)$^+$, 3], 202 ($C_{16}H_9^+$, 9), 193 ($C_{15}H_{13}^+$, 16), 192 ($C_{15}H_{12}^{\cdot+}$, 100), 191 ($C_{15}H_{11}^+$, 22), 165 ($C_{13}H_9$). Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.74; H, 6.41.

When the benzenesulfonic acid in the above ketalization reaction was substituted by 4-toluenesulfonic acid the mixture of products consisted of 39% of **3** (R = R′ = CH_3), 8% of **12**, and 15% of **13**. The application of concentrated H_2SO_4 as catalyst led to 91% of pure **12** that crystallized from ether and hexane even without chromatography.

1-[2′-(2-Methyl-1,3-dioxolan-2-yl)[1,1′-biphenyl]-2-yl]ethanone oxime (4, R = R′ = CH_3) was obtained in quantitative yield in the reaction of 820 mg (2.9 mmol) of **3** (R = R = CH_3) 0.6 g (8.6 mmol) of hydroxylamine hydrochloride, and 10 mL of 10% aqueous NaOH in 100 mL of EtOH at 40 °C for 2 h: colorless prisms (from ether), mp 130–131 °C; IR ($CHCl_3$) 3590 cm^{-1} (OH); 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.488 (s, 3, CH_3), 1.722 (s, 3, CH_3), 3.560–3.853 (m, 4, CH_2CH_2), 7.117 (dd, 1, $J_{3',4'}$ = 7.4 Hz, $J_{3',5'}$ = 1.5 Hz, H3′), 7.248–7.416 (m, 6, H4, H4′, H5, H5′, H6, H6′), 7.646 (dd, 1, $J_{3,4}$ = 7.4 Hz, $J_{3,5}$ = 1.1 Hz, H3); mass spectrum (70 eV, 70 °C), *m/z* (relative intensity) 282 [(M − CH_3)$^+$, 5], 250 ($C_{16}H_{12}NO_2^+$, 3.3), 223 ($C_{15}H_{13}NO^{\cdot+}$, 3), 210 ($C_{14}H_{12}NO^+$, 100), 194 ($C_{14}H_{10}O^{\cdot+}$, 23), 178 ($C_{14}H_{10}^{\cdot+}$, 13), 165 ($C_{13}H_9^+$, 10). Anal. Calcd for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71. Found: C, 73.02; H, 6.56; N, 5.07.

5,7-Dimethyl-5*H*-dibenz[*c*,*e*]azepine (6, R = R′ = CH_3). A quantity of 2.5 g (0.11 mol) of finely cut sodium was added under argon atmosphere during 4 h to a boiling solution of 1.28 g (4.3 mmol) of **4** (R = R′ = CH_3) in 200 mL of anhydrous *n*-amyl alcohol. The mixture was stirred at reflux for a further 90 min, cooled, diluted with water, and extracted with ether. After the usual work up and removal of the solvent under reduced pressure, 80 mL of toluene was added. The first half of this solvent was distilled off at atmospheric pressure and the second half at 20 mm. The resulting light yellow oil was dissolved in 100 mL of acetone and treated at room temperature for 20 h with 10 mL of concentrated HCl and 5 mL of water. The mixture was cooled to 0 °C and neutralized with solid NaOH. Water was added and the organic material extracted twice with ether and benzene. The concentrated organic solution was flash chromatographed on silica gel with a 20–50% solution of ether in hexane to yield 705 mg (74%) of **6** (R = R′ = CH_3) as a colorless oil; 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.776 (d, 3, J_{CHCH_3} = 6.8 Hz, CHCH_3), 2.344 (d, 3, $J_{homoallylic}$ = 1.2 Hz, CH_3), 3.787 (qd, 1, J_{CHCH_3} = 6.8 Hz, $J_{homoallylic}$ = 1.2 Hz, CHCH$_3$), 7.360–7.689 (m, 8, aromatic); 75-MHz ^{13}C NMR ($CDCl_3$) δ 18.749 (CHCH$_3$), 25.928 (N=CCH$_3$), 55.627 (CHCH$_3$),

(35) Hall, D. M.; Ladbury, J. E.; Lesslie, M. S.; Turner, E. E. *J. Chem. Soc.* **1956**, 3475.
(36) Bacon, R. G. R.; Lindsay, W. S. *J. Chem. Soc.* **1958**, 1382.
(37) Bavin, P. M. G. *Can. J. Chem.* **1960**, *38*, 911.

