and Mg and in triethylamine solution the composition can be represented by this single structure.

Similarly, the existence of RMgX in diethyl ether solution was established. When a diethyl ether solution of ethylmagnesium bromide, prepared from C_2H_5Br and Mg in diethyl ether, was added slowly to a large rapidly stirred volume of triethylamine, C_2H_5-$MgBr \cdot (C_2H_5)_3N$ was isolated in over 90% yield by fractional crystallization. The fact that no $MgBr_2 \cdot$ $(C_2H_5)_3N$ was isolated, although it is the most insoluble of the possible products, leads to the conclusion that the rate of solvation is greater than the rate of equilibration and therefore in diethyl ether solution ethyl magnesium bromide consists mainly, if not entirely, of RMgX species (as monomer or dimer).

Reaction of Ethyl Bromide and Magnesium in Triethylamine. To 16.0 g. (0.65 g.-atom) of triply sublimed magnesium metal was added 54.5 g. (0.50 mole) of ethyl bromide (distilled in a nitrogen atmosphere) dissolved in 400 ml. of triethylamine (freshly distilled over $NaAlH_4$ in a nitrogen atmosphere). The reaction was very exothermic; however, the temperature was not allowed to exceed 50°. The reaction produced a white solid suspended in a colorless liquid. The solid was filtered, dried under vacuum, and dissolved in 300 ml. of benzene (distilled over $NaAlH_4$ in a nitrogen atmosphere) in order to remove the unreacted magnesium. Fractional crystallization of the clear benzene solution was effected by slow removal of the benzene under vacuum. Four fractions were collected (fractions 1–4 in Table I), weighing 69.4 g. The triethylamine filtrate from the initial separation was fractionally crystallized into three fractions weighing 31.8 g. These fractions are labeled 5–7 in Table I. The deviation in analyses from one fraction to another is due to the extent of drying the fractions under vacuum. A better indication of fraction comparison can be obtained from consideration of the Mg:Br:N ratio.

Table I

Fractions	Sample wt., g.	Mg, %	Br, %	N, %	Mg:Br:N
1	15.0	11.2	36.6	6.55	1.00:0.99:1.02
2	10.1	11.5	39.2	6.71	1.00:1.04:1.01
3	32.4	13.4	41.8	7.47	1.00:0.93:0.95
4	11.7	12.3	37.9	7.10	1.00:0.94:1.00
5	9.1	10.6	34.8	5.87	1.00:1.00:0.94
6	12.0	10.8	35.1	6.12	1.00:0.99:0.98
7	10.7	12.2	38.2	6.98	1.00:0.95:0.99
Calcd. for $C_2H_5MgBr \cdot N(C_2H_5)_3$		10.4	34.1	5.97	1.00:1.00:1:00

Molecular Weight Measurements. The molecular weight of $C_2H_5MgBr \cdot N(C_2H_5)_3$ was determined ebullioscopically in triethylamine at 150 mm. The results are given in Table II.

Quenching of a Diethyl Ether Solution of Ethylmagnesium Bromide in Triethylamine. To 1 l. of freshly distilled triethylamine was added slowly at room temperature with rapid stirring 100 ml. of a 1.95 M solution of ethylmagnesium bromide in diethyl ether. The solvent was then removed under vacuum in order to remove all traces of diethyl ether, and the resulting

Table II

Concn., m	Δt, °C.	Solvent, g.	Solute, g.	Mol. wt.[a]
0.086	0.163	46.75	0.943	232
0.148	0.272	53.33	1.854	242
0.198	0.350	59.95	2.775	247

[a] Calculated value for $C_2H_5MgBr \cdot N(C_2H_5)_3$ as a monomer is 234.2.

solid was redissolved in triethylamine. Fractional crystallization produced three fractions with the analyses shown in Table III.

Table III

Fractions	Sample wt., g.	Mg, %	Br, %	N, %	Mg:Br:N
1	10.2	10.9	35.8	6.12	1.00:1.00:0.97
2	11.6	11.2	39.0	6.62	1.00:1.06:1.03
3	Residue 23.7	11.8	43.9	6.91	1.00:1.11:1.02

