The Isonitrile–Nitrile Rearrangement. A Reaction without a Structure–Reactivity Relationship

Michael Meier, Barbara Müller, and Christoph Rüchardt*

Institut für Organische Chemie und Biochemie der Universität Freiburg, D-7800 Freiburg, FRG

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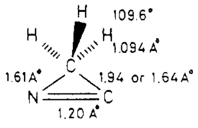
Reproducible rates of isomerization of aliphatic isonitriles to nitriles in solution can be measured by GLC or IR when free-radical inhibitors are added to suppress a competing radical chain reaction. The reactivities of 19 primary, secondary, tertiary, cyclic, bicyclic, bridgehead, benzyl, substituted-benzyl, α-carbomethoxymethyl, and triphenylmethyl isocyanides in this rearrangement reaction vary by only a factor of 67 in rate or by ±2 kcal mol^{-1} in $\Delta G^{\ddagger}$. This is explained by a tight hypervalent three-membered cyclic transition state in agreement with a previous prediction by ab initio calculation. The slower rate of 9-triptycyl isocyanide is proposed to be due to steric hindrance by the three peri hydrogens. Aromatic isocyanides isomerize about 10 times faster independent of polar para substituents and bulky ortho substituents. A hypervalent orthogonal transition state with retention of the aromatic sextet is proposed in contrast to the popular phenonium-type transition states for aryl migration in other 1,2-rearrangements. The reactivity data and the transition-state structures are discussed in context with other cationotropic 1,2-shifts.

The isonitrile–nitrile rearrangement (1)[1,2] discovered in 1873 by Weith[3] is formally a "cationotropic 1,2-shift".[4,5]

$$\underset{\textstyle 1}{\overset{+}{\mathrm{RN}}\equiv\overset{-}{\mathrm{C}}\mathrm{:}} \xrightarrow{\Delta} \mathrm{RC}\equiv\mathrm{N:} \qquad (1)$$

Owing to their noncatalytic nature, the isomerizations of methyl and a few other simple isocyanides proved to be excellent model reactions for testing kinetic theories of unimolecular gas-phase reactions,[1] thermal explosions,[6] and vibrational energy transfer.[7] RRKM theory was able to verify pressure and temperature effects on rates and lead to the proposal of structure 2 for the transition state by Rabinovitch.[1,2] To test and improve RRKM theory, theoretical studies of the transition-state structure in the methyl isocyanide rearrangement were undertaken by Hückel,[8] MNDO,[9] and ab initio calculations.[10,11] In the most recent ab initio self-consistent-field study[11b] of Schaefer et al., the transition state was precisely located by using gradient techniques. Although the resulting structure 4 is different from 2 suggested originally by Rabinovitch et al.,[1] the theoretical vibrational frequencies determined for 4 were in surprisingly good agreement with those deduced from experiment via the RRKM hypothesis. The comparison of transition-state structure 4 with structural data of methyl isocyanide 3[12] and acetonitrile 5[13] obtained by microwave spectroscopy allowed us interesting predictions for the structure–reactivity relationship of this rearrangement in general. During the reaction, neither the C≡N triple-bond length nor the H–C–H bond angle in the migrating methyl group is seriously changed. Only the N–C and C–C bonds are elongated in 4 in comparison to the starting material and product, 3 and 5, respectively. **Thus, neither steric nor electronic effects on rates of reaction 1 are predicted to be important, and therefore, no distinct structure–reactivity relationship is to be expected.** In addition, no appreciable separation of charge would be predicted in 4.[11]



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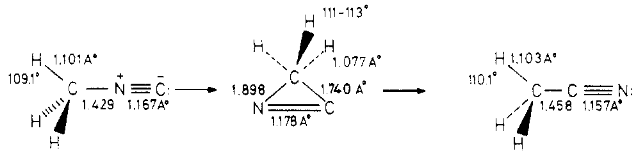

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Casanova et al.[14] found that cyclobutyl isocyanide isomerizes in the gas phase without skeletal rearrangement of the migrating group and that methyl, ethyl, isopropyl, and *tert*-butyl isocyanide isomerize with very similar rates and only slightly slower than phenyl, *p*-chlorophenyl, and *p*-methoxyphenyl isocyanides. They concluded that bond breaking and bond making are essentially synchronous and that little charge separation develops in the transition state. The observation of incomplete retention of the stereochemistry at the migrating group was supposed to be the result of base-catalyzed racemization[14,15] or of a homolytic dissociation recombination side reaction.[16]