122.812 (two overlapping signals), 126.932 (two overlapping signals), 127.842, 128.347, 129.207 (C1, C2, C3, C4, C8, C9, C10, C11), 135.955, 137.699, 139.039, 143.791 (C4a, C7a, C11a, C11b), 164.821 (*C*=N); mass spectrum (70 eV, 50 °C), *m/z* (relative intensity) 221 ($M^{\bullet+}$, 696), 220 [(M − H)$^+$, 100], 206 [(M − CH_3)$^+$, 64], 193 ($C_{14}H_{11}N^{\bullet+}$, 48), 178 ($C_{14}H_{10}^{\bullet+}$, 30), 165 ($C_{13}H_9^+$, 46). Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.69; H, 6.84; N, 6.28.

Reaction of 6 (R = R′ = CH_3) with *N*-Bromosuccinimide. A mixture of 100 mg (0.45 mmol) of the azepine **6** (R = R′ = CH_3), 86 mg (0.48 mmol) of NBS, and 50 mL of CCl_4 was refluxed for 35 min. The cooled reaction mixture was subjected to preparative TLC on alumina (a 3:7 mixture of ether–pentane serving as eluent) to give 42 mg of unreacted starting material, 8 mg (6%) of the monobromo compound **22** (R = R″ = H, R′ = Br), 33.3 mg (39%) of the dibromo derivative **22** (R = H, R′ = R″ = Br), and traces of **22** (R = R′ = R″ = Br) that proved difficult to separate from the dibromide. All bromo compounds were unstable and deteriorated under ambient conditions.

7-(Bromomethyl)-5-methyl-5*H*-dibenz[*c*,*e*]azepine (22, R = R′ = H, R″ = Br): yellow oil; 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.800 (d, 3, J_{CHCH_3} = 6.6 Hz, CHC*H*$_3$), 3.854 (qd, 1, J_{CHCH_3} = 6.6 Hz, $J_{homoallylic}$ = 1.1 Hz, C*H*CH$_3$), 4.170 (d, 1, J_{gem} = 10.3, BrC*H*H), 4.549 (dd, 1, J_{gem} = 10.3 Hz, $J_{homoallylic}$ = 1.1 Hz, BrCH*H*), 7.200–7.774 (m, 8, aromatic); mass spectrum (70 eV, 150 °C), *m/z* (relative intensity) 301, 299 ($M^{\bullet+}$, 0.5, 0.5), 286, 284 [(M − CH_3)$^+$, 6, 6], 220 [(M − Br)$^+$, 100], 206 [(M − CH_2Br)$^+$, 29], 178 ($C_{14}H_{10}^{\bullet+}$, 51), 165 ($C_{13}H_9^+$, 43).

7-(Dibromomethyl)-5-methyl-5*H*-dibenz[*c*,*e*]azepine (22, R = H, R′ = R″ = Br), yellow oil; 300-MHz ^{1}H NMR ($CDCl_3$) δ 1.808 (d, 3, *J* = 6.6 MHz, C*H*$_3$), 3.918 (q, 1, *J* = 6.6 Hz, C*H*CH$_3$), 6.499 (s, 1, C*H*Br$_2$), 7.361–7.719 (m, 5, aromatic), 8.056–8.240 (m, 3, aromatic); mass spectrum (70 eV, 120 °C), *m/z* (relative intensity) 381, 379, 377 ($M^{\bullet+}$, 6, 12, 6), 300, 298 [(M − Br)$^+$, 82, 82], 219 [(M − Br$_2$)$^{\bullet+}$, 100], 204 ($C_{15}H_{10}N^+$, 37), 190 ($C_{15}H_{10}^{\bullet+}$, 23), 165 ($C_{13}H_9^+$, 26).

The presence of **7-(tribromomethyl)-5-methyl-5*H*-dibenz[*c*,*e*]azepine (22, R = R′ = R″ = Br)** in the final fraction was established by virtue of the distinguished molecular ion peaks of the mass spectrum (*m/z* 461, 459, 457, 455; ratio of intensities 1:3:3:1).

