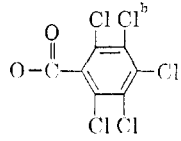


Haas and Bender,¹ who studied the reaction of nine *para*-substituted benzyl halides with the sodium salt of 2-nitropropane, showed that only *p*-nitrobenzyl chloride gives carbon-alkylation; all the other benzyl halides examined yield aldehydes, evidently arising from oxygen-alkylation.

It now has been found that the uniqueness of the *p*-nitrobenzyl system depends not only on the *p*-nitro group but also, and in a dramatic way, on the leaving group. For example, whereas *p*-nitrobenzyl chloride gives 95% carbon-alkylation the use of *p*-nitrobenzyl iodide results in 81% oxygen-alkylation; Table I summarizes our findings. Such dependence of the reaction course on the nature of the leaving group has not been demon-

TABLE I

NATURE OF REACTION OF $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$ WITH THE LITHIUM SALT OF 2-NITROPROPANE IN DMF AT -16° AS A FUNCTION OF X^a

X	C, %	O, %
NMe_3^b	93	0
	93	0
Cl	95	1
OTos	40	32
Br	17	65
I	7	81

^a All reactions were run to completion using 0.25 molar $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{X}$ and 0.5 molar lithium salt except for the pentachlorobenzoate ester reaction which was 0.035 molar in ester and 0.07 molar in lithium salt. All yields refer to pure products isolated except for the % 0 in runs employing the tosylate, bromide and iodide; here the aldehyde yields are by gas chromatography and are *ca.* 10-15% higher than the yields of pure *p*-nitrobenzaldehyde 2,4-dinitrophenylhydrazone isolated. Reaction times range from *ca.* 35 hr.

for X = NMe (slowest) to 0.5 hr. for X = I (fastest). Repetition of the *p*-nitrobenzyl iodide experiment using the X = Cl reaction time (20 hr.) did not alter the yield of carbon alkylate. ^b Run at 25° .

strated before, either in the alkylation of nitroparaffin salts, or in the alkylation of any other ambident² anions.

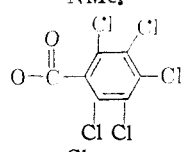
In contrast, the unsubstituted benzyl system shows no leaving group effect. The reactions of benzyl chloride, bromide, iodide or tosylate with the lithium salt of 2-nitropropane in DMF all give 82-84% yields of benzaldehyde and *ca.* 1% yields of the carbon alkylate (2-benzyl-2-nitropropane).

It is noteworthy that whenever carbon alkylation is observed in the *p*-nitrobenzyl system the reaction rate is much faster than for the corresponding benzyl compound whereas when the *p*-nitro group is unable to effectuate carbon alkylation of the 2-nitropropane anion it simultaneously fails to produce a large increase in rate relative to the corresponding benzyl compound (Table II).

This suggests that oxygen alkylation, the usual mode of reaction of a nitroparaffin anion, derives

(2) N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Ifland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).

TABLE II

Reaction rates $\frac{p\text{-O}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2\text{X}}{\text{C}_6\text{H}_5\text{CH}_2\text{X}}$	
NMe_3^+	>100
	>100
Cl	>100
OTos	8
Br	6
I	3

simply from nucleophilic displacement by the oxygen of the anion on the benzylic carbon; however, in the *p*-nitrobenzyl series, when X is a difficultly displaced group, a second mode of attack by the nitroparaffin anion has a chance to compete and it is this second process which is productive of carbon alkylation. The matter of mechanism is currently under investigation.

Aside from its obvious significance as regards the alkylation of other ambident anions, the properties herein reported for the *p*-nitrobenzyl system may very well be important in reactions involving non-ambident nucleophiles and this possibility is being explored.

(3) Sponsored by the U. S. Army Research Office (Durham).

