Registry No.—**2**, 19359-15-0; **6**, 19359-59-2; **7**, 19359-60-5; **8**, 19359-61-6; **9**, 19359-62-7; **10**, 19359-63-8; **12**, 19359-64-9; **14**, 19359-65-0; **16**, 19359-66-1; **20**, 19359-67-2; **22**, 19359-68-3; **23**, 19359-69-4; 4-chloro-5-ethoxymethylenaminopyrimidin-6-(1H)-one, 19359-70-7.

Acknowledgment.—The authors are indebted to Dr. W. J. Barrett and the members of the Analytical and Physical Chemistry Division of Southern Research Institute for the spectral and microanalytical determinations. Some of the analyses reported were performed by the Galbraith Microanalytical Laboratories, Knoxville, Tenn.

Base-Catalyzed Reactions. XXXIII.[1] Sodium- and Potassium-Catalyzed Reactions of Methylnaphthalenes with Ethylene

BOZIDAR STIPANOVIC AND HERMAN PINES

The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Received August 26, 1968

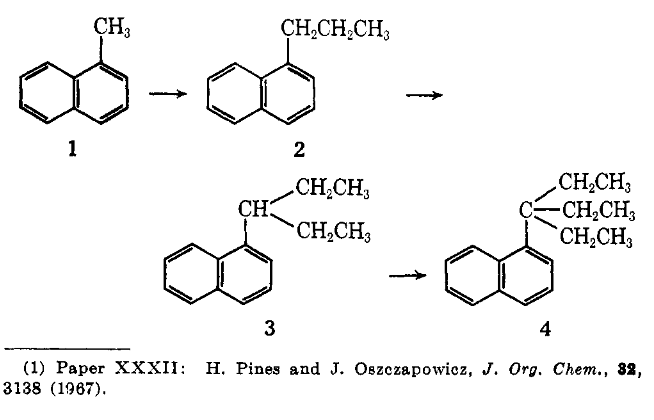
Sodium or potassium dispersed in 1- or 2-methylnaphthalene are active catalysts for the reaction of these hydrocarbons with ethylene, under pressure and at temperatures from 90 to 210°. To form an active sodium catalyst a promoter is needed, while in the case of potassium the initiator is not always required. The reaction in the presence of sodium results exclusively in side-chain ethylation (compounds **2–4**, **6**, and **8–10**). All hydrogen atoms at the α carbon of the side chain can be replaced with ethyl groups, though in case of 1-alkylnaphthalenes steric hindrance can considerably retard the reaction. The potassium-catalyzed reaction with ethylene is more complex. In addition to the side-chain ethylation reaction, products of cyclization (**12**, **17**, and **18**) and nuclear alkylation (**11** and **16**) were isolated. Also, all of these primary products undergo further alkylation (**13** and **14**) and formation of higher boiling hydrocarbons can take place.

The sodium- and potassium-catalyzed side-chain alkylation and alkenylation of alkylbenzenes and alkylpyridines have been the subject of extensive studies in this laboratory.[1,2] The present investigation is extended to the study of the reactions of ethylene with 1- and 2-alkylnaphthalenes, these being representatives of alkylpolycyclic hydrocarbons. The search of the literature had revealed only a noncatalytic reductive methylation of sodium 1- and 2-methylnaphthalenes with methyl bromide.[3]

The ethylation reactions were carried out under pressure using catalytic amounts of either sodium or potassium in the presence of small amounts of *o*-chlorotoluene as a promoter. The major reaction products were separated by a combination of fractional distillation and gas chromatography and the structures were established by nmr, by ir, and in some cases by means of mass spectra and synthesis.

Results

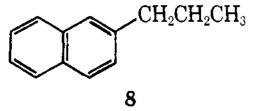
Sodium-Catalyzed Reactions.—Sodium has been found to be a very selective catalyst for the side chain ethylation of alkylnaphthalenes (Table I). With 1-methylnaphthalene (**1**), mono- and diadducts of ethylene were the only products obtained (expt 1 and 2). 3-(1-Naphthyl)pentane (**3**) underwent further ethylation very slowly and only after all of the *n*-propylnaphthalene (**2**) had reacted (expt 3). Prolonged heating and stirring for several hours resulted in the formation of only 2% 3-ethyl-3-(1-naphthyl)pentane (**4**).[4]



1 **2** **3** **4**

1,5-Dimethylnaphthalene (**5**) in the presence of sodium and an excess of ethylene produced 1,5-di(3-pentyl)naphthalene (**6**) in a 94% yield (expt 5).

2-Methylnaphthalene (**7**) formed mono- (**8**), di- (**9**), and triethylated (**10**) compounds; the last one was produced in a 62% yield (expt 7, Table I).



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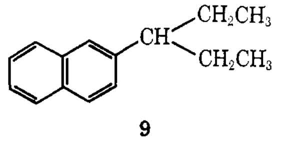

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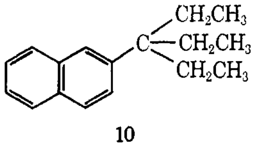

10

Unlike **1**, 2-methylnaphthalene (**7**) reacts readily with three molecules of ethylene to produce 3-ethyl-3-(2-naphthyl)pentane (**10**). The difference in the reactivity of **1** and **7** is due to steric effects which in 1-methylnaphthalene had been estimated to be 1.6 kcal/mol, greater than in *o*-xylene (0.5 kcal/mol) and almost equal to that of 1,2,3-trimethylbenzene (2.0 kcal/mol).[5] Molecular models show that in compound

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[1] Paper XXXII: H. Pines and J. Oszczapowicz, *J. Org. Chem.*, **32**, 3138 (1967).

[2] For general literature review, see H. Pines and L. A. Schaap, *Advan. Catal.*, **12**, 117 (1960).

[3] W. Hückel and R. Cramer, *Justus Liebigs Ann. Chem.*, **630**, 89, (1960); W. Hückel, and C. M. Jennewein, *Chem. Ber.*, **95**, 350 (1962).

[4] 1-Isopropylnaphthalene and 1-*sec*-butylnaphthalene were ethylated much more easily under the same conditions. More details about the products, 2-methyl-2-(1-naphthyl)butane and 3-methyl-3-(1-naphthyl)pentane, will be published in a separate paper.

[5] J. Packer, J. Vaughan, and E. Wong, *J. Amer. Chem. Soc.*, **80**, 905 (1958).

