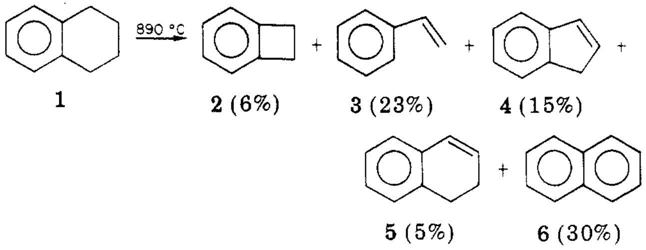
Communications

Flash Vacuum Pyrolysis of 2,3-Dialkyltetralins

Summary: The cleavage of alkyl groups from the 2- and 3-positions of tetralins is a facile process and the retro-Diels–Alder reaction of tetralins appears to be concerted.

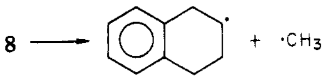
Sir: Recently there has been considerable interest in the thermal chemistry of tetralin (1)[1] because of its use as a hydrogen-donor solvent in coal liquefaction processes[2] and as the simpliest hydroaromatic compound 1 models one of the important structural features of coal.[3] Under our standard flash vacuum pyrolysis (FVP) conditions (700–900 °C, 0.1 torr),[4] the major products from 1 are 2–6.[5]



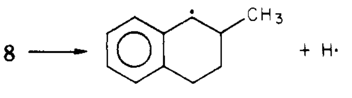
Products 2 and 4 are of particular interest. Compound 2 arises from *o*-quinodimethane which is the product of a retro-Diels–Alder reaction. At high temperatures 2 reacts further to form 3. Formation of 4 involves the formal loss of a CH_4 unit but the mechanism of this transformation is uncertain.

It was decided to examine the pyrolysis of a series of 2,3-dialkyltetralins to determine whether this substitution would enhance the retro-Diels–Alder reaction. Additionally, the effect of the substituents could possibly provide information about the formation of 4. In Table I are summarized the results of a study of the alkyl-substituted tetralins 7–11.[6] Two important points are apparent from these data: (1) cleavage of 2- and 3-alkyl groups is facile and (2) the retro-Diels–Alder product, 2, is produced in moderate yield from 1 and 8–10, but in low yield from 11.

For tetralins 8–11 almost none of the corresponding substituted naphthalene or anthracene is formed and in all cases 6 is a major product. Although surface effects are always a possibility under standard FVP conditions, unimolecular, gas-phase fragmentations or isomerizations are often observed,[8] and for lack of evidence to the contrary, we assume that our reactions are not surface-catalyzed ones. For 8 loss of the methyl group could involve initial homolytic cleavage of the methyl group bond, reaction 1, or initial loss of a benzylic hydrogen atom, reaction 2, followed by β-cleavage of the methyl group.



(1)

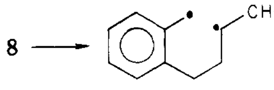


(2)

16

$$16 \longrightarrow 5 + \cdot CH_3$$

β-Cleavage of the related 2-methyl-1-indanyl radical occurs readily under FVP conditions.[1a] However, initial cleavage of the benzylic C–C bond, reaction 3, might be expected to be more favorable than either reaction 1 or 2, and the product of this cleavage, 17, would be expected to lose propene to give *o*-quinodimethane, the precursor of 2. The calculated[9] ΔH's, for reactions 1–3 at 300 K are 84, 79, and 66 kcal/mol, respectively, and the ΔS's at 300 K are 41, 24, and 15 cal/(mol deg), respectively. These values change very little up to 1100 K, and although they are for the overall reactions, they should reflect the same factors which affect the activation parameters of the reactions. Thus at higher temperatures, the loss of the methyl group from 8 could take place through a pathway initiated by reaction 1 or 2, and the favorable entropy change of these reactions, associated with losing a methyl group or hydrogen atom, provides an explanation for successful competition with reaction 3. The expected product from initial cleavage 1 or 2 is 5, which under our conditions is converted to 6 and 4 in an 8:1 ratio.[10]



(3)

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There is no evidence for concerted loss of the two methyl groups from 9. At a given temperature the percent conversion of 8 and 9 is almost equal and the yield of 2-methylnaphthalene (13) from 9 is significant. The major product is 6 but loss of the second methyl group from the expected intermediate 2-methyl-1,2-dihydronaphthalene should be facile.