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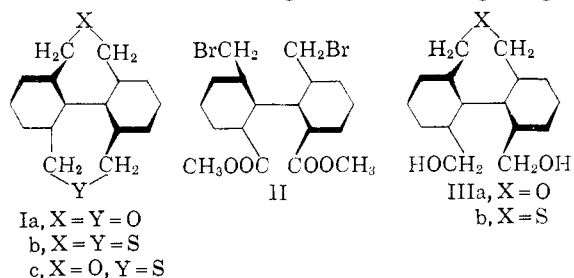
NATHAN KORNBLUM
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RECEIVED APRIL 14, 1961

A MODEL FOR ANGLE STRAIN CALCULATIONS. OPTICALLY ACTIVE SYMMETRICALLY BRIDGED BIPHENYLS^{1,2}

Sir:

The architecture of molecules of type I is uniquely suited for a comparison of theoretical and experimental evaluations of angle strain. A high degree



of constitutional symmetry in cases where X = Y minimizes the assumptions ordinarily entailed in calculations for less symmetrical molecules.³ We wish to report that calculated angle deformation energies in the transition state conformations for racemization of Ia and Ib account for the experimentally observed energy barriers.

(1) Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also thank the Alfred P. Sloan Foundation for partial support.

(2) Satisfactory elemental analyses were obtained for all substances reported. Chemical shifts are expressed for solutions in CDCl_3 with reference to external benzene.

(3) *E.g.*, K. E. Howlett, *J. Chem. Soc.*, 1250 (1955); *cf.* F. H. Westheimer, in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1956, Chapter 12.

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 Howlett³).

Use of bond bending constants^{3,4} 1.3, 1.0 and 0.7×10^{-11} erg. rad.⁻² molec.⁻¹ 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.*, $t_{1/2}$ ^{23,3} 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.*, $t_{1/2}$ ^{24,6} 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'-diphenate⁵ gives II (m.p. 105.5–106.5°), $[\alpha]^{24D} +21^\circ$ (C₆H₆), which is converted (Na₂S, then LiAlH₄) into IIIb, m.p. 123.5–124.5°, $[\alpha]^{23D} +58^\circ$ (chf.). The reaction of *solid* (+)-IIIb with PBr₃/C₆H₆ (trace of pyridine) at room temperature affords *directly* an equimolar mixture of Ib and of 2,2',6,6'-tetrakis-(bromo-methyl)-biphenyl (IV)⁶; it seems likely that sulfonium salts intervene in this disproportionation.⁷ Ib has m.p. 213.3–215.5° (dec.), λ_{max}^{EtOH} 242 m μ (11,800), 291 m μ (1040), $[\alpha]^{26D} +415^\circ$ (C₆H₆), n.m.r. spectrum in the aliphatic region exhibits two spin-coupled methylene protons, δ_A 3.00, δ_B 3.10, J_{AB} 0.212 p.p.m. The absolute configuration of (+)-Ib, shown in the figure, follows from the synthetic sequence.⁸

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 PBr₃/C₆H₆ (trace of pyridine) at room temperature affords a *single* substance, presumably the expected C₁₆H₁₄SBr₂ (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 Na₂S) and IV in PBr₃/C₆H₆, 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 Na₂S. 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 Ag₂O/aq. acetone, followed by LiAlH₄. Addition of (+)-IIIa to concd. H₂SO₄ 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.⁸ Racemic Ia may be prepared from IV and Ag₂O/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, λ_{max}^{EtOH} 255.5 m μ (16,300), n.m.r. spectrum in the aliphatic region exhibits two spin-coupled methylene protons, δ'_A , 1.85, δ'_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°, λ_{max}^{EtOH} 253.5 m μ (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, δ_A 2.84, δ_B 2.87, J_{AB} 0.30 (estd.), δ'_A 1.82, δ'_B 2.18, J'_{AB} 0.292 p.p.m.

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RECEIVED APRIL 24, 1961

SYNTHESIS OF SUBSTITUTED CYCLOBUTANE HYDROCARBONS BY POTASSIUM CATALYZED DIMERIZATION OF β -ALKYLSTYRENES¹

Sir:

We wish to report a novel dimerization reaction resulting in the formation of cyclobutanes. It was found that the dimerization of β -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 β -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 β -methylstyrenes, 45% of II, and of some higher boiling material. The yield of cyclobutanes based on converted β -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 C₁₈H₂₀; C, 91.46; H, 8.54. Found: C, 91.41; H, 8.62.

The cyclobutanes had λ_{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.