TABLE I

SODIUM-CATALYZED REACTIONS OF ALKYLNAPHTHALENES WITH ETHYLENE

Expt	Starting material[a]	Reaction temp, °C	Duration, hr	Convn,[a] %	Yields[b] of products,[c] % 2	3	4	6	8	9	10	Other
1	1-Methylnaphthalene (**1**)	210	8	53.1	49.8	47.1						3.1
2	1-Methylnaphthalene (**1**)	196	36	99.8	10.5	84.7						4.8
3	1-Methylnaphthalene (**1**)	208	48	100		91.7	2.1					6.2
4	1-*n*-Propylnaphthalene (**2**)	195	36	99.4		96.3						3.7
5[d]	1,5-Dimethylnaphthalene (**5**)	204	40	99.9				94.2				5.8
6	2-Methylnaphthalene (**7**)	178	10	75.9					25.8	64.8	3.0	6.3
7	2-Methylnaphthalene (**7**)	175	48	100					Trace	31.3	62.6	6.1

[a] Sodium (0.2–0.3 g) and *o*-chlorotoluene (0.2–0.4 ml) were stirred in 0.15 mol of alkylnaphthalene plus 0.0375 mol of *sec*-butylcyclohexane (internal standard) at 120° for 3–4 hr (12 hr expt 6 and 7). Initial pressure of ethylene was 30–35 atm. [b] Molar % based on reacted alkylnaphthalenes. [c] For the names of the compounds, consult Table VI. [d] About 0.1 g of sodium, 0.2 ml of *o*-chlorotoluene, 0.032 mol of starting material, and 0.0075 mol of *sec*-butylcyclohexane; after sodium was dispersed, the mixture was diluted with 10 ml of dry benzene.

TABLE II

ANALYTICAL DATA OF THE PRODUCTS OBTAINED IN THE PRESENCE OF SODIUM AS CATALYST

	Nmr Spectra,[a] δ, ppm					Analysis, %				
						Calcd		Found		
Compound[b]	CH_3	CH_2	CH	Aromatic protons	Bp, °C (mm)	C	H	C	H	Refract. index[c]
2	1.00 (3), t	1.77 (2), m 3.02 (2), t		7.20–8.16 (7), m	81–82 (1)					1.5923[d]
3	0.82 (6), t	1.82 (4), m	3.37 (1), m	7.30–8.32 (7), m	117–119 (4–5)	90.85	9.15	90.55	9.41	1.5782
4	0.63 (9), t	2.00 (6), q		7.00–8.44 (7), m	44–45[f]	90.20	9.80	90.42	9.97	
6	0.83 (12), t	1.84 (8), m	3.46 (2), m	7.29–7.64 (4), m 8.01–8.24 (2), q	171–172 (6) 33.5–34.5[f]	89.49	10.51	89.70	10.41	
8	0.95 (3), t	1.71 (2), m 2.71 (2), t		7.14–7.91 (7), m						1.5863[g]
9	0.78 (6), t	1.76 (4), m	2.45 (1), m	7.08–7.83 (7), m	102–104 (1.5)	90.85	9.15	91.08	9.19	1.5720
10	0.66 (9), t	1.77 (6), q		7.17–7.52 7.55–7.72 (7), m	133–134 (3–4)	90.20	9.80	89.74	10.08	1.6110

[a] Numbers in parentheses are proton integrations; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] For the names of the compounds, consult Table VI. [c] Measured at 20.0°. [d] Lit.[e] n^{20}_D 1.5922. [e] S. H. Morrell, G. B. Pickering, and J. C. Smith, *J. Inst. Petr.*, **34,** 677 (1948). [f] Melting point. [g] Lit.[e] n^{20}_D 1.5872.

3 there is a considerable interaction between the C-8 hydrogen and 3-pentyl group, which hinders further alkylation.

In the case of 1- and 2-methylnaphthalenes, monoethylated products could not be obtained free of the higher ethylated methylnaphthalenes. The rate of ethylation of the *n*-propyl group in naphthalene seems to be faster than that of the methyl group, which is in agreement with the data obtained from the study of the relative rates of ethylation of toluene *vs.* *n*-propylbenzene[6] and γ-picoline *vs.* γ-*n*-propylpyridine.[7]

The other minor products from the reaction of methylnaphthalenes with ethylene catalyzed by sodium were not isolated. However, the vpc relative retention times of these products were similar to those obtained in larger amounts in the presence of potassium.

The nmr spectra of the side-chain ethylated alkylnaphthalenes, obtained from the reactions catalyzed by sodium, gave unequivocal proof of their structures (Table II). Compounds **3**, **4**, **9**, and **10** have not been previously reported in the literature.

Potassium-Catalyzed Reactions.—The reaction of ethylene with 1- and 2-methylnaphthalene in the presence of potassium proceeded at temperatures of 90 to 160°, which is 50 to 100° lower than in the presence of sodium (Table III). Although the potassium-catalyzed reactions did not require *o*-chlorotoluene as a promoter, nevertheless its presence facilitated the ethylation.

The product obtained from the ethylation of methylnaphthalenes with potassium as a catalyst is much more complex than that derived from sodium (Table III). Besides the side-chain alkylation, cyclization and nuclear alkylation have also taken place. In addition all of these compounds also underwent further ethylation. Only 65 and 78% of the products from the reaction of 1- and 2-methylnaphthalene, respectively (expt 9 and 12, Table III), were identified. The remainder consisted of viscous material and tar. Besides **2** and **8**, compounds **11**, **12**, **16**, and **17** are the main products from the respective ethylation of methylnaphthalenes (see Scheme I).

The reaction of methylnaphthalenes with ethylene in the presence of potassium was accompanied by the formation of considerable amount of ethane, which diluted the ethylene and slowed down the rate of reaction. To complete the reaction the ethane–ethylene mixture was released during the course of the experi-

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(6) H. Pines and L. Schaap, *J. Amer. Chem. Soc.*, **80,** 3076 (1958).

(7) B. Notari and H. Pines, *ibid.*, **82,** 2945 (1960).

