

Synthesis and Oxygen-catalysed Racemization of 2,2'-Bismethoxycarbonyl-9,9'-bianthryl

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Summary The synthesis of 2,2'-bismethoxycarbonyl-9,9'-bianthryl and the results of attempts to measure the energy barrier to racemization are reported.

IN connection with other work, we were interested in measuring the energy barrier to racemization of an optically active 9,9'-bianthryl. To our knowledge, only one such compound, 3,3'-dicarboxyl-9,9'-bianthryl,[†] has previously been reported.¹ We report here the synthesis of optically active 2,2'-bismethoxycarbonyl-9,9'-bianthryl and the

2,2'-diacid, prior to esterification, was accomplished with quinidine to yield the (+)-diacid ($[\alpha]_D^{25} + 101^\circ$, c 0.65, acetone) and the (–)-diacid ($[\alpha]_D^{25} - 114^\circ$, c 0.65, acetone). Methylation with diazomethane yielded the corresponding (+)-diester ($[\alpha]_D^{25} + 114^\circ$, c 0.58, acetone) and (–)-diester ($[\alpha]_D^{25} - 133^\circ$, c 0.57, acetone).

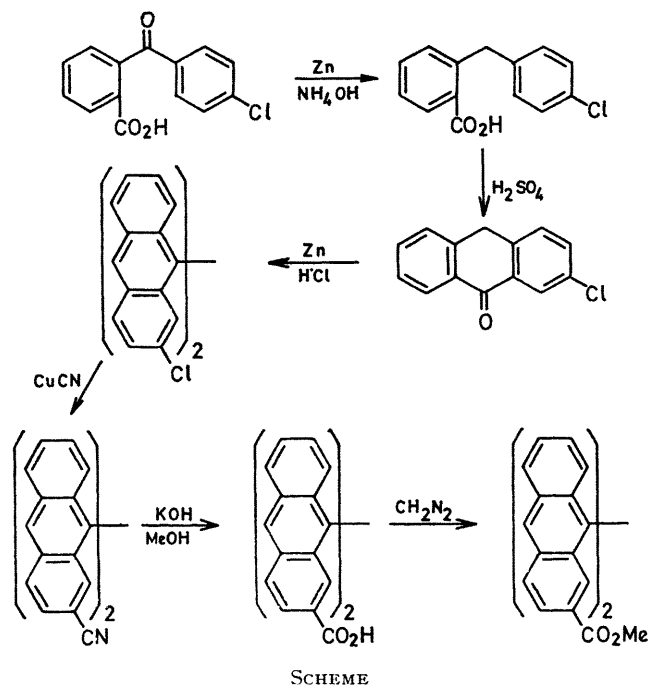
Under a nitrogen atmosphere, we were unable to racemize the diester. Thus, heating a solution of the diester in triglyme [1,2-bis-(2-methoxyethoxy)ethane] in a sealed tube under a nitrogen atmosphere at $224 \pm 1^\circ$ for 1.5 hr. or in dimethyl phthalate at $220.2 \pm 0.1^\circ$ for 6 hr. resulted in no change in rotation. Using the latter result, and assuming an error in polarimetry of 1%,[§] and applying the Arrhenius equation, the energy barrier is estimated to be at least 42 kcal.mole⁻¹.[¶]

A few of our racemization experiments gave erratic results. This led us to the discovery that the racemization of 2,2'-bismethoxycarbonyl-9,9'-bianthryl is catalysed by oxygen. Thus, heating a solution of the diester in dimethyl phthalate, through which oxygen had previously been bubbled for 10 min., in a sealed tube at $220.2 \pm 0.1^\circ$ for 2 hr. caused 13.3% racemization. A similar experiment in triglyme solution at $224 \pm 1^\circ$ for 1.5 hr. resulted in 83% racemization. In the latter case, the recovered material was shown to be chemically unchanged, within the limits of n.m.r. spectroscopy.

Although we do not have enough information yet to discuss the details of this oxygen catalysis, it would appear that a reversible addition of some species (either oxygen or a species derived from oxygen attack on the solvent) to one of the anthracene rings is involved. This would convert one of the central carbon atoms into a more tetrahedral-like structure. Such an intermediate would be expected to racemize more easily than 2,2'-bismethoxycarbonyl-9,9'-bianthryl.

We thank the National Science Foundation, The City University of New York, and The General Faculty Research Committee of The City College of New York for financial support, and Mr. Sidney Liebgold of The City College of New York for assistance.

(Received, September 19th, 1969; Com. 1417.)



results of our attempts to measure the energy barrier to racemization. The synthesis of 2,2'-bismethoxycarbonyl-9,9'-bianthryl is shown in the Scheme.[‡] Resolution of the

[†] We were unsuccessful in our attempts to repeat the earlier synthesis of this compound. Specifically, all attempts to oxidize 3,3'-dimethyl-9,9'-bianthryl to the corresponding diacid resulted mainly in tar formation.

[‡] Satisfactory spectroscopic and elemental analyses were obtained for all new compounds.

[§] A Perkin-Elmer Model 141 polarimeter with a 10 cm. cell was used to measure optical rotations. The observed rotation was 0.593° and was reproducible to within $\pm 0.002^\circ$.

[¶] For this calculation, we assumed an Arrhenius frequency factor of 10^{12} , close to that observed for 1,1'-binaphthyls.² The corresponding minimum energy barriers for Arrhenius frequency factors of 10^{11} and 10^{13} are 40 kcal. mole⁻¹ and 44 kcal. mole⁻¹, respectively.

¹ F. Bell and D. H. Waring, *J. Chem. Soc.*, 1949, 2689.

² A. S. Cooke and M. M. Harris, *J. Chem. Soc.*, 1963, 2365; Y. Badar, A. S. Cooke, and M. M. Harris, *ibid.*, 1965, 1412; *J. Chem. Soc. (C)*, 1966, 1315.