occurs in other systems and with other hydrogen donors as well.

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Reactions of Aromatic Radical Anions. I. Coupling of Alkyl Free Radicals Generated by Electron Transfer to Alkyl Iodides[1]

Sir:

The reaction of sodium naphthalenide (I)[2] with alkyl iodides in 1,2-dimethoxyethane (DME) solution occurs predominantly by initial electron transfer to yield alkyl free radicals. By this process, radicals can be generated in sufficiently high concentration that radical combination competes favorably with either hydrogen abstraction from solvent or further reduction to primary carbanion.

A DME solution approximately 1 *M*[3] in I was injected rapidly into a DME solution approximately 1 *M* in alkyl iodide protected from atmospheric oxygen and moisture by means of a rubber serum cap. The reaction is macroscopically instantaneous and exothermic. Complete reaction of the alkyl iodide was ensured by continuing the injection of radical-anion solution until its dark green color persisted in the reaction vessel. The products of the reaction (1) were analyzed by vapor phase chromatography without further work-up. Quantitative results were obtained by including an inert internal standard of known concentration in the alkyl iodide solution. Reactions were carried out at both ambient temperature and with the vessel containing the alkyl iodide solution immersed in a Dry Ice–acetone bath. No significant temperature effects were discerned. The yields of aliphatic hydrocarbons from *n*-amyl iodide and *n*-heptyl iodide are presented in Table I.

Table I. Per Cent Yield of Aliphatic Hydrocarbons from the Reaction of $Na^+C_{10}H_8^-$ with RCH_2CH_2I[a]

R	$R(CH_2)_4R$	RCH_2CH_3	$RCH{=}CH_2$
$CH_3(CH_2)_4-$	50	22	6
$CH_3(CH_2)_2-$	55	17	4

[a] Values reported are the average of several independent determinations. Yields in general are reproducible to ±10% of the value reported.

$$RCH_2CH_2I + Na^+C_{10}H_8\cdot^- \xrightarrow{DME} R(CH_2)_4R + RCH_2CH_3 + RCH{=}CH_2 \quad (1)$$

Either of two mechanisms, or a combination of both, can be postulated to explain these results.

$$RCH_2CH_2I + C_{10}H_8\cdot^- \longrightarrow RCH_2CH_2\cdot + C_{10}H_8 + I^- \quad (2)$$

Radical mechanism

$$2RCH_2CH_2\cdot \begin{cases} \xrightarrow{\text{combination}} R(CH_2)_4R & (3) \\ \xrightarrow{\text{disproportionation}} RCH_2CH_3 + RCH{=}CH_2 & (4) \end{cases}$$

$$RCH_2CH_2\cdot + CH_3OCH_2CH_2OCH_3 \longrightarrow RCH_2CH_3 + CH_3O\underset{\cdot}{C}HCH_2OCH_3 \quad (5)$$

Carbanion mechanism

$$RCH_2CH_2\cdot + C_{10}H_8\cdot^- \longrightarrow RCH_2CH_2^- + C_{10}H_8 \quad (6)$$

$$RCH_2CH_2^- + RCH_2CH_2I \begin{cases} \xrightarrow{\text{displacement}} R(CH_2)_4R + I^- & (7) \\ \xrightarrow{\text{elimination}} RCH_2CH_3 + RCH{=}CH_2 + I^- & (8) \end{cases}$$

$$RCH_2CH_2^- + CH_3OCH_2CH_2OCH_3 \longrightarrow RCH_2CH_3 + CH_3OCH{=}CH_2 + CH_3O^- \quad (9)$$

The alkene does not arise from a bimolecular elimination reaction of the alkyl iodide with I acting as a base, since the expected product of this reaction,[2] 1,4-dihydronaphthalene, is not formed in the reaction.