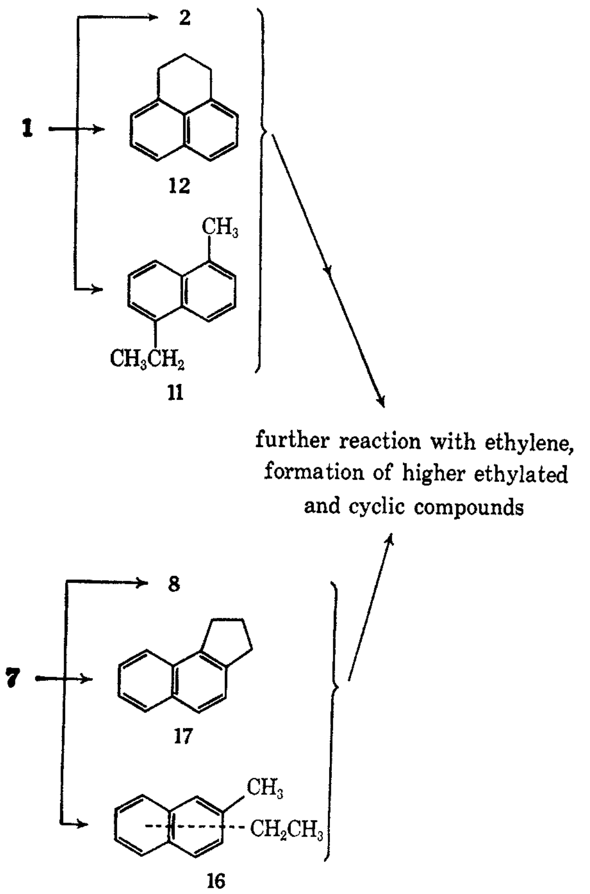
TABLE III

POTASSIUM-CATALYZED REACTIONS OF ALKYLNAPHTHALENES WITH ETHYLENE

Expt	Starting material[a]	Catalyst prepared,[b] °C, (hr)	Reaction temp, °C	Duration, hr	Ethane ratio[c]	Convn, %	Yields[d] of products,[e] % 2	3	11	12	13	14	15	Other + higher alkylated
8	1-Methylnaphthalene (**1**)	110(1.5)	165	4		41.5	18.3	2.2	4.0	9.7	12.3			53.4
9	1-Methylnaphthalene (**1**)	40 (3)	105	18	1.6	25.6	24.8	2.6	6.2	19.0	11.9			35.4
10	1-*n*-Propylnaphthalene (**2**)	90 (2)	160	12		49.3		19.8			25.7	9.0		46.9
11	3-(1-naphthyl)-pentane (**3**)	90 (2)	140	8		59.3						62.8	2.3	34.9
							8	9	10	16	17	18		
12	2-Methylnaphthalene (**7**)	40 (18)	90	36	0.7	49.4	22.4	2.4	0	10.4	41.7	3.1		21.7

[a] Alkylnaphthalene (0.15 mol) plus *sec*-butylcyclohexane (0.0375 mol) (internal standard); initial pressure of ethylene was 30–35 atm. [b] About 0.3–0.5 g of potassium in alkylnaphthalene was stirred without promoter, except in expt 8 and 11 where 0.2 and 0.4 ml, respectively, of *o*-chlorotoluene was added. [c] Molar ratio between the ethane produced and the total amount of cyclic plus higher alkylated product. [d] Molar per cent based on reacted alkylnaphthalene. [e] For the names of the compounds, consult Table VI.

SCHEME I



ment and the autoclave was recharged with fresh ethylene. The amount of ethane produced is an indicator of the extend of cyclization. Similar formation of ethane and cyclic compounds in the presence of potassium, but not in the presence of sodium, has been observed previously in connection with the ethylation of alkylbenzenes.[8] Cyclization in the presence of potassium had also been reported in the case of the rearrangement of ω-phenylalkenes.[9,10]

1-Methylnaphthalene yielded about 30% dihydrophenalene **12** and its ethyl derivative **13**, while 2-methylnaphthalene gave 45% indan-type compounds **17** and **18** (Table III). If we assume that at least the same distribution may exist among the unidentified higher boiling products, then the percentage of cyclic hydrocarbons formed would be even higher. Only one of the two possible cyclization compounds of 1- and 2-methylnaphthalene was found, as the attack was exclusively on the α position of the naphthalene ring; dihydrophenalene **12** and dihydrobenz[*e*]indene **17** were produced, respectively. The β position of the naphthalene ring seems inert to cyclization.

From expt 11 about 3% benz[*e*]indene **18**, a product of dehydrogenation of **17**, was also isolated; this type of dehydrogenation by alkali metals had been reported previously.[11–13] It is therefore very possible that phenalene itself must have undergone dehydrogenation (expt 8 and 9); however, owing to its high reactivity, it was not detected.

Previous studies have indicated that in base-catalyzed reactions alkylbenzenes having a benzylic hydrogen do not undergo nuclear alkylations with olefins.[2] However, in the case of methylnaphthalenes, ring alkylation in the presence of potassium did occur; 4–10% of the product consisted of ring-alkylated material (expt 8, 9, and 12). 2-Methylnaphthalene produced three isomeric methylethylnaphthalenes which were not separable into pure compounds by gas chromatography. Nuclear alkylation was the main reaction when 3-(1-naphthyl)pentane (**3**) was allowed to react with

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(8) L. Schaap and H. Pines, *J. Amer. Chem. Soc.*, **79**, 4967 (1957).

(9) H. Pines, N. C. Sih, and E. Lewicki, *J. Org. Chem.*, **30**, 1457 (1965).

(10) N. C. Sih and H. Pines, *ibid.*, **30**, 1462 (1965); H. Pines, J. A. Vesely, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **77**, 347 (1955).

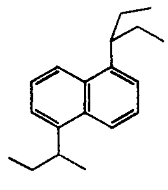
(11) H. Pines and H. E. Eschinazi, *ibid.*, **77**, 6314 (1955).

(12) M. Kolobielski and H. Pines, *ibid.*, **79**, 5820 (1957).

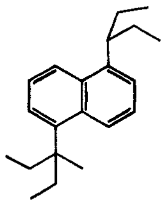
(13) T. M. O'Grady, R. M. Alm, and M. C. Hoff, Division of Petroleum Chemistry of the American Chemical Society, Preprints 4, No. 4, B65-B69, 1959.

ethylene (expt 11); about 63% compound **14** was produced.

From the same experiment, a small amount of pure compound was separated which had a higher boiling point than the main product to which structure **15** was assigned. The nmr spectrum of **15** represents almost a superimposure of the spectra of 3-(1-naphthyl)pentane (**3**) and 3-methyl-3-(1-naphthyl)pentane[4,14] (Figure 1).



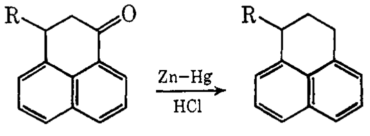
14



15

Analytical data of the products formed by the nuclear alkylation and cyclization using potassium as a catalyst are given in Table IV, where **13**, **14**, and **15** are new compounds. Some of the hydrocarbons were synthesized and their nmr and ir spectra were compared with those of the products of the reaction and found to be identical.

Dihydrophenalene **12** and ethyldihydrophenalene **13** were synthesized by a Clemmensen reduction of the corresponding ketones.[15] Compound **13** could not be synthesized directly from 1,2-dihydrophenalen-3-one **19** by means of a Grignard reaction because the dehydration of the corresponding alcohol leads to the isomerization of the ethyl group.[16]



19, R = H
20, R = C_2H_5
12, R = H
13, R = C_2H_5

Ketone **20** was prepared from 1-(1-naphthyl)-1-propanol (**21**), following the procedure of Bachmann and Edgerton.[17] Compound **11** was synthesized according to the method of Harvey, *et al.*,[18] with a few modifications. Hydrocarbon **14** was synthesized by reacting 1-methyl-5-ethylnaphthalene (**11**) with ethylene in the presence of sodium as a catalyst.

