CHEMISTRY LETTERS, pp. 45-48, 1972. Published by the Chemical Society of Japan

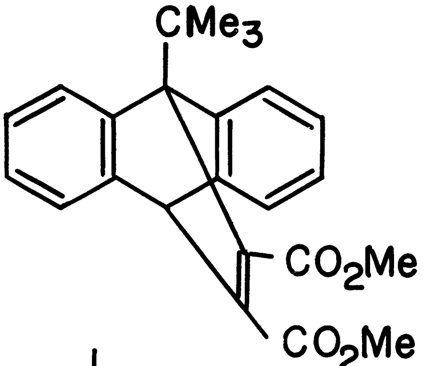
RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON. III.[1] ISOLATION OF ISOMERS DUE TO RESTRICTED ROTATION ABOUT AN sp^3-sp^3 CARBON BOND

Michinori Ōki and Gaku Yamamoto
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo

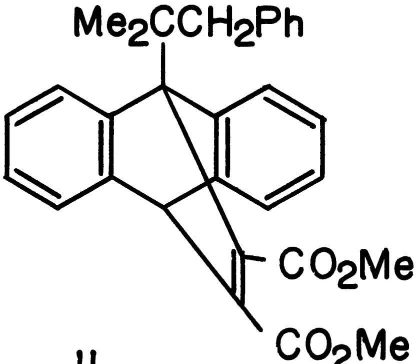
A dl pair and a meso form of dimethyl 9-(1,1-dimethyl-2-phenylethyl)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate are obtained as stable isomers at room temperature. These isomers must originate from restricted rotation about the C_9-C_α bond. Data for the thermal equilibrations and activation parameters for the interconversion are obtained.

Isolation of stereoisomers originating from the restricted rotation about a single bond between two sp^3-hybridized carbon atoms has been one of the most challenging problems in organic chemistry since the last century[2]. Since the early days of tetrahedron theory of carbon, the "free rotation" about a single bond had been assumed to accommodate the nonexistence of the optical isomers in a molecule of the type C_{xxyz}. Therefore, the average properties of the substance have been observed as far as we are discussing the macroscopic properties of the substance. It should be interesting to know the chemical and physical properties of each rotational isomer.

Since we have been able to show the possibility of isolation of this type of isomers at room temperature, if we consider the compounds such as dimethyl 9-*t*-butyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (I), in one of the preceding papers[2] of this series, our effort has been paid to realize the possibility. We now wish to present an unambiguous evidence for the isolation of rotational isomers due to restricted rotation about an sp^3-sp^3 carbon single bond: the



I

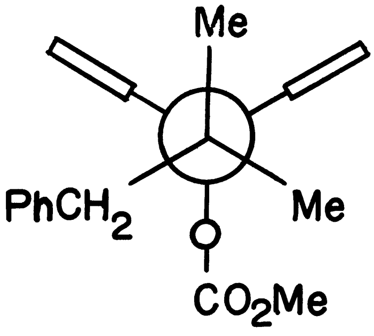


II

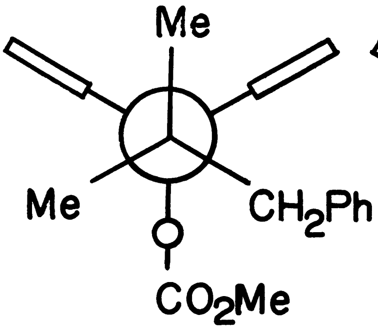
compound in question is dimethyl 9-(1,1-dimethyl-2-phenylethyl)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate (II) which is a phenyl derivative of I. This compound has no asymmetric carbon atom but afforded a dl isomer pair and a meso form as is described below.

Newman type projections of compound II through C_9-C_α bond are given by IIa, IIb, and IIc. IIa and IIb are the mirror images with each other, while IIc is optically inactive. Then the compound should give a dl isomer pair and a meso form, if the rotation about the bond in question is frozen. As to the NMR signals for the 1,1-dimethyl-2-phenylethyl group, two singlets (3H each) for the methyls and an AB quartet for the methylene protons are expected in the dl isomer, whereas one 6H singlet for the methyls and a 2H singlet for the methylene in the meso isomer.