The reactivity order found by Casanova et al.[14] is in sharp contrast with the order tertiary alkyl > secondary

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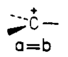
Table I. Kinetics of the Isonitrile–Nitrile Rearrangement[a]

R in RNC		yield,[b] %	s,/ n[c]	10^4k_1,[d] s^{-1}	$\Delta G^{\ddagger}$(250 °C), kcal mol^{-1}	$\Delta H^{\ddagger}$ ± SE, kcal mol^{-1}	$\Delta S^{\ddagger}$ ± SE, eu
1-C_8H_{17}	**8**	100	H, 5	2.95	36.4	38.4 ± 0.6	3.8 ± 1.3
$C_6H_5CH_2$	**9**	100	H, 5	4.16	36.3	35.4 ± 0.8	−1.7 ± 1.6
p-$O_2NC_6H_4CH_2$	**10**	96	M, 5	3.04	36.5	35.8 ± 0.3	−1.4 ± 0.6
p-$CH_3OC_6H_4CH_2$	**11**	101	H, 5	7.33	35.7	35.7 ± 0.1	0.1 ± 0.2
$C_6H_5C(CH_3)_2CH_2$	**12**	100	H, 5	0.86	37.8	36.1 ± 0.4	−3.3 ± 0.7
$H_3COOCCH_2$	**13**	101	M, 5	2.22	36.9	35.3 ± 0.9	−3.1 ± 1.9
$C_6H_{13}(CH_3)CH$	**14**	100	H, 5	0.97	37.6	37.2 ± 0.3	−0.8 ± 0.6
$C_6H_5(CH_3)CH$	**15**	101	H,[e] 6	1.25	37.4	37.2 ± 0.6	−0.3 ± 1.1
$[(CH_3)_2CH]_2CH$	**16**	96	H, 5	0.51	38.3	36.7 ± 0.9	−3.1 ± 1.9
cyclopropyl	**17**	98	H, 4	0.66	38.1	36.7 ± 0.4	−2.6 ± 0.7
$(H_3C)_3C$	**18**	78	Do, 6	0.16	39.1	(43.3 ± 0.4)	(8.1 ± 0.7)[36]
$C_5H_{11}(CH_3)_2C$	**19**	90	H, 5	0.18	39.2	38.7 ± 0.3	−1.0 ± 0.6
1-adamantyl	**20**	101	H, 5	0.22	39.0	39.4 ± 0.7	0.8 ± 1.5
1-bicyclo[2.2.2]octyl	**21**	100	H, 4	0.13	39.6	38.5 ± 0.4	−2.1 ± 0.8
1-bicyclo[2.2.1]heptyl	**22**	101	H, 5	0.27	38.8	39.4 ± 0.3	1.1 ± 0.6
3-homoadamantyl	**23**	98	H, 5	0.23	38.8	40.5 ± 0.4	3.2 ± 0.7
9-triptycyl	**24**	98	M, 5	0.001	44.1	43.0 ± 0.4	−2.1 ± 0.7
triphenylmethyl	**25**	100	H, 4	0.64	38.1	36.5 ± 1.0	−3.1 ± 2.1
exo-2MNB[f]	**26**	81[g]	H, 5	0.11	39.5	40.9 ± 0.2	2.7 ± 0.4
endo-2MNB[f]	**27**	95[g]	H, 5	0.12	39.8	38.2 ± 0.2	−3.0 ± 0.5
p-$CH_3C_6H_4$	**28**	100	H, 2[h]	10.3	35.3	35.9 ± 0.1	1.2 ± 0.3
2,4,6-$(CH_3)_3C_6H_2$	**29**	93	H, 5	15.3	35.0	35.0 ± 0.1	0.1 ± 0.3
o-(t-C_4H_9)C_6H_4	**30**	100	H, 5	2.59	36.6	36.3 ± 0.5	−0.6 ± 1.1

