

In the model for our calculations we assume that to a first approximation (a) over-all changes in non-bonded interaction from ground to transition state are negligible, (b) changes in the hexagonal geometry of the benzene rings are negligible, and (c) strain in the CCX angle is completely relieved by buckling, *i.e.*, by the folding of the CXC plane relative to the plane containing the biphenyl framework (a mode of relief not considered by Howlett<sup>3</sup>).

Use of bond bending constants<sup>3,4</sup> 1.3, 1.0 and  $0.7 \times 10^{-11}$  erg. rad.<sup>-2</sup> molec.<sup>-1</sup> for COC, CSC and CCC, respectively, yields calculated values for  $E_{act}$  of 22 and 42 kcal./mole for the racemization of Ia and Ib, respectively. In harmony with these estimates, we find that Ia racemizes in *o*-xylene according to the expression  $k_1 = 10^{11.7} e^{-20.2/RT}$  (*e.g.*,  $t_{1/2}$ <sup>23,3</sup> is 10.7 min.) whereas Ib remains optically unchanged on heating in *o*-xylene at 83.5° for at least 3 hours. Ic is intermediate: it racemizes in *o*-xylene according to the expression  $k_1 = 10^{13.2} e^{-30.0/RT}$  (*e.g.*,  $t_{1/2}$ <sup>24,6</sup> is 31.7 hr.).

The synthesis of Ib revealed a number of highly unconventional features which we desire to record at this time. Bromination (NBS) of dimethyl (-)-(R)-6,6'-dimethyl-2,2'-diphenate<sup>5</sup> gives II (m.p. 105.5–106.5°),  $[\alpha]^{24D} +21^\circ$  (C<sub>6</sub>H<sub>6</sub>), which is converted (Na<sub>2</sub>S, then LiAlH<sub>4</sub>) into IIIb, m.p. 123.5–124.5°,  $[\alpha]^{23D} +58^\circ$  (chf.). The reaction of solid (+)-IIIb with PBr<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> (trace of pyridine) at room temperature affords *directly* an equimolar mixture of Ib and of 2,2',6,6'-tetrakis-(bromo-methyl)-biphenyl (IV)<sup>6</sup>; it seems likely that sulfonium salts intervene in this disproportionation.<sup>7</sup> Ib has m.p. 213.3–215.5° (dec.),  $\lambda_{max}^{EtOH} 242$  m $\mu$  (11,800), 291 m $\mu$  (1040),  $[\alpha]^{26D} +415^\circ$  (C<sub>6</sub>H<sub>6</sub>), n.m.r. spectrum in the aliphatic region exhibits two spin-coupled methylene protons,  $\delta_A$  3.00,  $\delta_B$  3.10,  $J_{AB}$  0.212 p.p.m. The absolute configuration of (+)-Ib, shown in the figure, follows from the synthetic sequence.<sup>8</sup>

A novel aspect of the disproportionation is the fact that the reaction of *solid racemic* IIIb (m.p. 154.5–155.5°, prepared from racemic II, m.p. 131–134°) with PBr<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> (trace of pyridine) at room temperature affords a *single* substance, presumably the expected C<sub>16</sub>H<sub>14</sub>SBr<sub>2</sub> (found: C, 48.47; H, 3.63; S, 7.89; Br, 40.16). This substance remains unchanged on recrystallization. It is not formed from an equimolar mixture of racemic Ib (m.p. 266–267° (dec.), prepared from IV and Na<sub>2</sub>S) and IV in PBr<sub>3</sub>/C<sub>6</sub>H<sub>6</sub>, but it is quantitatively (infrared) disproportionated into an equimolar mixture of racemic Ib and IV by heating

(4) H. Siebert, *Z. anorg. u. allgem. Chem.*, **271**, 65 (1952).

(5) For absolute configuration, *cf.* K. Mislow, *Angew. Chem.*, **70**, 683 (1958).

(6) E. Bergmann and Z. Pelchowicz, *Bull. Research Council Israel*, **3**, No. 1/2, 91 (1953).

(7) *Cf.*, *e.g.*, F. E. Ray and I. Levine, *J. Org. Chem.*, **2**, 267 (1937); M. Kulka, *Can. J. Chem.*, **37**, 325 (1959) and references cited. Symmetrical intermediates are excluded from any possible mechanism since the produced Ib is optically active and apparently optically pure.

(8) The system of configurational designation proposed by R. S. Cahn, C. K. Ingold and V. Prelog, *Experientia*, **12**, 81 (1956), cannot be applied to this case. However, elimination from this system of the class of optically active atropisomers is under active consideration (V. Prelog, private communication).

above the melting point (149.5–155.5°, 4 min.). The compound gives racemic Ib with Na<sub>2</sub>S. The dramatic *difference in the chemistry of racemic and enantiomeric modifications* of IIIb appears to be without precedent and is the subject of further investigations.