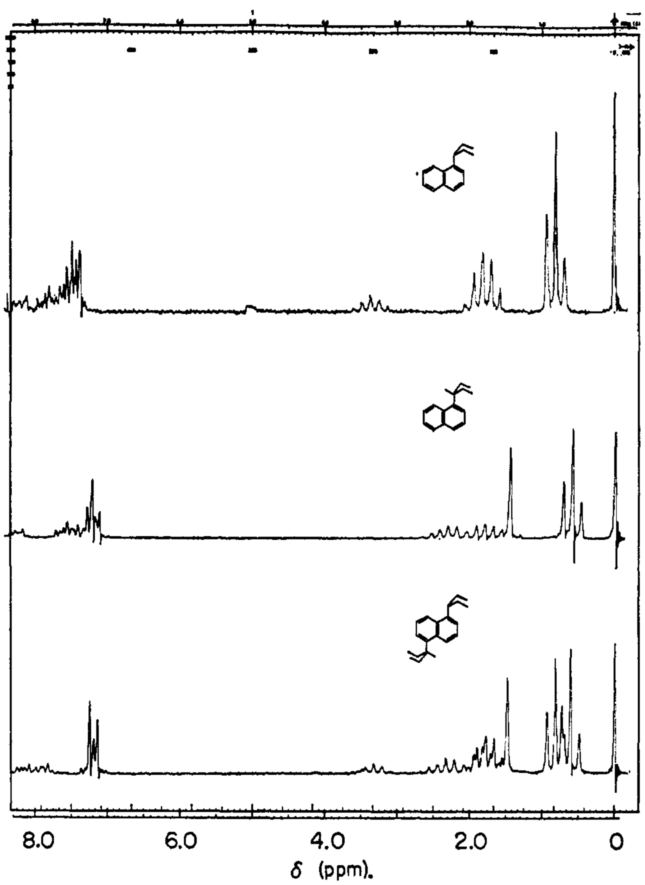
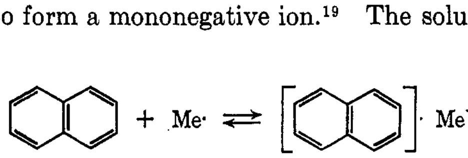


Figure 1.—Nmr spectra of 3-(1-naphthyl)pentane, 3-methyl-3-(1-naphthyl)pentane, and 1-(3-pentyl)-5-[(3-methyl)-(3-pentyl)]-naphthalene.

Discussion

The course of the reaction of alkylnaphthalenes with ethylene depends on alkali metal being used as a catalyst, which confirms the previously obtained results with alkylbenzenes,[8] and with ω-phenylalkenes.[9] Unlike alkylbenzenes, alkylnaphthalenes do not require the presence of a promoter to form an active potassium catalyst (expt 8, Table III). This can be attributed to the fact that fused polycyclic aromatic hydrocarbons undergo an addition reaction with a reactive alkali metal to form a mononegative ion.[19] The solutions of such ions in tetrahydrofuran and 1,2-dimethoxyethane were strongly paramagnetic[19b] and esr spectra unambiguously proved that the added electron is not localized on a particular carbon atom, but is distributed and delocalized over the whole π-electron system of the molecule.[19c] The electrontransfer from the alkali metal to the hydrocarbon may thus lead to uni- or divalent ions depending on the solvent.[19b]



(a)

Me = alkali metal

In the case of alkylnaphthalenes with at least one relatively acidic proton on the α-carbon atom (benzylic

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(14) The nmr spectrum indicated that the CH_2 hydrogens in 3-methyl-3-pentyl group are not magnetically equivalent (Figure 1). Nonequivalence apparently arises because the methylene group is attached to a carbon bearing three different substituents and an AB quartet of lines is further coupled to the adjacent methyl group. As a result of overlap, however, the full 16-line multiplet is not obtained. ("Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press, London–New York, 1967, pp 39, 121).

(15) L. F. Fieser and F. C. Novello, *J. Amer. Chem. Soc.*, **62**, 1855 (1940); L. F. Fieser and M. D. Gates, *ibid.*, **62**, 2334 (1940).

(16) D. H. Reid, *Quart. Rev.* (London), **19**, 274 (1965); V. Boekelheide and C. E. Larrabee, *J. Amer. Chem. Soc.*, **72**, 1240, 1245 (1950); M. Nakazaki, *U.S. At. Energy Comm. Repts.*, U.C.R.L. 3700 (1959).

(17) W. E. Bachmann and R. O. Edgerton, *J. Amer. Chem. Soc.*, **62**, 2219 (1940).

(18) J. Harvey, I. M. Heilbron, and D. G. Wilkinson, *J. Chem. Soc.*, 423, (1930).

(19) E. de Boer, *Advan. Organometal. Chem.*, (a) 115 (1964); (b) 117 (1964); (c) 140 (1964).

TABLE IV

ANALYTICAL DATA OF THE PRODUCTS OBTAINED IN THE PRESENCE OF POTASSIUM AS CATALYST

Compound[b]	Nmr spectra,[a] δ, ppm				Bp (mm) or mp, °C, or refractive index
	CH₃	CH₂	CH	Aromatic protons	
11	1.33 (3), t 2.72 (3), s	3.04 (2), q		7.00–7.50 7.55–7.97 (6), m	Mp 35–38[c]
12		1.99 (2), m 3.01 (4), t		6.93–7.55 (6), m	Mp 64–65[d]
13	0.96 (3), t	1.73 (2), m 1.95 (2), m 2.86 (3), m	2.96	7.00–7.30 (6), m	n^{20}D 1.6114
14	0.81 0.92 (9), q	1.36 (3), d	3.42 (2), m	7.20–7.64 7.83–8.10 (6), m	Bp 125–130 (1–1.5) n^{20}D 1.5637
15	0.61 0.82 (12), m 1.48 (3), m	1.78 1.82 2.33 (8), m	3.33 (1), m	7.15–8.42 (6), m	
17		2.18 (2), q 3.02 3.13 (4), q		7.13–7.81 (6), m	n^{20}D 1.6130[e]
18		3.40 (2), m		6.42–6.63 6.80–7.00 7.22–7.47 7.62–7.87 (8), m	

[a] Numbers in parentheses are proton integrations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. [b] For the names of the compounds, consult Table VI. [c] Lit.[18] mp 40.0°; identical with an synthetic sample (**11**; see Experimental Section). [d] Mp 65.1–65.4°: L. F. Fieser and E. B. Hershberg, *J. Amer. Chem. Soc.*, **60**, 1658 (1938). [e] $n^{19.7}$D 1.6323. [g] J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 1098 (1933).

type of proton), reactions b–d can occur. The species like IV and V can then initiate the catalytic side-chain alkylation.