[a] Rates were followed by the ampule technique in degassed solutions with addition of ~1.5 mol equiv of 1,1-diphenylethylene or nicotinonitrile over a temperature range of 40–50 °C; C_0 = 0.08–0.14 mol/L; GLC or IR (for **17**, **19**, and **25**) was used for measuring concentration. [b] Under conditions of kinetics. [c] s = solvent (H, hexadecane; Do, dodecane; M, mesitylene); n = number of kinetic runs used for calculating the activation parameters. [d] At 210 °C. Extrapolated value if outside temperature range of measurements. [e] One run was performed in 1,2-dichlorobenzene. [f] *exo*-2MNB = 2-*exo*-2-methylbicyclo[2.2.1]heptyl isocyanide; *endo*-2MNB = 2-*endo*-2-methylbicyclo[2.2.1]heptyl isocyanide. [g] >96% stereospecific. [h] For calculating the activation parameters, five further rate constants from ref 37 were used.

alkyl > primary alkyl > methyl found for the Criegee,[17] Beckmann,[18] and Lossen rearrangements[19] but is more similar to the Curtius[20] and pinacol rearrangements[21] (see also ref 5b). A possible reason for this difference in behavior is a variation of the transition states for these rearrangements between structures like **6** and **7** in which the migrating carbon is either carbenium-like (**6**) or hypervalent-carbonium-like (**7**).[5b,18a] The critical difference between transition states **6** and **7** lies in the different geometry of the migrating carbon and in its capability or incapability of entering into conjugation with attached groups.



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Another exceptional feature of the isonitrile–nitrile rearrangement is the independence of heat of reaction of the structure of the group R in 1. We have shown for a variety of alkyl, aryl, and even bridgehead isonitriles that the heat of isomerization is ΔH(isom) ~ 21 ± 2 kcal mol^{-1} in all cases.[22]

These unusual kinetic[14] and thermochemical results,[22] as well as the predictions from ab initio calculations mentioned before, suggested that a more detailed kinetic investigation of the structure–reactivity relationships of this interesting isomerization reaction would be rewarding. Our early attempts[23] to follow the rates in **solution** by using the ampule technique were frustrated by poor reproducibility, unexpected negative activation entropies, and complex product mixtures, including reduction products RH.[24] When we recognized that the free-radical chain (2 and 3) was responsible for these disturbing phenomena,

$$RNC + R^{\bullet} \rightarrow RN{=}\dot{C}R \qquad (2)$$

$$RN{=}\dot{C}R \rightarrow R^{\bullet} + NCR \qquad (3)$$

the problem could be solved by the addition of alkyl radical traps like 1,1-diphenylethylene or 3-cyanopyridine as proper inhibitors or by extremely careful degassing,[25] as an autoxidation step is apparently responsible for chain initiation. Almost quantitative yields of nitriles and reproducible rates were obtained under these conditions.[25–28] The fast isomerization of trityl isocyanide at 25 °C in **polar solvents** like acetonitrile was attributed to ionization and internal return,[29] but later an ionic chain reaction (4) was favored.[30,31]

$$(C_6H_5)_3C^+ + \overset{-}{C}{\equiv}\overset{+}{N}C(C_6H_5)_3 \rightarrow (C_6H_5)_3CCN + {}^+C(C_6H_5)_3 \qquad (4)$$

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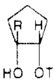
Table II. Structure–Reactivity Relationships for Cationotropic 1,2-Shifts[4]

reaction	k_{rel}				
	tert-butyl/ethyl	*tert*-butyl/1-norbornyl	benzyl/ethyl	phenyl/ethyl	$\rho(\sigma^+)$[h]
Criegee rearrangement[17] of $(CH_3)_2CROO$-pNb[a]	5000	555	36	2450[b]	−2.1
Beckmann rearrangement[18a] of $CH_3CR{=}NO$-picr[c]	150	11	6	685	−2.2
Lossen rearrangement[5] of $O{=}CRNHO$-BZ[d]	12			12	
pinacol rearrangement[21,e] of 	0.3			9	
Curtius rearrangement[20] of $O{=}CRN_3$[f]	0.3	0.7	2.6	0.04	0
isonitrile rearrangement of RNC[g]	0.06	0.7	1.4	3.5	0

[a] pNb = *p*-nitrobenzoate; 250 °C, CH_3OH. [b] This high value is partly due to the lack of ground-state conjugation of phenyl in this reaction in contrast to the other reactions. [c] picr = 2,4,6-trinitrophenyl. [d] BZ = benzoyl. [e] 100 °C, 0.035 sodium acetate in acetic acid. [f] 60 °C, nitrobenzene. [g] The rates of 1-octyl isocyanide and *tert*-octyl isocyanide have been used for this comparison instead of *tert*-butyl and ethyl isocyanide;[14] phenyl has been replaced by *p*-tolyl. [h] For R = S-$C_6H_4CH_2$.