α,α′-Diphenyl[1,1′-biphenyl]-2,2′-dimethanol (1, R = R′ = C_6H_5) was obtained in 76% yield when a solution of 20 g (0.11 mol) of **2** (R = R′ = H) in 150 mL of toluene was refluxed for 36 h with 267 mmol of phenylmagnesium bromide in 45 g of THF, 100 mL of benzene, and 400 mL of toluene; mp 194 °C (from ether) (lit.[38] 193–194 °C); 300-MHz ^{1}H NMR ($CDCl_3$) δ 3.730 (s, 2, O*H*), 5.641 (s, 2, C*H*), 7.316–7.189 (m, 18, aromatic).

When the reaction was conducted in pure THF (without benzene and toluene) an oil was formed, which upon trituration with hexane and ether gave 63% of colorless crystals of **5,7-dihydro-5,7-diphenyldibenz[*c*,*e*]oxepin** (11, R = R′ = C_6H_5), mp 174–175 °C (from ether–hexane); 300-MHz ^{1}H NMR ($CDCl_3$) δ 5.501 (s, 2, C*H*), 6.764 (d, 2, $J_{5,6}$ = 7.8 Hz, H6, H6′), 7.253–7.494 (m, 14, aromatic), 7.618 (d, 2, $J_{3,4}$ = 7.4 Hz, H3, H3′); mass spectrum (70 eV, 140 °C), *m/z* (relative intensity) 348 ($M^{\bullet+}$, 6), 258 [(M − C_6H_5CH)$^{\bullet+}$, 100], 242 [(M − C_7H_6O)$^{\bullet+}$, 39], 165 ($C_{13}H_9^+$, 33). Anal. Calcd for $C_{26}H_{20}O$: C, 89.62; H, 5.78. Found: C, 89.58; H, 5.66.

Reaction of [1,1-Biphenyl]-2,2′-diylbis(phenylmethanone) (2, R = R′ = C_6H_5) with Ethylene Glycol. A quantity of 5 g (14 mmol) of the ketone of mp 166–167 °C (prepared by Jones oxidation of the previous diol) was refluxed for 4 days with 10 mL of ethylene glycol, 0.2 mL of concentrated H_2SO_4 and 400 mL of benzene. The resulting mixture was flash chromatographed on silica gel with a gradient of solvents from pure hexane to pure CH_2Cl_2 to give 323 mg (5%) of **2,2′-[1,1′-biphenyl]-2,2′-diylbis(2-phenyl-1,3-dioxolane) (9, R = R′ = C_6H_5)**, 2.65 g (47%) of **[2′-[(2-phenyl-1,3-dioxolan)-2-yl][1,1′-biphenyl]-2-yl]-phenylmethanone (3, R = R′ = C_6H_5)** and 1.45 (29%) of unreacted starting material.

Monoketal 3 (R = R′ = C_6H_5): mp 157–159 °C (from ether); IR ($CHCl_3$) 1663 cm^{-1} (C=O); 300-MHz ^{1}H NMR ($CDCl_3$) δ 3.605 (m, 4, CH_2CH_2), 6.386 (d, 1, *J* = 7.4 Hz, aromatic), 7.379 (m, 16, aromatic), 7.889 (dd, 1, J_{ortho} = 7.0 Hz, J_{meta} = 1.5 Hz, aromatic); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity), 329 [(M − C_6H_5)$^+$, 6], 257 ($C_{19}H_{13}O^+$, 71), 149 ($C_9H_9O_2^+$, 100), 105 ($C_7H_5O^+$, 77), 77 ($C_6H_5^+$, 50). Anal. Calcd for $C_{28}H_{22}O_3$: C, 82.74; H, 5.45. Found: C, 82.81; H, 5.30.

Diketal 9 (R = R′ = C_6H_5): mp 147–149 °C; 300-MHz ^{1}H NMR ($CDCl_3$) δ 3.620 (m, 8, CH_2CH_2), 6.825 (dd, 2, J_{ortho} = 7.7 Hz, J_{meta} = 1.5 Hz, aromatic), 7.213 (m, 16, aromatic); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity) 373 [(M − C_6H_5)$^+$, 40], 257 ($C_{19}H_{13}O^+$, 9), 149 ($C_9H_9O_2^+$, 100), 105 ($C_7H_5O^+$, 57), 77 ($C_6H_5^+$, 23). Anal. Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 79.89; H, 5.94.