E. C. Ashby

Georgia Institute of Technology
Atlanta, Georgia 30332

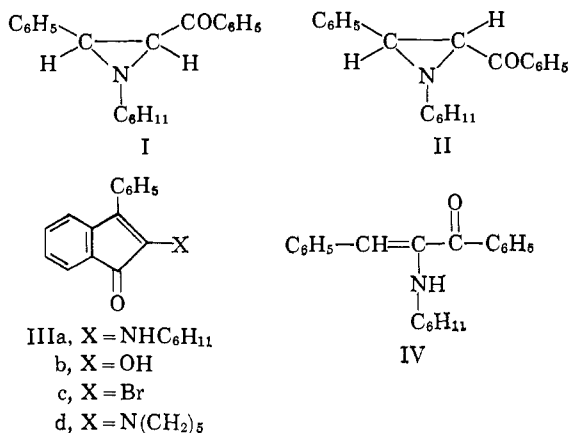# A Novel Rearrangement of Ethylenimine Ketones

Sir:

The epimerization of ethylenimine ketones under the influence of sodium alkoxides has been reported recently,[1,2] the *cis*-ethylenimine ketones (I) being formed in good yields from the *trans* isomer (II). In a further study of the effect of basic reagents on ethylenimine ketones, we have found that N-methylanilinolithium effects a novel rearrangement of *cis*-1-cyclohexyl-2-phenyl-3-benzoylethylenimine (I) to 2-cyclohexylamino-3-phenylindenone (IIIa). Thus treatment of 4 g. (0.0066 mole) of I in 20 ml. of anhydrous ether with 0.04 mole of N-methylanilinolithium in ether (prepared from N-methylaniline and butyllithium), followed by hydrolysis with methanol, leads to the formation of 0.78 g. (19.5%) of IIIa as a deep purple solid, m.p. 119–120°. *Anal.* Calcd. for $C_{21}H_{22}NO$: C, 82.86; H, 7.28; N, 4.60. Found: C, 83.09; H, 7.16; N, 4.62.

The structure of IIIa was established by consideration of its spectral data and hydrolysis to 3-phenylindandione (IIIb). The infrared spectrum of IIIa in CCl_4 shows characteristic NH absorption at 3370 cm.$^{-1}$ and a strong carbonyl band at 1720 cm.$^{-1}$. The mass spectrum yields a molecular weight of 303 for the parent ion and exhibits a cracking pattern fully consistent with structure IIIa. These data exclude structure IV, which has a molecular weight of 305 and would be expected to exhibit carbonyl absorption in the infrared below 1700 cm.$^{-1}$.[3]

(1) A. B. Turner, H. W. Heine, J. Irving, and J. B. Bush, Jr., *J. Am. Chem. Soc.*, **87**, 1050 (1965).
(2) R. C. Badger, Ph.D. Thesis, The University of Nebraska, Nov. 1963.

I   II

IIIa, X = NHC$_6$H$_{11}$
b, X = OH
c, X = Br
d, X = N(CH$_2$)$_5$

$C_6H_5-CH=C-\overset{\displaystyle O}{\overset{\|}{C}}-C_6H_5$
$\underset{\underset{C_6H_{11}}{|}}{\overset{|}{N}H}$

IV

The ultraviolet spectrum of IIIa exhibits maxima at 265 mμ (ϵ 57,600) and 525 (13,900); the latter undoubtedly is responsible for the dark purple color. We suggest that this latter maximum is associated with the considerable electron delocalization implied by forms such as V,[4] which involves electron mobility between the oxygen and nitrogen atoms implied by the arrow in V.

V   VI

VII
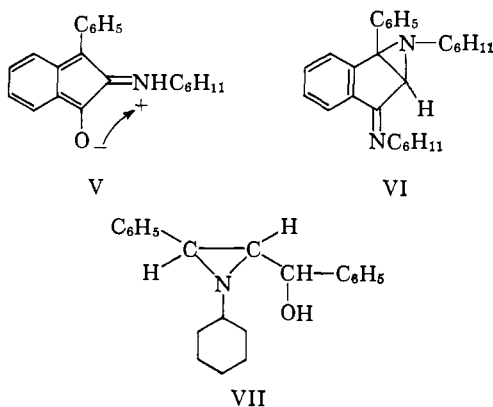
Treatment of IIIa with concentrated sulfuric acid at 0° and then addition of the brown solution thus formed to water at 70° resulted in hydrolysis of the cyclohexylamino group and precipitation of 3-phenylindandione (IIIb) in 84.5% yield, m.p. 145-147°, $\nu_{OH}^{CCl_4}$ 3500 cm.$^{-1}$, $\nu_{C=O}^{CCl_4}$ 1725 cm.$^{-1}$, $\lambda_{max}^{CH_3OH}$ 252 mμ (ϵ 32,000), and δ_{OH}^{DMSO} 10.6 p.p.m. The diketone was identical in all respects with an authentic sample prepared by the method of Koelsch.[5]