Kinetics

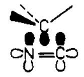
Results. For the kinetic measurements, ≈0.1 M solutions of isocyanides[32] in thoroughly degassed (three melt and freeze periods) sealed ampules were prepared. To suppress the free-radical chain (2 and 3), ≈1.5 mol equiv of 1,1-diphenylethylene or 3-cyanopyridine was added. The decreasing isocyanide concentrations were followed either by GLC[33a] or by IR.[33b] Quantitative product analyses were performed by GLC with the aid of authentic samples of nitriles and using internal standards.[34] A nonlinear-least-squares program was used[35] for calculating the rate constants and the activation parameters. The results are recorded in Table I. The high yields of nitriles, the clean first-order kinetics, and the activation entropies $\Delta S^{\ddagger}$ all ca. 0 eu are are good evidence for a uniform mechanism of the rearrangements of isocyanides **8–17** and **19–30**.

Discussion. The remarkable feature of the results given in Table I for the aliphatic series is the small change in rate (a factor of ≤67 in *k*) and the constancy of $\Delta G^{\ddagger}$(250 °C) at 38 ± 2 kcal mol^{-1} despite the great variation in structure from **8** to **27** (with the exception of **24**; see below). Primary octyl isocyanide (**8**) isomerizes just three times faster than the secondary (**14**) and only sixteen times faster than the tertiary isomer (**19**). The rates of isomerization of sterically crowded isocyanides **12** and **16** are reduced only by a factor of less than three when compared with those of the corresponding unstrained models **8** and **14**, respectively. The ring strain of the tertiary bicyclic isocyanides **26** and **27** or of cyclopropyl isocyanide **17** leads only to a reduction in rate less than twofold. Most remarkable is the almost complete lack of a bridgehead effect on the rates. 3-Homoadamantyl (**23**), 1-adamantyl (**20**), 1-bicyclo[2.2.2]octyl (**21**), and 1-bicyclo[2.2.1]heptyl isocyanide (**22**) react with a rate almost identical with that of tertiary octyl isocyanide (**19**). **This essential independence of rate on large variation in structure must mean that bond angles and steric constraints[38] do not change on the way from ground state to transition state.**

Similarly, the lack of a rate enhancement by conjugating α-substituents like phenyl (**9**, **15**, **25**) or carbomethoxy (**13**) is evidence that the α-carbon does not obtain carbenium-like unsaturated character at the transition state as would be expected if the transition-state structure corresponded to **6** ($\mathrm{a{=}b} \mathrel{\hat{=}} \mathrm{C{\equiv}N^-}$). The transition state, more likely, is hypervalent as required by the tight three-center structure **7** ($\mathrm{a{-}b} \mathrel{\hat{=}} \mathrm{C{=}N^-}$).

In most reactions, triphenylmethyl derivatives react faster by many powers of ten over their trypticyl counterparts. The most exceptional single comparison in Table I is therefore the small rate factor of 640 and the corresponding small difference in activation enthalpy $\Delta\Delta G^{\ddagger}$ = 6 kcal mol^{-1} for the isomerization of triphenylmethyl isocyanide (**25**) and 9-triptycyl isocyanide (**24**). The largest part of this difference, apparently, is not caused by phenyl conjugation in the transition state of **25** or by a typical bridgehead effect (cf. **22**). Probably the three peri hydrogens in **24** are aligned in such a way that the three-membered cyclic transition state cannot be reached from the linear arrangement in the isocyanide without steric hindrance.