[2′-(2-Phenyl-1,3-dioxolan-2-yl)[1,1′-biphenyl]-2-yl]-phenylmethanone Oxime (4, R = R′ = C_6H_5) and [1,1′-Biphenyl]-2,2′-diylbis(phenylmethanone) Dioxime (10, R = R′ = C_6H_5). The crude reaction mixture of 5 g of **2** (R = R′ = C_6H_5) and 10 mL of ethylene glycol was refluxed with 9 g of hydroxylamine hydrochloride, 16 g of NaOH, and 25 mL of water. After 6 h water was added and the organic material extracted with ethyl acetate. The resulting oil was flash chromatographed on silica gel with a 3:7 mixture of ether–hexane to yield 320 mg (5%) of **10** (R = R′ = C_6H_5), 3.13 g (53%) of a mixture of the two isomers of oxime **4** (R = R′ = C_6H_5), (which could be separated by repeated chromatographies with the same eluent into the cis and trans compounds of mp 136–139 °C and 173–174 °C, respectively), and 1.72 g (31%) of mixture of the isomer of dioxime **10** (R = R′ = C_6H_5).

4 (R = R′ = C_6H_5) (mixture of isomers): IR ($CHCl_3$), 3535 cm^{-1} (OH); 300-MHz ^{1}H NMR ($CDCl_3$) δ 3.673 (m, 4, CH_2CH_2), 6.560 (dd, 1 J_{ortho} = 7.4 Hz, J_{meta} = 0.7 Hz, aromatic), 6.587–7.271 (m, 15, aromatic), 7.344 (dd, 1, J_{ortho} = 7.0 Hz, J_{meta} = 1.1 Hz, aromatic), 7.488 (dd, 1, J_{ortho} = 7.72 Hz, J_{meta} = 1.1 Hz, aromatic); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity), 421 ($M^{\bullet+}$, 6), 344 [(M − C_6H_5)$^+$, 15], 301 [(M − C_7H_6NO)$^+$, 100], 272 ($C_{19}H_{14}NO^+$, 54). Anal. Calcd for $C_{28}H_{23}NO_3$: C, 79.79; H, 5.50; N, 3.32. Found: C, 79.57; H, 5.43; N, 3.42.

10 (R = R′ = C_6H_5) (isomers): mp 185–186 °C (from ether); IR (KBr), 3540 cm^{-1} (OH); 300-MHz ^{1}H NMR ($CDCl_3$) δ 6.315 (d, 1, *J* = 7.4 Hz), 6.492 (dd, 2, J_a = J_b = 7.4 Hz), 6.768–7.258 (m, 11), 7.066 (s, 2, O*H*), 7.49 (d, 1, *J* = 7.7 Hz), 7.540 (d, 1, *J* = 7.7 Hz), 7.636 (d, 1, *J* = 7.7 Hz); mass spectrum (70 eV, 160 °C), *m/z* (relative intensity) 392 (M^+, 2), 272 [(M − C_7H_6NO)$^+$, 100], 254 ($C_{19}H_{12}N^+$m 24), 105 ($C_7H_5O^+$, 40). Anal. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.17; N, 7.17. Found: C, 79.19; H, 5.80; N, 6.86.

5,7-Diphenyl-5*H*-dibenz[*c*,*e*]azepine (6, R = R′ = C_6H_5). To a solution of 250 mg (0.6 mmol) of **4** (R = R′ = C_6H_6) was added in the following order 25 mL of concentrated ammonia solution, 1 g of ammonium acetate, and 1 g of zinc powder. The mixture was refluxed and the progress of the reaction monitored by the development of orange coloration on ninhydrine treated TLC plate (silica gel; 30% ether in hexane as eluent). When all the starting material disappeared, the solids were filtered off and washed with hot EtOH. The solvent was removed under reduced pressure and the residue extracted with $CHCl_3$. The yellow oil obtained after the usual workup was dissolved in 20 mL of acetone and 5 mL of water containing 50 mg of 4-toluenesulfonic acid. The mixture was refluxed for 10 h (disappearance of the ketal was followed by ninhydrine treated TLC). The acid was neutralized with 3% aqueous NaOH and the acetone distilled off. The residue was dissolved in ether, washed with water, and dried to give 172 mg (84%) of **6** (R = R′ = C_6H_5): prismatic crystals, mp 206–207 °C (from ether–hexane); 300-MHz ^{1}H NMR (toluene-d_8) δ 5.183 (s, 1, C*H*), 6.916–7.787 (m, 18, aromatic); 75-MHz ^{13}C NMR ($CDCl_3$) δ 65.795 (*H*CC_6H_5), 125.927, 126.559, 127.191, 128.000 (two overlapping signals), 128.303, 128.404 (two overlapping signals), 128.910, 129.036, 129.718, 129.769, 129.946, 130.123 (aromatic tertiary carbon atoms), 134.243, 137.630, 140,638, 141.169, 141.649, 145.364 (aromatic quaternary carbon atoms), 165.611 (*C*=N); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity) 345 ($M^{\bullet+}$, 100), 344 [(M − H)$^+$, 76], 267 [(M − C_6H_6)$^{\bullet+}$, 25]; 242 ($C_{19}H_{14}^{\bullet+}$, 31). Anal. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.07. Found: C, 90.32; H, 5.52; N, 3.92.