An independent synthesis of IIIa was undertaken involving the addition of cyclohexylamine to 2-bromo-3-phenylindenone (IIIc).[6] However, when 1 mole of IIIc was treated with 4 moles of cyclohexylamine in benzene, a white solid was obtained which we believe, on the basis of spectral and analytical data, to have structure VI (73%), m.p. 157.5-158.5°, $\nu_{C=N}$ 1658 cm.$^{-1}$, and $\lambda_{max}^{isooctane}$ 252 mμ (ϵ 17,950). Anal. Calcd. for C$_{27}$H$_{32}$N$_2$: C, 84.33; H, 8.39; N, 7.29. Found: C, 84.10; H, 8.46; N, 7.16. All attempts to partially hydrolyze VI to IIIa have been unsuccessful. However, hydrolysis in concentrated sulfuric acid, as in the case of IIIa, results in the formation of IIIb.

(3) N. H. Cromwell, et al., J. Am. Chem. Soc., 71, 3337 (1949).
(4) N. H. Cromwell and R. S. Johnson, ibid., 65, 316 (1943).
(5) C. F. Koelsch, ibid., 58, 1321 (1936).
(6) R. Weisz and S. Luft, Monatsh., 48, 338 (1927).

Secondary amines on the other hand readily form purple compounds analogous to IIIa. Thus treatment of 1 g. (0.0035 mole) of IIIc with 1.19 g. (0.014 mole) of piperidine in benzene at room temperature yields in 4 days 32.7% IIId, m.p. 77-79°. Anal. Calcd. for C$_{20}$H$_{19}$NO: C, 83.01; H, 6.62; N, 4.84. Found: C, 83.45; H, 6.74; N, 4.79. The infrared spectrum exhibits strong carbonyl absorption at 1710 cm.$^{-1}$. In the ultraviolet IIId absorbs strongly at 271 mμ (ϵ 31,000) and 521 (1700). These values are consistent with those found for IIIa and thus lend further support for the structure of IIIa. Hydrolysis of IIId in concentrated sulfuric acid again leads to IIIb identical in all respects with authentic material.

Surprisingly enough, trans-ethylenimine ketone II is unchanged by N-methylanilinolithium. Neither t-butylaminolithium nor cyclohexylaminolithium have any effect on I or II. Diisopropylaminolithium does effect the rearrangement of I to IIIa in low yield (<5%). This reagent with II effectively reduces the carbonyl group, yielding the corresponding carbinol VII (60.2%), m.p. 141-142°, identical in all respects with that obtained through lithium aluminum hydride reduction of II. Anal. Calcd. for C$_{21}$H$_{25}$NO: C, 82.04; H, 8.20; N, 4.56. Found: C, 82.41; H, 8.12; N, 4.70. The detailed mechanism by which I is transformed into IIIa is currently under investigation and will be discussed in a later communication.

A. E. Pohland, M. C. McMaster
R. C. Badger, N. H. Cromwell
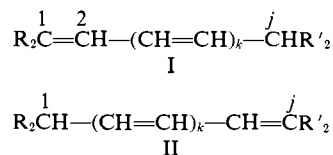Department of Chemistry, University of Nebraska
Lincoln, Nebraska
Received April 8, 1965

Selection Rules for Sigmatropic Reactions

Sir:

We define as a sigmatropic change of order [i,j] the migration of a σ-bond, flanked by one or more π-electron systems, to a new position whose termini are $i - 1$ and $j -$ atoms removed from the original bonded loci, in an uncatalyzed intramolecular process. Thus, the well-known Claisen and Cope rearrangements are sigmatropic changes of order [3,3]. It is our purpose here to point out that orbital symmetry relationships must play a determinative role in the course of sigmatropic transformations similar to that operative in electrocyclic reactions[1] and concerted cycloadditions.[2]

Consider first the [1,j] sigmatropic migration of hydrogen within an all-cis polyolefin framework (I → II). There are two conceivable ways in which

$$\overset{1}{\underset{}{R_2C}}=\overset{2}{\underset{}{CH}}-(CH=CH)_k-\overset{j}{\underset{}{CH}}R'_2$$

I

$$\overset{1}{\underset{}{R_2CH}}-(CH=CH)_k-CH=\overset{j}{\underset{}{C}}R'_2$$

II

(1) R. B. Woodward and R. Hoffmann, J. Am. Chem. Soc., 87, 395 (1965).
(2) R. Hoffmann and R. B. Woodward, ibid., 87, 2046 (1965).