As we can find no marked structure–reactivity relationship, the isonitrile–nitrile rearrangement (1) can now be considered properly prototypical for a sigmatropic 1,2-rearrangement via a nonpolarized, tight, hypervalent three-centered transition state (**31**). This is in excellent agreement with the predictions from ab initio calculation (cf. 4).[39]



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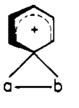
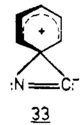
We can now look to the nature of the transition state in other types of 1,2-cationotropic rearrangements. Many structure–reactivity relationships have been obtained.[4,5] A comparison of the rate effects of α-branching, bridgehead structures, α-phenyl substitution, and polar substituents in migrating benzyl groups on the rates of alkyl migration can provide insight into the gradation of transition-state structures. Some relevant data from the literature are collected in Table II. In the reactions chosen for this comparison in Table II, the migration of the alkyl groups is always part of the rate-determining step. If we consider again the extremes for the transition state, i.e., a carbenium-like structure **6** and a hypervalent or carbonium-like structure **7**, one comes to the conclusion that for the four rate ratios in Table II one expects a larger variation in rate the more the transition state resembles structure **6**.[40] The decrease of rate ratios in Table II in the order Criegee > Beckmann > Lossen > Pinacol > Curtius > isonitrile rearrangement gives a consistent picture of increasing tightness of the transition-state structure in this direction. For the Curtius and isonitrile rearrangement, **7** has the advantage over **6** of keeping charge separation small. The higher carbenium character in the Criegee rearrangement is probably a reflection of the high π-bond energy of the carbonyl group.

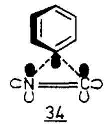
An additional point of interest in Table II is the large ratio of k_{rel} for phenyl/ethyl for the Criegee[17] and Beckmann rearrangements for which neighboring-group participation and the phenonium structure **32** of the transition state have been convincingly proposed.[41] However, in the isonitrile rearrangement, phenyl migrates only 3.5 times faster than 1-octyl. Para substitution[14] as well as ortho substitution (cf. **29** and **30** in Table I) lead to only small rate changes. A phenonium-like transition state like **32**, i.e., **33**, is clearly excluded by the lack of phenyl or phenyl-substituent effects[14] (see Table II). Of the remaining possibilities, the orthogonal arrangement **34** of the aromatic ring and the C═N group is favored over the planar arrangement **35**, which would be slightly destabilized by ortho substitution. Transition-state structure **34** for the isonitrile rearrangement with a three-center bond and a hypervalent sp^2-hybridized carbon has the advantage over **32** of requiring no charge separation and retaining the aromatic sextet. The slightly larger migration aptitude of phenyl over 1-octyl (see Table I) may be due to the better overlap of the sp^2 vs. the sp^3 orbital of the migrating carbon in **34** and **31**, respectively. This ratio would probably be even larger than 3.5 were the conjugation between the phenyl ring and the isonitrile group in phenyl isonitrile[22] not lost in the activation process.[1,37]

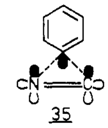


32



33


34


35

For the ^{15}N-inversion during solvolysis reactions of α-^{15}N-labeled diazonium ions,[42] a hetero analogue of the isonitrile rearrangement, a phenyl cation–nitrogen ion–molecule pair intermediate has been proposed recently. Its structure is more related to **34** than to **33**, but the three-center-bonding component is weaker. This is probably due to the high heat of formation of the N_2 molecule.

Experimental Section

The isocyanides **8**,[43] **9–12**,[44] **14**,[45] **15**,[15b] **17**,[46] **18**,[14,24] **20**,[24] **25**,[29,47] **26**,[18a] **27**,[18a] **28**,[37] and **29**[22] have been reported previously in the literature; **13** was commercially available and purified by distillation.

Most of the nitrile samples used for identification of the reaction products were known compounds and either prepared by literature procedures or commercial samples. Two nitriles were isolated from preparative experiments and identified by spectral means.

2,4-Dimethyl-3-isocyanopentane (16) was prepared from *N*-formyl-3-amino-2,4-dimethylpentane[48] with $POCl_3$–pyridine[32a] (87%): bp 110 °C (100 mm); IR (film) 2145 cm^{-1}; MS, 110.09726 (calcd for $C_7H_{12}N$, 110.09697; $M^+ - CH_3$), 83.07355 (calcd for C_5H_8N, 83.07350; $M^+ - C_3H_7$); GLC (SE 30, 15%, 2m) >99% pure.

