

Davis Avnir and Jochanan Blum*

Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel

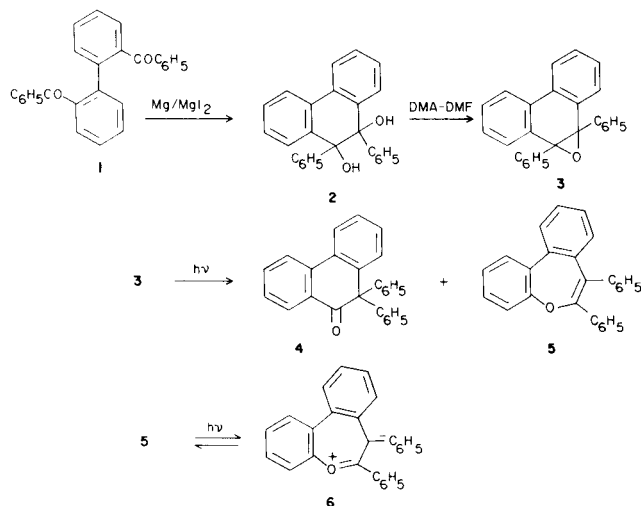
Received April 4, 1980

The synthesis of the title compound is described. Pinacol reduction of 2,2'-dibenzoylbiphenyl followed by dehydration of the *trans*-diol, so formed, with dimethylformamide dimethyl acetal yielded 55% of the oxirane. Irradiation of the oxide in methylene chloride at 254 nm gave 10,10-diphenyl-9-(10*H*)phenanthrone as the major photoproduct.

J. Heterocyclic Chem., 17, 1349 (1980).

The biochemical interest in disubstituted K-region arene oxides has been discussed in a previous paper (1) and a general synthesis of these compounds by oxidative entry into the K-bond has been described (2,3). We now wish to report: (i) an alternative synthesis based on reductive construction of the K-region by which the previously unattainable (2) 1a,9b-dihydro-1a,9b-diphenylphenanthro[9,10-*b*]oxirene (3) could be obtained, and (ii) the photochemical behavior of 3 upon uv-irradiation.

Pinacol reduction of 2,2'-dibenzoylbiphenyl (1) by magnesium and magnesium iodide afforded a 3:5 mixture of *cis*- and *trans*-9,10-diphenylphenanthrene-9,10-diol (2). Separation of the *trans*-isomer followed by treatment with excess dimethylformamide dimethyl acetal gave epoxide 3 in 55% yield.



Irradiation of 3 in nitrogen purged methylene chloride at 254 nm to full conversion resulted in the formation of 64% of 10,10-diphenyl-9-(10*H*)phenanthrone (4) and 35% of 6,7-diphenyldibenz[*b,d*]oxepin (5).

It should be recalled that while oxepins have been reported to be either the only or the major singlet state photoproducts of unsubstituted arene oxides (4)(5), phenanthrols (usually the by-products) were assumed to result from triplet state processes affected by sensitizers (6).

Thus, the photoconversion of 1a,9b-dihydro-1a,9b-dimethylphenanthro[9,10-*b*]oxirene in benzene into a pinacolone derivative has been attributed to solvent sensitization (7). We have shown, however, that the yield of 4 is not affected by added sensitizers. Moreover, when the photolysis of 3 was carried out in acetone or in benzene (with or without benzophenone), oxepin 5 was virtually the only product.

In contrast to the photolysis of the unsubstituted parent epoxide (8), we did not observe any significant change in the course of the reaction upon irradiation of 3 with uv-light of different wave length.

Interestingly, uv-light evokes reversible photochromism in solid 5 adsorbed on silica gel matrices. A distinguished orange coloration appears when a sample is irradiated at 254 nm for 2 minutes (22°). The color bleaches in visible light but is regenerated upon renewal of the uv-irradiation. As similar photochromism of vicinal diaryl oxiranes (10) has been attributed to the stabilization of carbonyl ylides (11), we assume that the orange color formed in our experiments is associated with the transformation of 5 into the ylid 6. However, unlike the photochromism of some indonone oxide derivatives (12) the phenomenon is detectable at ambient temperature only in the solid state.

EXPERIMENTAL

1a,9b-Dihydro-1a,9b-diphenylphenanthro[9,10-*b*]oxirene (3).

2,2'-Dibenzoylbiphenyl (1) (13) was converted into a 3:5 mixture of *cis*- and *trans*-9,10-diphenylphenanthrene-9,10-diol (2) in 83% yield by pinacol reduction with magnesium/magnesium iodide (14). Separation of the required *trans*-isomer was accomplished by titration of the mixture with 1-propanol followed by recrystallization of the soluble material once from acetic acid (15) and once from benzene, m.p. 182° [lit. (14) m.p. 178-180°]; ir (Nujol): 3560 cm⁻¹.