$$\underset{\text{I}}{C_{10}H_7CH_3} + Me\cdot \longrightarrow \underset{\text{II}}{|C_{10}H_7CH_3|\cdot{}^-Me^+} \qquad \text{(b)}$$

$$\underset{\text{II}}{|C_{10}H_7CH_3|\cdot{}^-Me^+} + \underset{\text{I}}{C_{10}H_7CH_3} \longrightarrow \underset{\text{III}}{|C_{10}H_8CH_3|\cdot} + \underset{\text{IV}}{C_{10}H_7CH_2{}^-Me^+} \qquad \text{(c)}$$

$$\underset{\text{III}}{|C_{10}H_8CH_3|\cdot} + \underset{\text{II}}{|C_{10}H_7CH_3|\cdot{}^-Me^+} \longrightarrow \underset{\text{V}}{|C_{10}H_8CH_3|^-Me^+} + \underset{\text{I}}{C_{10}H_7CH_3} \qquad \text{(d)}$$

Me = alkali metal

Potassium having a lower ionization potential than sodium is able to transfer the electron to a naphthalene molecule and form an anion radical. However, promoters are necessary for the reactions in the presence of sodium since radical anions are formed less readily with this metal, particularly in the nonpolar solutions, and at higher temperature.[19–21]

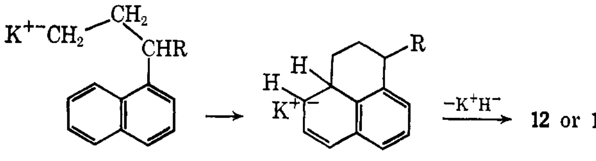
High selectivity of the sodium-catalyzed ethylation of alkylnaphthalenes is an indication that only carbanions at the α-carbon atom of the side chain are involved in the addition to ethylene (eq e and f). A monoethylated product can further undergo an abstraction of the secondary proton and then add to another molecule of ethylene. This mechanism is similar to the one proposed previously to explain the side-chain alkylation of toluene with olefins.[2,22]

$$ClC_6H_4CH_3 \xrightarrow[(-NaCl)]{2Na} C_6H_5CH_2{}^-Na^+ \xrightarrow{C_{10}H_7CH_3} C_{10}H_7CH_2{}^-Na^+ + C_6H_5CH_3 \qquad \text{(e)}$$

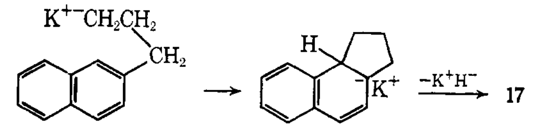
$$C_{10}H_7CH_2{}^-Na^+ \xrightarrow{CH_2{=}CH_2} C_{10}H_7CH_2CH_2CH_2{}^-Na^+ \xrightarrow{C_{10}H_7CH_3} C_{10}H_7CH_2CH_2CH_3 + C_{10}H_7CH_2{}^-Na^+ \qquad \text{(f)}$$

The potassium-catalyzed reaction of alkylnaphthalenes and ethylene is more complex than that with sodium. More than 15 compounds were formed from the reaction of 1-methylnaphthalene with ethylene. The great difference between the catalytic properties of the alkali metals as catalysts may be related to the ionic characters of the carbon-metal bonds. Organolithium compounds are least ionized while cesium-carbon bonds show a large extent of ionic character.[23] A more ionic species is probably more dissociated and the carbanion is thus of higher reactivity.[9] It also appears probable that the extent of ion pairing[24] and the field effect of the cation[25] may determine to a certain degree the catalytic properties of an alkali metal.

The formation of 1,2-dihydrophenalene (**13**) (eq g)



(g)



(h)

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(22) H. Pines and V. Mark, *ibid.*, **78**, 4316 (1956).

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(24) K. H. J. Buschow, J. Dielman, and G. J. Hoijtink, *J. Chem. Phys.*, **42**, 1993 (1965); N. H. Velthorst and G. J. Hoijtink, *J. Amer. Chem. Soc.*, **87**, 4529 (1965).

(25) E. Warhurst and R. Whittaker, *Trans. Faraday Soc.*, **62**, 707 (1966).

TABLE V
DESCRIPTION OF VAPOR PHASE CHROMATOGRAPHIC COLUMNS

Column	Liquid phase	Solid support	Mesh	Length, m	Outside diameter, in.
A	15% silicone gum SE-30	Gas Pack WAB	60–80	2.13	0.25
B	15% silicone gum SE-30	Gas Pack WAB	60–80	2.44	0.375
C	15% Versamid	Gas Pack WAB	60–80	2.44	0.375
D	15% Carbowax 20M	Chromosorb P	60–80	2.13	0.25
E	15% LP-122 silicone gum rubber GE-SE-52	Chromosorb W	60–80	10.00	0.25

TABLE VI
RELATIVE RETENTION TIMES OF IDENTIFIED REACTION PRODUCTS[a]

Reaction product	Compound no.	Column[b,c]		
		A[d]	A[e]	D[d]
Standard		1.00	1.00	1.00
1-Propylnaphthalene	**2**	1.45		1.15
3-(1-Naphthyl)pentane	**3**	2.11		1.36
3-Ethyl-3-(1-naphthyl)pentane	**4**	3.97	1.95	2.57
1,5-Di(3-pentyl)naphthalene	**6**		3.25	
2-Propylnaphthalene	**8**	1.48		1.16
3-(2-Naphthyl)pentane	**9**	2.20		1.48
3-Ethyl-3-(2-naphthyl)pentane	**10**	4.36		3.05
1-Methyl-5-ethylnaphthalene	**11**	1.68		1.45
1,2-Dihydrophenalene	**12**	2.18		2.37
1-Ethyl-1,2-dihydrophenalene	**13**	3.49		3.24
1-(2-Butyl)-5-(3-pentyl)naphthalene	**14**		2.90	
1-(3-Pentyl)-5-[(3-methyl)-3-pentyl]naphthalene	**15**		4.44	
2-Methyl-*x*-ethylnaphthalene	**16**	1.50		1.27
2,3-Dihydro-1H-benz[*e*]indene	**17**	2.24		2.28
*x*H-Benz[*e*]indene[f]	**18**	2.36		

[a] F & M 720 chromatograph; helium flow 100 ml/min at 35 psi; injection port and detector temperature 300°. [b] Column temperature 220°. [c] Description of the columns in Table V. [d] Biphenyl as a standard. [e] Fluorene as a standard. [f] 1H- and/or 3H-benz[e]indene.