2-Isocyano-2-methylheptane (19). *N*-Formyl-2-amino-2-methylheptane was prepared from 2-methylheptan-2-ol by the Ritter reaction[49] (67%): bp 87–88 °C (0.2 mm). Anal. Calcd for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68.51; H, 12.32; N, 9.17. Isocyanide **19** was obtained with $POCl_3$–pyridine[32a] (76%): bp 79–80 °C (20 mm); IR (film) 2122 cm^{-1}. Anal. Calcd for $C_9H_{17}N$: C, 77.64; H, 12.31; N, 10.06. Found: C, 77.45; H, 12.07; N, 10,06; GLC (SE 30, 15%, 2m) >99% pure.

1-Bicyclo[2.2.2]octyl Isocyanide (21). *N*-Formyl-1-bicyclo[2.2.2]octylamine was prepared from 1-bicyclo[2.2.2]octylamine hydrochloride[50] and the mixed anhydride of formic and acetic acid[15b] (87%): mp 194 °C (from CH_2Cl_2–petrol ether). Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.55; H, 9.62; N, 9.10. Isocyanide **21** was obtained in the usual way[32a] (56%): mp 139 °C (petrol ether); IR (KBr) 2138 cm^{-1}. Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 80.08; H, 9.81; N, 10.28; GLC (SE 30, 15%, 2m) >99% pure.

1-Bicyclo[2.2.1]heptyl Isocyanide (22) was prepared by treating *N*-formyl-1-bicyclo[2.2.1]heptylamine[23,50] with $POCl_3$–pyridine[32a] (73%): bp 80 °C (16 mm); mp 62 °C; IR (KBr) 2120 cm^{-1}. Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.04; H, 9.13; N, 11.37; GLC (SE 30, 15%, 2m) >99% pure.

3-Homoadamantyl Isocyanide (23). *N*-Formyl-3-homoadamantylamine was prepared from 3-homoadamantylamine[50] by the usual procedure[15a] (56%): mp 101–103 °C (ether–petrol ether). Anal. Calcd for $C_{12}H_{19}NO$: C, 74.57; H, 9.91; N, 7.25. Found: C, 74.17; H, 9.81; N, 7.17. Isocyanide **23** was obtained from it with $POCl_3$–pyridine[32a] (67%): mp 173 °C (CH_2Cl_2–petrol ether); IR (KBr) 2120 cm^{-1}. Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 81.99; H, 9.44; N, 7.48; GLC (SE 30, 15%, 2m) >99% pure.

9-Triptycyl Isocyanide (24). *N*-Formyl-9-triptycylamine was prepared from 9-triptycylamine[51] by the usual procedure[15b] (78%): mp 320 °C (sublimes). Treatment with $POCl_3$ and pyridine in methylene chloride[32a] gave isonitrile **24** (77%): mp 281 °C dec; IR (KBr) 2140 cm^{-1}. Anal. Calcd for $C_{21}H_{13}N$: C, 90.30; H, 4.69; N, 5.01. Found: C, 90.14; H, 4.82; N, 4.96; GLC (SE 30, 15%, 0.5m) >99% pure.

***o*-*tert*-Butylphenyl Isocyanide (30).** 2-*tert*-Butylaniline[52] was heated in toluene with formic acid, and the water formed was removed in a Dean–Stark trap.[53] The *N*-formyl-2-*tert*-butylaniline obtained[54] was transformed to isocyanide **30** with $POCl_3$

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[40] This analysis seems to be safe because steric ground-state effects apparently are not present in the model systems used.

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in *tert*-butyl alcohol–potassium *tert*-butoxide[53] (31%): bp 63 °C (0.4 mm); IR (film) 2120 cm^{-1}. Anal. Calcd for $C_{11}H_{13}N$: C, 83.02; H, 8.18; N, 8.80. Found: C, 82.98; H, 8.30; N, 8.75.

Rate Measurements. Solutions (0.05–0.12 M) of the isonitriles, an *n*-alkane standard for GLC,[34] and a 1.6 molar excess of 1,1-diphenylethylene or 3-cyanopyridine were treated with ultrasound and nitrogen (99.99% pure) for removing oxygen. Samples of this solution (0.15 mL) were distributed over a series of 2-mL glass ampules[33a] and again degassed by repeated freezing in liquid nitrogen, evacuating, aerating with pure nitrogen, and thawing. Finally, the ampules were sealed under nitrogen and (10–15/experiment) thermostated at the indicated temperature (±0.2 °C).[33a] For analysis, the ampules were removed at definite times and chilled. The reactions were followed up at least to 80% completeness and analyzed either by GLC[55] or IR.[33b] The first-order rate constants were obtained by least-squares fitting of the concentration data.[35] Details and a listing of the rate constants are found in ref 55 and 56, and the activation parameters are recorded in Table I.