Preparation of IIIa, m.p. 139–140.5°,  $[\alpha]^{23D} +32^\circ$  (chf.), is effected by treatment of (+)-II with Ag<sub>2</sub>O/aq. acetone, followed by LiAlH<sub>4</sub>. Addition of (+)-IIIa to concd. H<sub>2</sub>SO<sub>4</sub> at -20°, followed by a conventional workup in which the temperature is kept as low as possible, gives (+)-Ia, initial  $[\alpha]_{435}^0$  ca. +230° (*o*-xylene); the absolute configuration, shown in the figure, follows from the synthetic sequence.<sup>8</sup> Racemic Ia may be prepared from IV and Ag<sub>2</sub>O/aq. acetone, or from racemic or active IIIa and TsCl/pyridine, or from IIIa and TsOH in refluxing benzene. It has m.p. 189–191° after sublimation,  $\lambda_{max}^{EtOH} 255.5$  m $\mu$  (16,300), n.m.r. spectrum in the aliphatic region exhibits two spin-coupled methylene protons,  $\delta'_A$ , 1.85,  $\delta'_B$  2.23,  $J'_{AB}$  0.192 p.p.m.

Closure of (+)-IIIb (TsCl/pyridine) gives (R)-Ic, m.p. 161–162°,  $[\alpha]^{25D} +333^\circ$  (*o*-xylene). Racemic Ic, m.p. 161–162°,  $\lambda_{max}^{EtOH} 253.5$  m $\mu$  (10,900), is similarly prepared from racemic IIIb. The n.m.r. spectrum in the aliphatic region exhibits two pairs of spin-coupled methylene protons,  $\delta_A$  2.84,  $\delta_B$  2.87,  $J_{AB}$  0.30 (estd.),  $\delta'_A$  1.82,  $\delta'_B$  2.18,  $J'_{AB}$  0.292 p.p.m.

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#### SYNTHESIS OF SUBSTITUTED CYCLOBUTANE HYDROCARBONS BY POTASSIUM CATALYZED DIMERIZATION OF $\beta$ -ALKYLSTYRENES<sup>1</sup>

Sir:

We wish to report a novel dimerization reaction resulting in the formation of cyclobutanes. It was found that the dimerization of  $\beta$ -methylstyrene in the presence of catalytic amounts of potassium produces high yields of an almost equimolar mixture of stereoisomers of 1,3-dimethyl-2,4-diphenylcyclobutane (II).

The dimerization reaction was carried out in a flask provided with a high-speed stirrer. Two grams of potassium metal was dispersed in 96 g. of methylcyclohexane at 100° and to this was added 24 g. of  $\beta$ -methylstyrene consisting of 65% of the *trans*- and 35% of the *cis*-isomer. After 3 hours of stirring at 100° the product consisted of 50% of recovered  $\beta$ -methylstyrenes, 45% of II, and of some higher boiling material. The yield of cyclobutanes based on converted  $\beta$ -methylstyrene amounted to about 90%.

The two stereoisomeric species of the substituted cyclobutane (II) were detected by means of gas chromatography. The combined isomers distilled at 118–122° at 0.5 mm.,  $n_D^{20}$  1.5455, and did not show any olefinic unsaturation.

*Anal.* Calcd. for C<sub>18</sub>H<sub>20</sub>: C, 91.46; H, 8.54. Found: C, 91.41; H, 8.62.

The cyclobutanes had  $\lambda_{max}$  2590 Å.,  $\epsilon = 1015$ .

(1) Paper XXII of the series "Base Catalyzed Reactions" for paper XXI see J. Shabtai and H. Pines, *J. Org. Chem.*, in press.

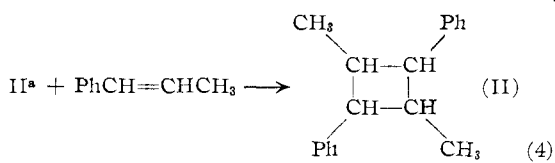
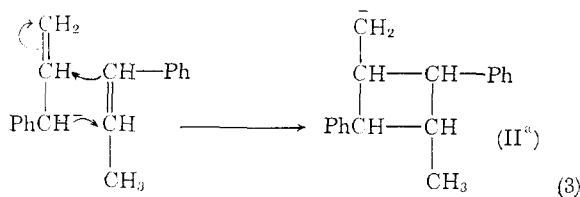
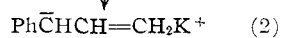
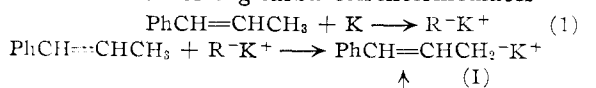
The position of the B-band was practically identical with that observed in the spectra of a number of 1,3-diphenylalkanes (*ca.* 2600 Å.). The molecular extinction, however, was about twice that shown by the latter class of compounds.