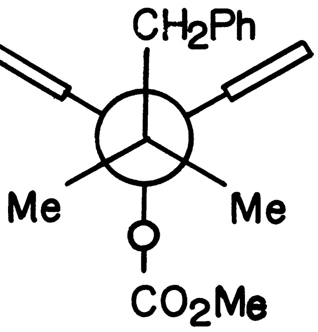
Treatment of 1,1-dimethyl-2-phenylethylmagnesium chloride$^{3)}$ with anthrone followed by dehydration with phosphorus pentoxide afforded 9-(1,1-dimethyl-2-phenylethyl)anthracene (III)$^{4)}$, mp 125-127°C, NMR (CCl_4, 60MHz): δ 1.74 (6H, s), 3.68 (2H, s), 7.01 (5H, s), 6.9-8.2 (9H, m). Heating III with dimethyl acetylenedicarboxylate in toluene for 5 hr gave colorless needles, mp 200-201°C (from chloroform-



IIa



IIb



IIc

methanol) in almost quantitative yield. This compound was identified with the meso form IIc because its NMR spectrum was consistent with the assignment (see Table I for the data), giving a single peak for the two methyl groups.

The compound thus obtained was heated in chlorobenzene at 150°C for a period of 10 hr, the change being monitored by NMR spectra. The NMR spectra indicated that, besides the signals due to IIc, a set of new signals appeared and increased in intensity until an equilibrium was reached. The new set of signals was consistent with the assumption that the isomers IIa and IIb were formed: two singlets for C-Me groups and an AB quartet for the benzylic CH_2. At the equilibrium the ratio (IIa + IIb)/IIc was 3.0 ± 0.1 irrespective of the temperature in the range of 111-152°C. This would mean that the two isomers have about the same enthalpy and the equilibrium is in favor of (IIa + IIb) because of the favorable mixing entropy and other factors.

Table I. Chemical Shifts[a)]

	meso isomer		dl isomer	
	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
C-Me	1.78 (6H, s)	1.90 (6H, s)	1.83 (6H, br s)[b)]	1.83 (3H, s)
				1.97 (3H, s)
O-Me	3.65 (3H, s)	3.25 (3H, s)	3.72 (3H, s)	3.28 (3H, s)
	3.72 (3H, s)	3.39 (3H, s)	3.75 (3H, s)	3.43 (3H, s)
CH_2	3.75 (2H, s)	3.70 (2H, s)	3.64 (2H, q: J_{AB} 13.8Hz, δ_{AB} 18.1Hz)	3.90 (2H, q: J_{AB} 14.4Hz, δ_{AB} 4.9Hz)
CH	5.57 (1H, s)	5.70 (1H, s)	5.56 (1H, s)	5.69 (1H, s)
aromatic	6.9-8.1 (13H, m)	6.7-8.1 (13H, m)	6.7-8.1 (13H, m)	6.6-8.1 (13H, m)

a) Obtained for _ca_. 10% (w/v) solution at 34°C and 60MHz, and given in parts per million relative to internal TMS.

b) Apparent singlet with half width of 2.1Hz, suggesting the existence of two slightly shifted singlets.

The equilibrated mixture was chromatographed through silica gel and eluted with benzene. The dl isomer was eluted faster than the meso isomer and was purified through crystallization from methanol. The dl isomer was obtained as colorless granules, mp 149-151°C. NMR spectral data of this isomer are also given in Table I.

On heating the dl isomer in chlorobenzene at 138°C for 40 hr, a mixture resulted which gave the identical NMR spectrum with that of the equilibrium mixture obtained from the meso isomer. Thus these results together with the spectral data suggest that the compounds obtained here are readily interconvertible. These data are best accommodated by assuming the independent existence of the rotational isomers at room temperature and the interconversion among the rotamers at higher temperaure.

Time dependence of the relative intensities of the signals was followed at four different temperatures between 111-152°C. The preliminary results indicated that the Arrhenius activation energy is ca. 33 kcal/mol and the frequency factor 10^{13} sec^{-1}. These data support the claim that the isolation of the rotational isomers was possible at room temperature.

Since the dl isomer is favored at the equilibrium, the preferred formation of the meso isomer in the Diels-Alder reaction should be attributed to the kinetic control. The approach of dimethyl acetylenedicarboxylate from the direction which bisects the Me-C-Me angle will form the meso isomer whereas that from the direction bisecting the Me-C-CH_2Ph will produce the dl isomer. The former approach should give the smaller activation energy because of the less steric requirement.

Optical resolution of the dl isomer is in progress.

References.

1) The preceding paper: M. Ōki and N. Nakamura, Bull. Chem. Soc. Japan, 44, 1880 (1971).

2) For some of the recent papers pertaining to the restricted rotation about a single bond, see the Part I of this series: M. Ōki and M. Suda, Bull. Chem. Soc. Japan, 44, 1876 (1971).

3) W. G. Brown, C. J. Mighton, and M. Senkus, J. Org. Chem., 3, 62 (1938).

4) Satisfactory analyses were obtained for all new compounds.

(Received October 11, 1971)