Product analysis was conducted by GLC (2 m, 15% silicone, SE 30) with *n*-alkanes as integration standards.[34] The products were identified by retention-time comparison with authentic samples or by GLC–MS.

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Electrochemical Reduction and Intramolecular Cyclization of 1-Iodo-5-decyne and 1-Bromo-5-decyne at Vitreous Carbon Cathodes in Dimethylformamide

Rui-lian Shao and Dennis G. Peters*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

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In dimethylformamide containing tetramethylammonium perchlorate, cyclic voltammograms for reduction of 1-iodo-5-decyne and 1-bromo-5-decyne at a vitreous carbon electrode each consist of a single irreversible wave due to two-electron scission of the carbon–halogen bond. Preparative-scale electrolyses of 1-iodo-5-decyne yield pentylidenecyclopentane, 5-decyne, 1-decen-5-yne, and a small amount of 5-decyn-1-ol, whereas reduction of 1-bromo-5-decyne affords mainly 5-decyne and 1-decen-5-yne along with a modest quantity of pentylidenecyclopentane. Differences in product distributions correlate with the extent to which the 5-decyn-1-yl radical persists as a transient species. Pentylidenecyclopentane arises via intramolecular cyclization of the 5-decyn-1-yl radical followed by hydrogen atom abstraction, 5-decyne is formed via protonation of the 5-decyn-1-yl carbanion by either water or the tetramethylammonium cation, and 1-decen-5-yne and 5-decyn-1-ol are obtained, respectively, via E2 and S_N2 reactions between unreduced starting material and hydroxide ion (generated by deprotonation of water). In the presence of a proton donor (diethyl malonate or hexafluoroisopropyl alcohol), the quantities of pentylidenecyclopentane and 5-decyne rise noticeably and the yield of 1-decen-5-yne falls dramatically.

In a previous paper[1] we described the electrochemical behavior of 1-iodo-5-decyne and 1-bromo-5-decyne at mercury cathodes in dimethylformamide containing tetraalkylammonium salts as supporting electrolytes. It was found that 1-iodo-5-decyne undergoes stepwise reduction (first to the 5-decyn-1-yl radical and then to the corresponding carbanion) and that the distribution of products depends on the potential of the cathode. At potentials that give rise to the 5-decyn-1-yl radical, the principal product is di-5-decynylmercury (>85%), and only a small quantity of pentylidenecyclopentane (<5%) is obtained. At potentials for which the carbanion intermediate is predominant, the major species formed are 5-decyne (>40%) and 1-decen-5-yne (>20%), whereas the yields of di-5-decynylmercury (<15%) and pentylidenecyclopentane (<1%) decrease as the potential is made more negative.

In studying the electrochemistry of 1-bromo-5-decyne, we discovered that this compound exhibits just a *single* polarographic wave corresponding to generation of the 5-decyn-1-yl anion. However, the product distribution reflects the existence of *two* regimes of behavior. At potentials on the *rising part* of the polarographic wave, the major products are di-5-decynylmercury (>65%) and 5-decyne (>17%); but the lack of any change in yields when a proton donor is added to the system indicates that these two compounds are derived from a transient *radical* intermediate. On the other hand, when 1-bromo-5-decyne is electrolyzed at potentials on the *plateau* of the polarographic wave, the main products are 5-decyne (>47%) and 1-decen-5-yne (>23%); if a proton donor (diethyl malonate) is introduced, the amount of 5-decyne rises (>80%) and the quantity of 1-decen-5-yne falls (<1%)—results which clearly implicate a *carbanion* intermediate.

In the present research, we have examined the electrochemical reduction of 1-iodo-5-decyne and 1-bromo-5-decyne at vitreous carbon electrodes in dimethylformamide containing tetramethylammonium perchlorate. We have sought to complement our recent work[2] on the reduction of alkyl halides in such systems and, in particular, to probe

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