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(1) (a) Franz, J. A.; Camaioni, D. M. *J. Org. Chem.* **1980**, *45*, 5247. (b) Berman, M. R.; Comita, P. B.; Moore, C. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5692. (c) Benjamin, B. M.; Hagaman, E. W.; Raaen, V. F.; Collins, C. J. *Fuel* **1979**, *58*, 386. (d) Hooper, R. J.; Battaerd, H. A. J.; Evans, D. G. *Ibid.* **1979**, *58*, 132. (e) Bredael, P.; Vinh, T. H. *Ibid.* **1979**, *58*, 211. (f) Tominaga, H.; Yahagi, U. *J. Fac. Eng., Univ. Tokyo, Ser. A* **1977**, *15*, 68. (g) Loudon, A. G.; Maccoll, A.; Wonk, S. K. *J. Chem. Soc. B* **1970**, 1733. (h) Badger, G. M.; Kimber, R. W. L.; Novotny, J. *Aust. J. Chem.* **1962**, *15*, 616.

(2) Schlupp, K. F.; Wien, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 341–346.

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(4) Trahanovsky, W. S.; Ong, C. C.; Lawson, J. A. *J. Am. Chem. Soc.* **1968**, *90*, 2839. The pyrolysis tube was cleaned before each run by passing O_2 through the hot tube for several minutes.

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(6) Compounds 7–9 were synthesized by standard methods. Compounds 10 (mp 61–62 °C) and 11 (mp 53.5–54.5 °C) were prepared in >98% isomeric purity by reduction (H_2, Pd/C, EtOH) of the corresponding 9-ketone. The *cis*-9-ketone was obtained by a series of reactions starting with a Friedel–Crafts reaction of benzene and *cis*-1,2-cyclohexanedicarboxylic acid anhydride. Treatment of the *cis*-9-ketone with $NaOCH_3/HOCH_3$ isomerized it to the trans isomer. The ^1H NMR of 10 matched one reported for an octahydroanthracene with unspecified stereochemistry synthesized by another route.[7]

(7) Eloranta, J. *Finn. Chem. Lett.* **1974**, 112.

(8) Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980.

(9) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(10) Morello, M. P.; Bohlen, D. H., unpublished results.

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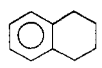
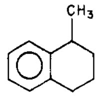
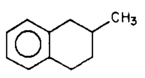
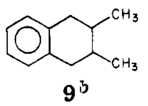
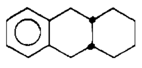
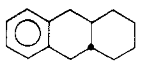
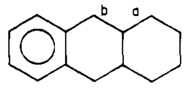
Table I. Relative Yield (%)[a] of Products of Alkyltetralin Pyrolysis

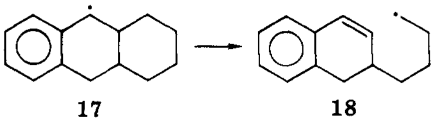
	reactant											
												
	1		**7**		**8**		**9**[b]		**10**		**11**	
temp, °C	737	888	732	891	797	890	737	888	758	860	752	854
benzocyclobutene (**2**)	6	6			7	5	8	4	24	15	trace	5
styrene (**3**)	10	23	4	2	5	15	trace	19	trace	19	trace	8
indene (**4**)	5	15	6	13	7	10	4	7	trace	3	trace	4
1,2-dihydronaphthalene (**5**)	55	5	26	6	18	4	trace	1				
naphthalene (**6**)	10	31	29	67	35	41	29	42	14	14	25	24
1-methylnaphthalene (**12**)		trace	3	1	1	1	3	2	1	3	5	6
2-methylnaphthalene (**13**)		trace	5	1	5	2	31	10	11	16	16	21
Σ minor products	13	20	27	10	22	22	25	15	44[c]	30[d]	48[e]	32[f]
% conversion[g]	6	89	60	99	30	84	12	95	18	78	17	67
Σ recovered material[g]	103	77	95	87	98	88	95	77	94[h]	86[i]	95[j]	87[k]