and 2,3-dihydro-1H-benz[*e*]indene (**17**) (eq f) could be explained according to the earlier proposed mechanism as an intramolecular alkylation of the aromatic ring by a carbanion.[8] Potassium hydride from the cyclization reaction may add to an ethylene and form ethylpotassium, which by abstraction of a proton from an α-carbon atom leads to the formation of a carbanion and ethane (eq i). A concerted mechanism for such a cyclization reaction has been recently proposed.[26]

$$K^+H^- + CH_2{=}CH_2 \longrightarrow CH_3CH_2^-K^+ \xrightarrow{C_{10}H_7CH_3} CH_3CH_3 + C_{10}H_7CH_2^-K^+ \quad \text{(i)}$$

$$R = H, \text{alkyl}$$

Product **18** resulting from the dehydrogenation of **17** was isolated from the reaction of 2-methylnaphthalene (expt 12, Table III). This dehydrogenation could be explained by a mechanism suggested previously.[11]

The nuclear alkylation, one of three major reactions of alkylnaphthalenes and ethylene in the presence of potassium, was also found to occur in ethylation reactions of alkylbenzenes, although in relatively small yields. For this reaction two possible carbanion mechanisms were suggested.[8,22] The formation of ethylpotassium by the addition of potassium hydride to ethylene may result either in a direct attack of the ethyl carbanion on the aromatic nucleus, or in a metalation of the aromatic ring. The arylpotassium thus formed could then add to ethylene.[27]

The addition of an aromatic mononegative ion to ethylene could also be assumed and there is some evidence in favor of such a mechanism. The structure of the isolated product **14** from the reaction of 1-methylnaphthalene suggests that the carbon atom in position 5 is presumably more reactive than the others. This is in agreement with the calculated higher spin densities at the α rather than at the β position of the symmetrically substituted dimethylnaphthalene mononegative ions.[28] It is, however, difficult to visualize such a reaction as a catalytic process. Only a catalytic reaction can lead to the formation of more than 60% ring-alkylated compound **14** (expt 11, Table III) and for that reason the mechanism involving ethylpotassium is favored.

Experimental Section

The pure reaction products were separated by means of preparative vapor phase chromatography (columns B and C, Table V). The structures of various hydrocarbons were determined from the nmr spectra, while the ir spectra[29] were compared with those of synthesized compounds or with known spectra from the literature. The vpc columns are described in Table V, and the retention times of identified products are given in Table VI. All melting and boiling points are uncorrected.

Apparatus and General Procedure.—In a three-necked, round-bottom flask with a thermocouple well, equipped with a high speed stirrer,[30] condenser with a drying tube, and an inlet for inert gas (nitrogen or helium), was placed 0.15 mol of alkylnaphthalene and 0.0375 mol of *sec*-butylcyclohexane as an in-

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[26] G. G. Eberhardt, *J. Org. Chem.*, **29**, 643 (1964).

[27] Recently, R. L. Eppley, and J. A. Dixon [*J. Amer. Chem. Soc.*, **90**, 1606 (1968)] have found that *t*-butyllithium reacts with naphthalene, initially forming a complex $(RLi)_2(C_{10}H_8)$. Subsequent reaction of this complex leads to the formation of 1- and 2-*t*-butylnaphthalene. A similar intermediate complex might be found in the reaction of ethylpotassium and alkylnaphthalene.

[28] F. Gerson, P. Wiedmann, and E. Heilbroner, *Helv. Chim. Acta*, **47**, 1951 (1964).

[29] The ir spectra were taken in a microcell with capillary thickness (liquid products) and in KBr pellet (solids) with a Baird Model 4-55 spectrophotometer. Nmr spectra were measured in carbon tetrachloride using tetramethylsilane as an internal standard with a Varian A-60.

[30] H. Pines and N. C. Sih, *J. Org. Chem.*, **30**, 280 (1965).

ternal standard. Under a nitrogen (or helium in case of potassium) atmosphere approximately 0.01–0.02 g-atom of alkali metal was cut (under dry *n*-pentane) and placed into the flask. Then, if necessary, 0.2–0.4 ml of *o*-chlorotoluene was added and the reaction mixture was heated to the desired temperature and stirred until a dark brown or black suspension was formed (the reaction conditions for particular experiments are given in Table I and III). The mixture was then cooled and transferred (under nitrogen) to a Magne-Dash autoclave of 100-cc capacity. After flushing the air with nitrogen, ethylene was introduced from a calibrated charger (pressure of about 30 atm at room temperature). The autoclave content was agitated and heated to that temperature at which the pressure started to decrease. At the end the autoclave was cooled down to room temperature. In some experiments the gaseous products, after releasing the pressure, were collected in a gas bottle and analyzed on column E (Table V) at room temperature.

The remaining alkali metal and organometallic catalyst was decomposed with abs ethanol (under nitrogen). The resulting reaction mixture was dissolved in ether, washed with water and salt solution, dried over anhydrous magnesium sulfate, and finally distilled in vacuum under nitrogen. The samples for the vpc analysis were taken before distillation. The conversions and molar per cent compositions of the products were calculated according to the internal standard. Thermal conductivity coefficients for separated and identified products were taken into account for those calculations.

Reagents.—1-Methylnaphthalene (Aldrich, bp 240–243°) and 2-methylnaphthalene (Aldrich, mp 34–36°) were distilled and stored under nitrogen until they were used for the reaction. 1,5-Dimethylnaphthalene was supplied by courtesy of Dr. A. W. Weitkamp, American Oil Co., Whiting, Ind. 3-(1-Naphthyl)-pentane was synthesized from 1-methylnaphthalene and ethylene in the presence of sodium as a catalyst.

3-(1-Naphthyl)pentane (3).—A mixture of 71.0 g (0.5 mol) of 1-methylnaphthalene, about 1–1.5 g (0.1 g-atom) of freshly cut (under dry *n*-pentane) metallic sodium, and 0.5 ml of *o*-chlorotoluene were placed in the previously described apparatus (250-cc capacity). The reaction mixture was stirred at 110–120° under a slow stream of nitrogen for 4 hr. The content was then cooled down and transferred into a 250-cc Magne-Dash autoclave, and after flushing the air with nitrogen ethylene was introduced (about 32 atm). The reaction was carried out at 205° for 48 hr. More ethylene was added during that time. After the reaction was completed, unreacted ethylene was released and the sodium and organosodium compounds destroyed with ethanol. The reaction products were dissolved in ether, washed, dried ($MgSO_4$), and distilled. After a small amount of 1-propylnaphthalene was distilled off, the main reaction product, a viscous, colorless liquid, 3-(1-naphthyl)pentane, distilled at 133–134° (4–5 mm). The yield was 69.8 g (82.2%).

Synthesis of the Reaction Products. A. 1,2-Dihydrophenalene (12). 1,2-Dihydrophenalen-3-one (19).—Ketone 19 was synthesized according to the method of Fieser and Gates,[15] with the modification that 1-bromoethylnaphthalene was used as a starting material: 52% over-all yield, mp 80–82°. The bromide was prepared in 91% yield, mp 54–55°, by the method of Horner and Winkelmann.[31]

1,2-Dihydrophenalene (12).—This hydrocarbon was prepared in 66% yield, mp 64.5–65.5°, by the Clemmensen reduction[15] of 19.