Substantial support for the structure of a symmetrically substituted dimethyldiphenylcyclobutane assigned to the dimer was obtained by an examination of its nuclear magnetic resonance spectrum. The spectrum showed the presence of  $\text{CH}_3\text{CH}<$  and the absence of  $\text{CH}_3\text{CH}_2$ - groupings in the molecule. The sharpness of the phenyl group signal was related to the equivalency of the two benzene rings. A third shift was attributed to the presence of tertiary hydrogen.

The conclusive proof for the structure of the dimer was obtained by a hydrogenolysis reaction using platinum-alumina as catalyst. The reaction was carried out in a flow system at 235° in the presence of a stream of hydrogen. The product was composed only of 1,3-diphenyl-2-methylpentane, which shows that compound (II) consisted of stereoisomers of 1,3-dimethyl-2,4-diphenylcyclobutane. 1,3-Diphenyl-2-methylpentane, which was synthesized independently by Claisen-Schmidt condensation of propiophenone and hydrogenolysis of the resulting keto-olefin, distilled at 113–114° at 0.4 mm.,  $n_D^{20}$  1.5365.

*Anal.* Calcd. for  $\text{C}_{18}\text{H}_{22}$ : C, 90.67; H, 9.21. Found: C, 90.55; H, 9.30.

The formation of I can be explained by a chain mechanism involving carbanion intermediates



The general steps in this mechanism are similar to those described previously.<sup>2</sup> Step 3 of the mechanism implies that a cyclobutane ring, because of a certain internal strain, has a stabilizing effect upon the primary carbanion  $\text{II}^a$ .

When the dimerization was carried out at 135° in ethylcyclohexane the initial product of the reaction was 1,5-diphenyl-4-methyl-1-pentene ( $\text{PhCH}=\text{CHCH}_2\text{C}(\text{CH}_3)\text{HCH}_2\text{Ph}$ ), (III), which then through a depolymerization and resynthesis is converted to (II). The course of this reaction was followed by gas chromatography. Compound III distilled at 140–141° at 0.5 mm.,  $n_D^{20}$  1.5710. The structure was proved by a combination of

(2) M. Kolobieski and H. Pines, *J. Am. Chem. Soc.*, **79**, 5820 (1957).

ultraviolet spectroscopy, ozonization and comparison of the selectively hydrogenated dimer with a synthetic sample of 1,5-diphenyl-2-methylpentane.

1,1,3,3-Tetramethyl-2,4-diphenylcyclobutane (IV) in over 90% yield was obtained on reaction of  $\beta,\beta$ -dimethylstyrene at 110° in the presence of potassium, using methylcyclohexane as a solvent. Compound IV melted at 133°. Its structure was confirmed by n.m.r. spectroscopy, which showed the presence of three sharp peaks, corresponding to the phenyl,  $\text{CH}_3$ - and  $\text{CH}$ - groupings, in the proper relative intensities.

*Anal.* Calcd. for  $\text{C}_{20}\text{H}_{24}$ : C, 90.84; H, 9.16. Found: C, 90.91; H, 9.50.

The outlined reaction, which represents a novel approach to the synthesis of cyclobutane derivatives, is presently applied to a study of related compounds having functional groups.

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#### THE DECOMPOSITION OF ACETYL PEROXIDE: THE EFFECT OF IODINE

Sir:

In an earlier publication<sup>1</sup> one of us proposed that the formation of cyclohexyl acetate from the decomposition of acetyl peroxide in cyclohexene solution is a result of acetoxy radical addition to cyclohexene. This proposal was quite contrary to the generally accepted behavior of acetoxy radicals, as was pointed out<sup>1</sup> at the time.

This general point of view is based to some extent on the undeniable fact that acetate groups are not widely found in the products of decomposition of acetyl peroxide. More substantial evidence as to the non-existence or very transient nature of acetoxy radicals has been provided by Szwarc<sup>2,3</sup> and by Walling.<sup>4</sup> That is, Szwarc has computed the heat of formation of the acetoxy radical, and its value is regarded as indicating that dissociation of the radical is the favored process. Walling<sup>4</sup> has reported that the decomposition of acetyl peroxide in moist carbon tetrachloride solution containing iodine gives carbon dioxide, methane and methyl iodide in contrast to benzoyl peroxide,<sup>5</sup> which gives benzoic acid almost quantitatively.

The two pieces of evidence<sup>3,4</sup> just referred to are used with increasing frequency in classifying the acetoxy radical as either non-existent or transient. Most recently, Martin and Drew<sup>6</sup> have pro-

(1) H. J. Shine and J. R. Slagle, *J. Am. Chem. Soc.*, **81**, 6309 (1959).

(2) A. Rembaum and M. Szwarc, *ibid.*, **77**, 3486 (1955).

(3) L. Jaffee, E. J. Prosen and M. Szwarc, *J. Chem. Phys.*, **27**, 416 (1957).

(4) C. Walling and R. B. Hodgdon, Jr., *J. Am. Chem. Soc.*, **80**, 228 (1958).

(5) G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

(6) J. C. Martin and E. H. Drew, *ibid.*, **82**, 1234 (1961).