A solution of 1.00 g. of *trans*-2 and 0.73 g. of freshly distilled dimethylformamide dimethyl acetal in 40 ml. of dry dimethylformamide was heated at 128° (bath temperature) for 20 hours. A second portion of 0.30 g. of the reagent was added and the heating continued for further 20 hours. The mixture was cooled to 90° and poured into 100 ml. of water. The precipitate was dissolved in a mixture of methylene chloride-benzene (1:1). The solution was washed with water, dried, concentrated and chromatographed on silica gel (benzene-petrol ether as eluent) to

yield 512 mg. (55%) of colorless **3**, m.p. 223°; uv (methylene chloride): λ max (log ϵ) 236 (4.22), 269 (4.07 sh), 279 (4.19), 288 (4.02 sh), 303 nm (3.54); pmr (deuteriochloroform): δ 6.75-7.67 (m, 16H), 8.17-8.30 (m, 2H); ms: (70 eV, 90°) m/e (relative intensity) 346 (12.5), 328 (3.3), 318 (2.0), 241 (15.3), 105 (100), 77 (15.3).

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.14; H, 5.23. Found: C, 90.40; H, 5.15.

Photochemical Conversion of **3** into 10,10-Diphenyl-9-(10H)phenanthrone (**4**) and 6,7-Diphenyldibenz[*b,d*]oxepin (**5**).

In a typical experiment a solution of 130 mg. of **3** in 190 ml. of spectroscopical grade degassed methylene chloride was placed in a quartz well and irradiated at room temperature with fifteen 15W Rayont lamps (254 nm) located around the well at a distance of 12 cm. After 70 minutes all of the starting epoxide disappeared (determined by tlc). The solvent was removed and the residue subjected to preparative tlc on 2 mm. Merck silica gel on glass plates using a mixture of benzene and methylcyclohexane (1:1) as eluent. The band of $R_f = 0.1$ afforded 82.6 mg. (64%) of **4**; m.p. and mixed m.p. with an authentic sample (2) 194-195°. The band of $R_f = 0.4$ yielded 45.2 mg. (35%) of oxepin **5**, m.p. 183° [from benzene-methylcyclohexane (1:20)]. The ir spectrum was free of C=O and OH bands; uv (methylene chloride): λ max (log ϵ) 307 nm (4.19) (16); pmr (deuteriochloroform): δ 6.90-7.30 (m, 13H), 7.46-7.75 (m, 5H); ms: (70 eV, 120°) m/e (relative intensity) 346 (32.5), 344 (13.0), 315 (8.0), 313 (5.5), 269 (3.8), 149 (15.8), 105 (100), 77 (12.3).

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.14; H, 5.23. Found: C, 90.34; H, 5.39.

When the above irradiation of **3** was carried out for 90 minutes in (a) methanol-methylene chloride (12:5), (b) acetone (c) benzene (with or without benzophenone) the only photoproduct was oxepin **5**.

REFERENCES AND NOTES

- (1) M. Bucker, H. R. Glatt, K. L. Platt, D. Avnir, Y. Ittah, J. Blum and F. Oesch, *Mutation Res.*, **66**, 337 (1979).
- (2) D. Avnir, A. Grauer, D. Dinur and J. Blum, *Tetrahedron*, **31**, 2457 (1975).
- (3) D. Avnir and J. Blum, *J. Heterocyclic Chem.*, **13**, 619 (1976).
- (4) See e.g., D. M. Jerina, B. Witkop, C. L. McIntosh and O. L. Chapman, *J. Am. Chem. Soc.*, **96**, 5578 (1974).
- (5) B. J. Dowty, N. E. Brightwell, J. L. Laster and G. W. Griffin, *Biochem. Biophys. Res.*, **57**, 452 (1974).
- (6) G. W. Griffin, S. K. Sata, N. E. Brightwell, K. Ishikawa and N. S. Bhacca, *Tetrahedron Letters*, 1239 (1976).
- (7) K. Ishikawa and G. W. Griffin, *ibid.*, 427 (1977).
- (8) K. Shudo and T. Okamoto, *Chem. Pharm. Bull.*, **21**, 2809 (1973).
- (9) Silica gel has been shown previously to be a useful support for the exercise of photochromism; e.g., T. R. Evans, A. F. Toth and P. A. Leermakers, *J. Am. Chem. Soc.*, **89**, 5060 (1967).
- (10) Cf., e.g., G. W. Griffin, K. Nishiyama and K. Ishikawa, *J. Org. Chem.*, **42**, 180 (1977) and references therein.
- (11) N. R. Bertoniere and G. W. Griffin, in "Organic Photochemistry", Vol. III, O. L. Chapman, Ed., Marcel Dekker, New York, N.Y., 1973, p. 139.
- (12) D. R. Arnold and Y. C. Chang, *J. Heterocyclic Chem.*, **8**, 1097 (1971).
- (13) R. G. R. Bacon and W. S. Lindsay, *J. Chem. Soc.*, 1382 (1958).
- (14) W. E. Bachmann, *J. Am. Chem. Soc.*, **54**, 1969 (1932).
- (15) During the recrystallization of **2** from acetic acid the temperature should not reach the boiling point otherwise pinacolone rearrangement might take place.
- (16) Cf., e.g., M. J. S. Dewar, *Tetrahedron*, **26**, 4269 (1970).