When a solution of 200 mg of **6** (R = R′ = C_6H_5) in 5 mL of anhydrous THF was treated for 4 h at −78 °C (argon atmosphere)

(38) Bergmann, E. D.; Pelchowicz, Z. *J. Org. Chem.* **1954**, *19*, 1387.

with LDA (from 200 mg diisopropylamine in 2 mL of THF and 0.77 mmol of BuLi in hexane), followed by quenching with D_2O at −40 °C, **5-deuterio-5,7-diphenyldibenz[*c*,*e*]azepine** (**20**, R = C_6H_5) was obtained. (Only the ^1H NMR signal at 5.183 ppm disappeared).

5,7-Diphenyldibenz[*c*,*e*]azepin-5-ol (25). A solution of 120 mg (0.35 mmol) of **6** (R = R′ = C_6H_5) in 7 mL of chlorobenzene was stirred vigorously under ambient atmosphere at 60 °C with 10 mL of 50% aqueous NaOH containing 160 mg of tetrabutylammonium bromide. After 4 h the temperature was raised to 85 °C and stirring was continued for another 20 h. Phase separation and evaporation of the chlorobenzene under reduced pressure followed by flash chromatography on silica gel (with 20% ether in pentane as eluent) afforded 104 mg (83%) of **25** as colorless crystals; mp 136–137 °C (from ether–pentane); 300-MHz ^1H NMR (acetone-d_6) δ 6.889 (s, 5), 7.028–7.729 (m, 12), 8.338 (dd, $J_{3,2}$ = 1.8 Hz, $J_{3,4}$ = 7.1 Hz, H4); mass spectrum (70 eV, 100 °C), *m/z* (relative intensity) 361 ($M^{\bullet+}$, 5), 360 [$(M - H)^+$, 16], 344 [$(M - OH)^+$, 2], 282 ($C_{20}H_{12}NO^+$, 3), 257 ($C_{19}H_{15}N^{\bullet+}$, 55), 256 ($C_{19}H_{14}N^+$, 100), 241 ($C_{19}H_{13}^+$, 4), 178 ($C_{13}H_8N^+$, 27).

When the procedure was repeated under exclusion of air, the entire starting material was recovered unchanged.

Crystals for X-ray analysis were obtained by slow recrystallization (during 10 days) from acetone. The crystal unit consisted of two independent pairs [**25(i)** and **25(ii)**] that differed only in the relative angle of the two phenyl groups. Data were measured on a PW110/20 Philips four-circle computer-controlled diffractometer. Mo K_α (λ = 0.71069 Å) radiation with a graphite crystal monochromator in the incident beam was used. The unit cell dimensions were obtained by a least-squares fit of 15 centered reflections in the range of 9° < θ < 12°. Intensity data were collected using the ω–2θ technique to a maximum 2θ of 45°. The scan width, Δω, for each reflection was 1° with a scan time of 20 s. Background measurements were made for another 20 s at both limits of each scan. Three standard reflections were monitored every 60 min. No systematic variations in intensities were found.

