Novel Rearrangements in Carbodi-imide Chemistry[1]

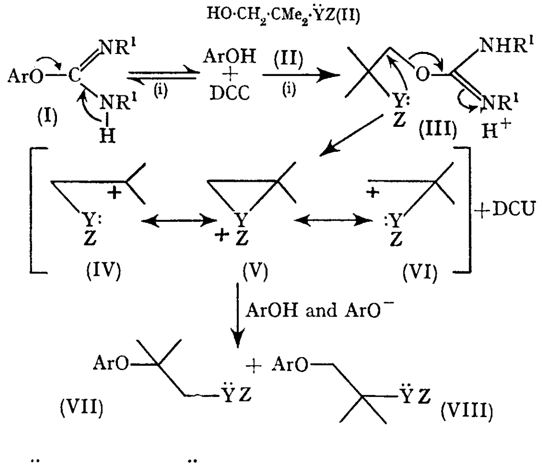
By F. L. BACH* and E. COHEN

(*Lederle Laboratories, a Division of American Cyanamid Co., Pearl River, New York,* 10965)

WE report here the unexpected formation of isomeric aryl branched 2-dialkylaminoethyl ethers when a phenolic substance is allowed to react with *NN'*-dicyclohexylcarbodi-imide (DCC) and an appropriately substituted 2-dialkylaminoethanol. Following the experimental conditions outlined in the Scheme, alkylation of *p*-nitrophenol using DCC and 2-dimethylamino-2-methylpropan-1-ol (IIa)† resulted in the formation of (VIIa) and (VIIIa) produced in a ratio of 9 : 1.‡

These unusual results may be attributed to the formation of an unsymmetrical ethylenimonium ion (Va) by way of an intramolecular displacement (neighbouring group participation[2]) initiated by the NMe_2 group of (IIIa). Once formed, the very reactive cyclic ethylenimonium ion (Va) would be vulnerable to nucleophilic attack by a phenol or phenoxide ion to afford (VIIa) and (VIIIa).§

We next searched for a similar rearrangement using an alcohol with sulphur on the β-carbon atom. The compound chosen was 2-n-hexylthio-2-methylpropan-1-ol (IIb)† which was allowed to react with



a, $\ddot{Y}Z$ = NMe_2; b, $\ddot{Y}Z$ = n-$C_6H_{13}S$; Ar = *p*-nitrophenyl, R^1 = cyclohexyl, (i) = equimolecular amounts of reactants heated (95—98°) in a sealed tube under argon for *ca.* 60 hr.

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† The purity of (IIa) and (IIb) was established by n.m.r. spectral analysis.

‡ Isomer ratios were determined by comparing n.m.r. signal intensities of the -$CH_2\ddot{Y}Z$ protons in (VIIa) and (VIIb) with the OCH_2 protons in (VIIIa) and (VIIIb); g.l.c. techniques were also used.

§ Preliminary experiments indicate that the ratio of (VIIa) to (VIIIa) is *not* due to thermodynamic equilibrium.

p-nitrophenol and DCC using the experimental conditions described in the Scheme. Work-up and analysis of the reaction mixture revealed the presence of (VIIb) and (VIIIb) in an approximate ratio of 9 : 1.‡

Based on the concept that ring-opening and ring-closing reactions of cyclic ethylenimonium and ethylene sulphonium ion intermediates are S_N2-like,[3] it is difficult to rationalize the predominance of (VIIa) and (VIIb). However, it has been proposed that intermediates (Va) and (Vb) are resonance hybrids[4] having considerable carbonium-ion like character due to forms (IVa) and (IVb). Accepting this and using an argument analogous to the one recently suggested by Winstein,[5] we propose that the resonance structure (IV) makes a substantial contribution to the transition stage for reactions of (V) and thus affects the ratio of C–$\ddot{Y}$Z cleavages.

We thank Mr. W. Fulmor for assistance with n.m.r. studies and Mr. C. Pidacks for developing useful gas–liquid and liquid–liquid partition column chromatographic techniques.

(*Received, February* 21*st*, 1968; *Com.* 210.)

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[1] For previous part in this series see F. L. Bach, *J. Org. Chem.*, 1965, **30**, 1300.

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[4] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 828.

[5] E. L. Allred and S. Winstein, *J. Amer. Chem. Soc.*, 1967, **89**, 3991.