

Anodic Fragmentation of Branched Alkanes

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Summary Branched alkanes produce acetamidated fragments when oxidized in $\text{CH}_3\text{CN}-\text{Et}_4\text{N}^+\text{BF}_4^-$ at -45° .

REACTIONS which cleave the carbon-carbon bonds of alkanes are both unusual and interesting; we report the anodic fragmentation of branched alkanes. This process involves direct oxidation of the hydrocarbon at a platinum anode in acetonitrile. Products isolated after work-up are acetamidated fragments.

The procedure is described for the conversion of 2,3-dimethylbutane to 2-propylacetamide. A three compartment cell¹ was used containing acetonitrile-tetraethyl-

ammonium fluoroborate as anolyte and catholyte. The reference electrode was a silver wire immersed in 0.1 M AgNO_3 -acetonitrile, and the anode was platinum gauze. The cell was maintained at -45° and at a controlled anode potential of 3.6 V the background current was 20 mA. Addition of 2.7 mmol of 2,3-dimethylbutane gave an initial current of 100 mA and electrolysis was continued until the current fell to 45 mA. The potential was pulsed to *ca.* zero for 1 s every 10 s. The reaction required 2.5 h and utilized 4.7 mF. The product was isolated by concentrating the anolyte, adding water and continuously extracting it with chloroform. 2-Propylacetamide (1 mmol)

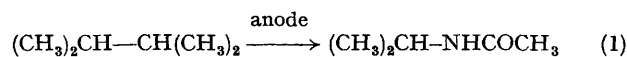
TABLE. Oxidation Products^a and Peak Potentials^b

Reactant (mmol)	E_p /(V)	Coulometry/ (mF)	Products ^c
2,3-dimethylbutane (2.7)	3.80	4.7	2-propylacetamide
2,2,4-trimethylpentane (1.8)	3.05, 3.40	4.7	t-butylacetamide, 2-propylacetamide, 2-butylacetamide
2,2-dimethylbutane (4)	3.90	4.5	t-butylacetamide
2,3,4-trimethylpentane (3)	3.35, 3.80	6.8	2-propylacetamide, t-pentyl acetamide, iso- pentyl acetamide
t-butylcyclohexane (2) ^d	3.00	4.6	t-butylacetamide, cyclohexylacetamide
n-octane (3)	3.50	5.0	2-octylacetamide, 3-octylacetamide, 4-octyl- acetamide

^a All oxidations in $\text{CH}_3\text{CN}-(\text{C}_2\text{H}_5)_4\text{N}^+\text{BF}_4^-$ at Pt at -45° . The oxidation potential was 3.6 V vs. Ag/AgNO₃ except where noted.

^b Peak potentials from cyclic voltammetry on Pt at 0.5 V/s sweep rate. All oxidations were irreversible up to 100 V/s. ^c Major products identified by n.m.r. and g.l.c. comparison with authentic samples. ^d Oxidized at 3.0 V.

was identified by n.m.r. and g.l.c. It was contaminated with acetamide.



The Table shows that fragmentation of branched alkanes is the rule under these conditions. This is in contrast to the anodic substitution reactions observed by Clark, Fleischmann, and Pletcher² for n-alkanes at room temperature.

The product yields were quantified in several cases, but attempts to improve the yield have not been pursued. t-Butyl cyclohexane gave the highest yield providing 63% t-butyl acetamide and 47% cyclohexylacetamide based on the initial amount of hydrocarbon. These results demonstrate that in general tertiary and secondary fragments will be preferred over primary. Indeed, n-alkanes do not cleave even under the low temperature conditions employed here. Low temperatures are, however, necessary to cleave branched alkanes since it is found that oxidations of branched alkanes at room temperature gave poor yields (<5%) of substitution products and no fragmentation. Systems which will allow the oxidations to be performed at temperatures below -45° are under study.

The mechanism supported for n-alkanes³ and adaman-

tan³ involves direct electron transfer from hydrocarbon to the electrode. Branched alkanes oxidize at somewhat lower potentials than n-alkanes. It therefore seems likely that direct oxidation of substrate, not a process involving electrolyte oxidation⁴ is involved. The case of t-butylcyclohexane is particularly clear on this point since the oxidation can be performed at potentials well below background and good yields of both fragments result. Our working hypothesis is that initial electron transfer is followed by fragmentation and further oxidation resulting in carbonium ions. There is clear precedent for carbonium ions as precursors of acetamides in acetonitrile³ and the products from 2,2,4-trimethylpentane and 2,3,4-trimethylpentane point to carbonium ion rearrangements.

Within this scheme one might postulate that low temperatures favour processes with positive ΔS^\ddagger such as unimolecular decomposition of an initially formed cation radical. This overall scheme rationalizes all the data including the selectivity toward formation of highly substituted fragments, but more evidence is clearly needed to understand the reaction. The analogy with mass spectroscopy should, however, be noted.

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² D. Clark, M. Fleischmann, and D. Pletcher, *J.C.S. Perkin II*, 1973, 1578.

³ V. R. Koch and L. L. Miller, *J. Amer. Chem. Soc.*, in the press.

⁴ L. L. Miller and V. Ramachandran, *J. Org. Chem.*, in the press.