The final step (5, 9) in each mechanism is required to account for the fact that alkane is formed in excess of alkene. We have detected the presence of methyl vinyl ether in the product mixture, but this in no way serves to distinguish between the two mechanisms, since the fate of the radicals derived from solvent produced by the radical mechanism might well be further reduction (10) followed by fragmentation (11).

$$C_{10}H_8\cdot^- + CH_3O\underset{\cdot}{C}HCH_2OCH_3 \longrightarrow C_{10}H_8 + CH_3O\underset{-}{C}HCH_2OCH_3 \quad (10)$$

$$CH_3O\underset{-}{C}HCH_2OCH_3 \longrightarrow CH_3OCH{=}CH_2 + CH_3O^- \quad (11)$$

We have sought to differentiate between the radical and carbanion mechanisms by investigating the yield of coupled products in the reaction of I with an equimolar mixture of *n*-propyl iodide and isopropyl iodide. Potentially, three isomeric hexanes can be formed in this reaction.

$$CH_3CH_2CH_2I + CH_3CHICH_3 + C_{10}H_8\cdot^- \longrightarrow \underset{\text{II}}{CH_3(CH_2)_4CH_3} + \underset{\text{III}}{CH_3(CH_2)_2CH(CH_3)_2} + \underset{\text{IV}}{(CH_3)_2CHCH(CH_3)_2} \quad (12)$$

If coupling occurs by combination (3), the three hexanes should be formed in a statistical ratio, $[\text{III}] = 2([\text{II}][\text{IV}])^{1/2}$, which reflects only the concentration of the two isomeric propyl radicals.[4,5] This prediction, which has received extensive experimental verification, derives from the fact that radical coupling requires essentially no activation energy.[4] If coupling occurs by displacement (7), no such statistical product distribution would be expected. In a wide variety of nucleophilic displacement reactions which vary in absolute

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[1] Presented in part at the 11th Conference on Reaction Mechanisms, McMaster University, Hamilton, Ontario, June 22–25, 1966, and at the 1st Middle Atlantic Regional Meeting, American Chemical Society, Philadelphia, Pa., Feb 3–4, 1966, Abstracts, p 120.

[2] N. D. Scott, J. F. Walker, and V. L. Hansely, *J. Am. Chem. Soc.*, **58**, 2442 (1936).

[3] Solutions of I were prepared by adding 1 equiv of sodium to a DME solution 1 *M* in naphthalene. The virtually equal yield of naphthalene and dihydronaphthalene formed on quenching aliquots of these solutions in water indicated that essentially complete conversion of naphthalene to I had occurred.

[4] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 108 (1961); A. F. Trotman-Dickenson, *Ann. Rept. Chem. Soc.*, **55**, 41 (1958).

[5] The tacit but necessary assumption that both radicals are produced at the same rate is supported by data which suggest that the rate of reaction of both halides with I should be diffusion controlled [D. J. Morantz and E. Warhurst, *Trans. Faraday Soc.*, **51**, 1375 (1955)].

rate constant over several powers of ten, the rate for displacement on propyl in all cases exceeds that on isopropyl by at least a factor of ten.[6] In addition, for nucleophiles of high basicity, the competing E2 elimination reaction intrudes much more severely in attack on isopropyl than on propyl halides.[7] Both considerations lead to the conclusion that a carbanionic mechanism would discriminate against the formation of 2,3-dimethylbutane (IV), which could be formed only by displacement on isopropyl iodide.

Table II. Relative Yields of Isomeric Hexanes from Reaction of $Na^+C_{10}H_8\cdot^-$ with an Equimolar Mixture of 1- and 2-Iodopropanes

Temp	IV, %	III, %	II, %	[III]/([II] × [IV])$^{1/2}$
Ambient	25.4 ± 1.5	49.8 ± 0.6	26.8 ± 2.0	1.98
Ambient[a]	23.3	52.2	24.5	2.18
−78°	23.2 ± 0.3	51.8 ± 0.9	25.0 ± 0.6	2.15
(Average)	24.1	51.1	24.8	2.09

[a] Sufficient I added to react with only *ca.* one-half alkyl iodide present. Duplicate experiment was not carried out.