B. 1-Ethyl-1,2-dihydrophenalene (13). 1-(1-Naphthyl)propan-1-ol (21).—Carbinol 21 was synthesized from 0.1 mol of 1-bromonaphthalene and 0.1 mol of propionaldehyde *via* a Grignard reaction, according to the procedure described.[32] The yield of alcohol 21 was 82%, bp 139–142° (2–2.5 mm), $n^{20}D$ 1.6096.[33]

1-Bromo-1-(1-naphthyl)propane (22).—Bromide 22 was prepared from 0.08 mol of 21 according to the method of Bachmann and Edgerton:[17] yield 72%, mp 37–38.5°.[33]

β-(1-Naphthyl)valeric acid (23).—Acid 23 was synthesized from 0.052 mol of 22 and diethyl sodiomalonate:[17] yield 69%, mp 69–70°.[33]

1-Ethyl-1,2-dihydrophenalen-3-one (20).—Acid 23 (0.038 mol) was cyclized by means of hydrogen fluoride according to Ansell and Berman.[33] A brown oil (6.9 g) was obtained, which was chromatographed in *n*-hexane on an alumina column (4 × 15 cm). Ketone 20 was eluted by a 4:1 *n*-hexane–ether solution. The column and the elute were kept under nitrogen, and he column was protected from the light. After the solvent was distilled off, 4.05 g (50%) of 20 was obtained: 2,4-dinitrophenylhydrazone mp 182.5–184°.[33]

1-Ethyl-1,2-dihydrophenalene (13).—A mixture of 25 g of amalgamated zinc, 50 ml of methyl alcohol, 50 ml of benzene, 10 ml of concentrated hydrochloric acid, and 4.0 g of ethyldihydrophenalenone (20) was refluxed for 9 hr. During that period an additional 10 ml of hydrochloric acid were added in two portions. After cooling, the aqueous layer was extracted with ether, washed, dried ($MgSO_4$), and concentrated. 1-Ethyl-1,2-dihydrophenalene (13) was separated from 10–15% of impurities by a preparative vpc using column B (Table V) at 210° and helium flow of 100 ml/min: $n^{20}D$ 1.6110. *Anal.* Calcd for $C_{15}H_{16}$: C, 91.78; H, 8.22. Found: C, 92.02; H, 8.15.

C. 1-Methyl-5-ethylnaphthalene (11). Diethyl 2-Methylbenzylmalonate (24).—2-Methylbenzylbromide (0.4 mol) was added slowly to a paste of ethyl sodiomalonate prepared from 0.75 mol of diethyl malonate in 200 ml of benzene and 0.4 g-atom of sodium. The mixture was stirred and refluxed for 12 hr and cooled and the sodium bromide was washed with water. Ester 24, obtained in 89% yield, distilled at 151–154° (4–5 mm): $n^{20}D$ 1.4910. *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.37; H, 7.64.

1-Methylhydrocinnamic Acid (26).—Ester 24 (0.35 mol) was hydrolyzed for 4 hr at reflux temperature with 1 mol of potassium hydroxide in 200 ml of water. The solution was cooled and neutralized with dilute hydrochloric acid, using congo red as an indicator. On filtration a quantitative yield of 1-methylbenzylmalonic acid 25 was obtained. Without further purification the acid 25 (0.34 mol) was heated for ~0.5 hr at 170–180°, until the evolution of carbon dioxide ceased. The residue was recrystallized from an acetic acid–water solution and 49.5 g (88%) of 1-methylhydrocinnamic acid, mp 103–104°,[34] was obtained.

3-(1-Methylphenyl)propan-1-ol (27).—Acid 26 (0.3 mol) was placed in a thimble of a continuous extractor and reduced with 0.26 mol of lithium aluminum hydride in 300 ml of ether.[35] Alcohol 27, 94.5% yield, distilled at 109–111° (3 mm): urethan mp 57–58° [lit.[18] bp 136° (15 mm), urethan mp 58°].

3-(1-Methylphenyl)-1-bromopropane (28).—To 0.28 mol of 27, cooled with ice, was added dropwise 46 g of phosphorus tribromide. After standing overnight the reaction mixture was kept for 1.5 hr in a warm-water bath, then poured on ice, and extracted with ether. Bromide 28, yield 85% distilled at 121–123° (15 mm) [lit.[18] bp 124° (17 mm)].

γ-(1-Methylphenyl)butyric acid (29).—From 0.115 mol of bromide 28 and potassium cyanide, according to the procedure of Harvey, *et al.*,[18] acid 29 was obtained in 84% yield: mp 59–60° (lit.[18] mp 60°).

3,4-Dihydro-5-methyl-1(2H)-naphthalenone (30).—A solution of 0.095 mol of 29 in 150 g of anhydrous hydrogen fluoride was stirred for 8 hr at room temperature, then poured on ice, and extracted with ether. After it was washed (H_2O, $NaHCO_3$) and dried ($MgSO_4$), the ethereal extract was distilled. Ketone 30 was obtained in 89% yield: bp 117–120° (3–4 mm), mp 48–50° [lit.[36] bp 115–117° (3 mm), mp 50–51°[18]].

1-Methyl-5-ethylnaphthalene (11).—Compound 11 was prepared from 0.075 mol of ketone 30 by the procedure of Harvey, *et al.*[18] The tertiary alcohol, obtained by allowing 30 to react with ethylmagnesium bromide, was dehydrated with boiling acetic anhydride to 1-ethyl-5-methyl-3,4-dihydronaphthalene. The latter was then heated with selenium metal at 300° for 24 hr. A solid obtained after distillation over sodium was purified *via* picrate. Compound 11 in the form of white crystals was obtained in 61% over-all yield: mp 38–39° (lit.[18] mp 40°). The synthetic hydrocarbon was identical with 1-methyl-5-ethylnaphthalene separated from the reaction (Table IV).

D. 1-(2-Butyl)-5-(3-pentyl)naphthalene (14).—A mixture of 5 g (0.0294 mol) of 1-methyl-5-ethylnaphthalene (11) and 6.5 g (0.0706 mol) of toluene was stirred for 5 hr with 0.2 g of sodium and 0.35 ml of *o*-chlorotoluene at 110° in a slow stream of nitro-

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[31] L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 349 (1959).

[32] H. Gilman, N. B. St. John, and F. Schulze, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 425.

[33] M. F. Ansell and A. M. Berman, *J. Chem. Soc.*, 1792 (1954).

[34] W. E. Bachmann and E. K. Raunio, *J. Amer. Chem. Soc.*, **72**, 2530 (1950).

[35] R. F. Nystrom and W. G. Brown, *ibid.*, **69**, 2548 (1947).