[a] Relative yield X = (absolute yield X)/(Σ all products). Absolute yields are averages of two GLC runs against an internal standard. FID response factors were determined for the major products and estimated for the minor ones. [b] This was an 80:20 trans-cis mixture. [c] Includes 10% 2-ethylnaphthalene (**14**) and 4% 2-vinylnaphthalene (**15**). [d] Includes 5% **14** and 4% **15**. [e] Includes 14% **14** and 6% **15**. [f] Includes 5% **14** and 5% **15**. [g] Absolute yield (%). [h] Includes 1% **11**. [i] Includes 4% **11**. [j] Includes 2% **10**. [k] Includes 4% **10**.

Loss of the four-carbon unit from **10** and **11** to give **6** probably does not involve initial cleavage of C–C bond a since cleavage of C–C bond b would be expected to be more favorable. The entropy changes of both reactions are similar but the enthalpy changes favor cleavage of bond b which produces the more stable benzyl radical. Thus initial loss of a benzylic hydrogen atom to form **17** would seem more likely. Loss of C_1–C_4 fragments from **18** would lead to **6**, **13**, and 2-ethyl- (**14**) and 2-vinylnaphthalene (**15**).



10 or 11



17 18

A concerted loss of cyclohexene readily explains the marked difference in the importance of the retro-Diels–Alder reaction for **10** and **11** since **11** would have to produce the high energy *trans*-cyclohexene.[11] However, the two-step mechanism cannot be rigorously excluded since stability or conformational differences of **10** and **11** could explain the difference in the importance of the retro-Diels–Alder reaction. Also, the two-step mechanism probably becomes important at higher temperatures and accounts for the production of **2** and **3** from **11** at 850 °C.

As a comparison to the 2-alkyltetralins, 1-methyltetralin (**7**) was pyrolyzed. The predominant product was **6**, presumably formed by direct cleavage of the benzylic methyl group. This cleavage occurs readily as evidenced by the fact that at 800 °C 90% of **7** but only 30% of **8** was converted to products.

There have been scattered reports of the thermal, gas-phase cleavage of alkyl groups,[12] but all involve the cleavage of methyl groups attached to benzylic or quaternary centers in contrast to the cleavages reported in this manuscript.

Acknowledgment. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, Budget Code AK-01-03-021 under Contract W-7405-ENG-82.

Registry No. 1, 119-64-2; **2**, 694-87-1; **3**, 100-42-5; **4**, 95-13-6; **5**, 447-53-0; **6**, 91-20-3; **7**, 1559-81-5; **8**, 3877-19-8; *cis*-**9**, 10074-96-1; *trans*-**9**, 10074-97-2; **10**, 64363-88-8; **11**, 77341-12-9; **12**, 90-12-0; **13**, 91-57-6; **14**, 939-27-5; **15**, 827-54-3; *cis*-1,2,3,4,4a,9a-hexahydro-9-(10*H*)-anthracenone, 72036-02-3; *trans*-1,2,3,4,4a,9a-hexahydro-9-(10*H*)-anthracenone, 3586-86-5.

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Received January 22, 1981

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Direct One-Step Conversion of Alcohols into Nitriles[1]

Summary: Alcohols are converted into nitriles in good to excellent yields by treatment with 2 equiv of NaCN/Me_3SiCl and a catalytic amount of NaI in DMF/CH_3CN.

Sir: The conversion of alcohols into nitriles is a useful and often employed synthetic reaction sequence. It is frequently used to obtain the homologous carboxylic acid by hydrolysis of the resulting nitrile as well as the homologous amine or aldehyde by reduction. The classical methods for alcohol to nitrile conversion proceed via sulfonate ester and/or halide intermediates (Scheme I). The nucleophilic displacement of OSO_2R' by cyanide or halide is often accompanied by the undesirable side reaction of elimination to produce olefins. Other newer methods utilize various phosphorus[2] and boron[3] derivatives as intermediates to

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(1) Publication No. 573 from the Institute of Organic Chemistry.

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