The relative yields of the isomeric hexanes formed in the reaction of I with an equimolar mixture of *n*-propyl iodide and isopropyl iodide are presented in Table II. Three striking features of these data are worthy of note: (1) the statistical product distribution, (2) the absence of any discrimination in the formation of 2,3-dimethylbutane, and (3) the fact that all three hexanes are formed with equal activation energy, as indicated by the insensitivity of the product distribution to a change in temperature of 100°. On all counts we are forced to the conclusion that the reaction of I with alkyl iodides results in the formation of alkyl free radicals which possess sufficient lifetime to combine by a free-radical process.

Table III. Per Cent Yield[a] of Aliphatic Hydrocarbons from Reaction of $Na^+C_{10}H_8\cdot^-$ with $CH_3(CH_2)_4X$

Products	Cl	Br	I
n-Pentene	43.9	29.2	17.3
1-Pentene	0[b]	0[b]	3.7
n-Decane	0	5.0	55.7
Total	43.9	34.2	76.7
$\pi^{1/2}$ (CH_3CH_2X)[c]	−2.7 v	−2.08 v	−1.67 v
$\Delta\pi^{1/2}$ [d]	−0.2 v	+0.42 v	+0.83 v

[a] In general the yield is reproducible to ±10% of the value reported. [b] A minute, unresolved shoulder on the trailing edge of the pentane peak in the vapor phase chromatogram admits the possibility of the presence of trace amounts of 1-pentene. [c] Polarographic half-wave potential [M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949)]. Data for the *n*-amyl halides are unavailable. [d] For definition, see text.

This conclusion is supported further by the pronounced influence of the halide in determining the product distribution in the reaction of I with a series of *n*-amyl halides (Table III). The decane:pentane product ratio decreases dramatically in the order iodide > bromide > chloride, a trend readily explicable in terms of the radical coupling mechanism. The reaction which gives rise to the excess of pentane over pentene, whether abstraction of hydrogen atoms from solvent (5) or further reduction to the anion (6) followed by proton abstraction (9),[8] is most certainly only first order in radical concentration. Thus pentane is formed at a rate less sensitive to the concentration of alky radicals than that for decane formation, a process second order in radical concentration. The concentration of alkyl radicals is a function of their rate of formation, which in turn is a function of the activation energy for electron transfer from radical anion to alkyl halide. At least qualitatively, it would seem reasonable to expect this activation energy to parallel the difference in reduction potential between electron acceptor (alkyl halide) and reducing agent (radical anion). These differences[9] ($\Delta\pi^{1/2}$) decrease in an order which directly corresponds to the decane:pentane product ratio (Table I).

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(6) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Company, Inc., New York, N. Y., 1962, pp 11–13; *Chem. Rev.*, **56**, 571 (1956).

(7) See, for example, M. L. Dahr, E. D. Hughes, C. K. Ingold, and S. Masterman, *J. Chem. Soc.*, 2055 (1948).

(8) This latter alternative is suggested by two recent investigations closely related to the work reported here: (a) J. F. Garst, W. Ayers, and R. C. Lamb, *J. Am. Chem. Soc.*, **88**, 4260 (1966); (b) S. J. Cristol and R. V. Barbour, *ibid.*, 4261 (1966).

(9) The polarographic half-wave potential for naphthalene reduction is −2.50 v [H. A. Latinen and S. Wawzonek, *J. Am. Chem. Soc.*, **64**, 1765 (1942)].

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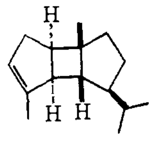
The Total Synthesis of the (±)-Bourbonenes

Sir:

The sesquiterpenoid hydrocarbons α- and β-bourbonene, isolated from *Geranium bourbon* oil, have been shown to possess the stereostructures **1** and **2**, respectively.[1,2] We wish to report a total synthesis of the bourbonenes which supports these structural assignments.



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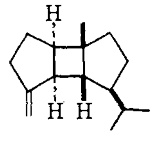

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2-Isopropylcyclopentanone, prepared by treatment of the cyclohexylimine of cyclopentanone with

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(1) J. Křepinský, Z. Samek, and F. Šorm, *Tetrahedron Letters*, 3209 (1966).

(2) J. Křepinský, Z. Samek, F. Šorm, and D. Lamparsky, *ibid.*, 359 (1966).