[36] I. Ochiai, T. Okamoto, M. Sekijima, M. Nishikawa, and K. Shono, *Pharm. Bull.* (Tokyo), **5**, 48 (1957); *Chem. Abstr.*, **51**, 16387 (1957).

gen. The dark brown reaction mixture was then cooled and transferred to a 100-ml capacity Magne-Dash autoclave with an agitator. After this was flushed with nitrogen, 40 atm of ethylene was introduced and the autoclave was heated at 208° until the uptake of ethylene ceased. The sodium was then decomposed with ethanol and the reaction product was dissolved in ether, washed, dried ($MgSO_4$), and distilled. Title compound **11** distilled at 125–128° (1–1.5 mm) and was purified by preparative vpc: $n^{20}D$ 1.5640. *Anal.* Calcd for $C_{19}H_{26}$: C, 89.70; H, 10.30. Found: C, 89.98; H, 10.28. The synthetic sample was identical with the isolated product **14** (expt 10 and 11, Table III).

Registry No.—Ethylene, 74-85-1; **2**, 2765-18-6; **3**, 3042-56-6; **4**, 19990-00-2; **6**, 19990-01-3; **8**, 2027-19-2; **9**, 3042-57-7; **10**, 19990-03-5; **11**, 17057-92-0; **12**, 479-58-3; **13**, 19990-06-8; **14**, 19990-07-9; **15**, 19990-08-0; **17**, 4944-94-9; **18**, 232-54-2; **24**, 6619-57-4.

Base-Catalyzed Reactions. XXXIV.[1] The Alkali Metal Catalyzed Side-Chain Aralkylation of 2- and 4-Alkylpyridines with Styrene, α-Methylstyrene, and *cis*- and *trans*-β-Methylstyrene

Herman Pines and Nelson E. Sartoris[2]

The Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University,
Evanston, Illinois 60201

Received September 25, 1968

The sodium- and potassium-catalyzed side-chain aralkylation reactions of 2- and 4-alkylpyridines with styrene, α-methylstyrene, and *cis*- and *trans*-β-methylstyrene were performed using the alkylpyridines in a 5:1 molar excess. For the most part, the reactions proceed readily at 0–25° to yield monoaddition products *via* a Michael-type addition mechanism, as well as di- and triaddition products in some cases. As the length and branching of the alkylpyridine are increased, the yields of the higher adducts decrease. The yields of the higher adducts, as well as the relative rates of reaction, also decrease as the steric hindrance of the reacting olefin increases on going from styrene to α-methylstyrene to β-methylstyrene. 4-Alkylpyridines react more readily than 2-alkylpyridines. Also formed, in some cases, are diaddition products resulting from a chain-lengthening process. With 2- and 4-picoline and 2- and 4-ethylpyridine, *trans*-β-methylstyrene reacts faster than *cis*, due to the greater conjugation of the *trans* olefin. With 4-isopropylpyridine, however, the results are reversed.

The sodium- and potassium-catalyzed side-chain aralkylations of alkylbenzenes having a benzylic hydrogen have been studied extensively in our laboratory.[3] These reactions proceed in the presence of a promoter at 100–125° to give the expected monoaddition products, and diadducts in some cases, *via* a carbanion mechanism. As the length and branching of the alkylbenzene is increased, and as the steric hindrance of the olefin increases on going from styrene to α-methylstyrene to β-methylstyrene, the yields of the aralkylation products decrease while the competitive dimerization and polymerization of the olefin increases.[4] The potassium-catalyzed aralkylation of *n*-alkylbenzenes with β-methylstyrene at 105° gives only fair yields (19–52%) of the monoaddition products, while isopropylbenzene fails to react with β-methylstyrene. Instead, the β-methylstyrene undergoes dimerization by both anionic and anionic free-radical mechanisms.[5,6]

It has been reported that alkylpyridines can undergo alkali metal catalyzed side-chain alkylation reactions similar to the side-chain alkylations of alkylbenzenes.[3,7] The sodium- and potassium-catalyzed aralkylation reactions of 2- and 4-alkylpyridines with styrene, α-methylstyrene, and *cis*- and *trans*-β-methylstyrene were studied in order to compare the results with those of the analogous reactions with alkylbenzenes.

Discussion of Results

The reactions of 2- and 4-alkylpyridine with styrene, α-methylstyrene, and *cis*- and *trans*-β-methylstyrene were carried out in the presence of catalytic amounts of sodium and potassium. Details and results of the aralkylations are given in Tables I and II. The course of the reactions was followed by vapor phase chromatography. The products were separated by preparative gas chromatography and their structures were established by nmr and ir spectroscopy, elemental analyses, and occasionally by comparison with known compounds.

The metallic sodium or potassium was dispersed in the alkylpyridine for 3–5 hr to ensure complete dispersion, resulting in the formation of a seemingly homogeneous solution of organoalkali metal catalyst, R^-M^+. The olefin was then added dropwise. For the most part the reactions proceed readily at 0–25°.

The mechanism of the aralkylation is proposed to be similar to that of the side-chain aralkylation of alkylbenzenes[8] and the side-chain alkenylation of 4-alkylpyridines.[7d] The initial step is suspected to be the formation of a radical anion.[1]

The aralkylation reaction can be described by the following equation. If R_1 and/or R_2 = H, further aralkylation of the alkylpyridine does occur, resulting in the formation of normal di- and triadducts. The diaddition products can also be formed to a smaller extend *via* a chain-lengthening process similar to that which has previously been reported.[8,9]

In Table I are listed the results of the reactions of various alkylpyridines with styrene and α-methylstyrene. As the length and branching of the alkylpyri-

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[1] (a) Paper XXXIII: B. Stipanovic and H. Pines, *J. Org. Chem.*, **34**, 2106 (1969); (b) paper V of the series Alkylation of Heteroaromatics.

[2] Predoctoral Fellow, National Institutes of Health, 1964–1968.

[3] For literature references, see H. Pines and L. Schaap, *Advan. Catalysis*, **12**, 116 (1960).

[4] J. Shabtai and H. Pines, *J. Org. Chem.*, **26**, 4225 (1961).

[5] J. Shabtai, E. M. Lewicki, and H. Pines, *ibid.*, **27**, 2618 (1962).

[6] J. Shabtai and H. Pines, *ibid.*, **29**, 2408 (1964).

[7] (a) H. Pines and D. Wunderlich, *J. Amer. Chem. Soc.*, **81**, 2568 (1959); (b) H. Pines and B. Notari, *ibid.*, **82**, 2209 (1960); (c) *ibid.*, **82**, 2945 (1960); (d) H. Pines and J. Oszczapowicz, *J. Org. Chem.*, **32**, 3183 (1967).

[8] H. Pines and D. Wunderlich, *J. Amer. Chem. Soc.*, **80**, 6001 (1958).

[9] H. Pines and N. Sih, *J. Org. Chem.*, **30**, 280 (1965).