Intensities were corrected for Lorentz and polarization effects. All non-hydrogen atoms were found by using the results of the MULTAN direct method analysis.[39] After several cycles of refinements[40] the positions of the hydrogen atoms were calculated, and added with a constant isotropic temperature factor of 0.5 Å to the refinement process. Refinement proceeded to convergence by minimizing the function $\sum w(|F_o| - |F_c|)^2$, where the weight, w, is $1/\sigma(F_o)^2$. A final different Fourier synthesis map showed several peaks less than 0.5 eÅ^{-3} scattered about the unit cell without a significant feature.

The discrepancy indices, $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ and the other pertinent crystallographic data are as follows: formula, $C_{26}H_{19}NO$; molecular weight 361.4; space group $P2_1/n$; a = 16.850 Å; b = 20.565 Å; c = 11.565 Å; α = 90°; β = 101.44°; γ = 90°; V = 3928 Å^3, Z = 8; ρ_{calcd} = 1.22 g cm^{-3}; μ(Mo Kα) = 0.40 cm^{-1}; number of unique reflections 4922; reflections with $I \geq 3\sigma(I)$ = 2595; R = 0.086; R_w = 0.096. The positional and thermal parameters, selected angles, and bond lengths obtained are summarized in Tables 1–10 of the supplementary material of this paper and a stereoscopic view of **25(i)** is given in Figure 1.

1-Benzyl-1a,9b-dihydrophenanthro[9,10-*b*]azirine (26). To a cold solution (0 °C) of 2.0 g (7.3 mmol) of the bromide **8** (R = R′ = H, X = Br)[20] in 60 mL of anhydrous ether was added 2.0 g (19 mmol) of freshly distilled benzylamine in 20 mL of the same solvent. The mixture was heated to 25 °C and stirred at this temperature for 60 min. Washing with cold 5% aqueous $NaHCO_3$ and water followed by removal of the solvent and HPLC separation on an Altech R.P. 18 column (80% aqueous MeOH served as eluent) afforded 185 mg (9%) of **26** (R = H) of properties identical with those of an authentic sample.[1]

5-Methyl-6-benzyl-5*H*-dibenz[*c*,*e*]azepinium Bromide (27, R = CH_3, R′ = $CH_2C_6H_5$). A solution of 2.0 g (6.9 mmol) of bromide **8** (R = H, R′ = CH_3, X = Br) and 1.4 g (13.8 mmol) of benzylamine in 150 mL of anhydrous benzene was stirred under reflux for 20 h. The colorless precipitate (2.3 g, 88%) proved to be pure **27**, R = CH_3, R′ = $CH_2C_6H_5$: mp dec 210 °C; 200-MHz ^1H NMR ($CDCl_3$) δ 1.081 (d, 3, J = 7 Hz, CH_3), 5.323 (q, 1, J = 2 Hz, $CHCH_3$), 5.799 (s, 2, $CH_2C_6H_5$), 7.231–8.467 (m, 13, aromatic), 10.292 (s, 1, CH=N). Anal. Calcd for $C_{22}H_{20}BrN$: C, 69.85; H, 5.33; Br, 21.12; N, 3.70. Found: C, 70.05; H, 4.87; Br, 21.20; N, 3.62.

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Supplementary Material Available: Tables of crystallographic data for compound **25** (9 pages). Ordering information is given on any current masthead page.

(39) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. MULTAN 78. *A System of Computor Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*, Universities of York, England and Louvain, Belgium.

(40) All crystallographic computing was done on a Cyber 74 computer at the Hebrew University, Jerusalem, using the SHELX 1977 structure determination package.

Electroorganic Chemistry. 99. β-Acetoxylation and β-Halogenation of *N*-Methoxycarbonyl Cyclic Amines[1]

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Anodic oxidation of *N*-(methoxycarbonyl)pyrrolidines (n = 1) and -piperidines (n = 2) (**A**) gave α,β-disubstituted compounds **B**, in which the α-substituent was an acetoxy, hydroxy, or methoxy group and the β-substituent was an acetoxy group or halogen atom. The α-substituents of **B** were easily removed by $NaBH_4$ under acidic conditions to give β-substituted compounds **C**. A reaction mechanism involving the formation of α,β-unsaturated intermediate **E** followed by anodic oxidation of **E** or attack of halogen-active species on **E** has been presented for the anodic α,β-disubstitution.

Functionalization of a less reactive methylene group is one of the most interesting current topics, while generally effective methods have not always been found yet. One of the methods hitherto exploited may be remote oxida-

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