[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSIY OF WISCONSIN]

Catalytic Dehydrogenation of Hydroaromatic Compounds in Benzene. V. Application to Pyrrolidines and Piperidines

BY HOMER ADKINS AND LESTER G. LUNDSTED

A catalytic method of dehydrogenating hydroaromatic compounds in benzene in the liquid phase[1] has been evaluated against representative pyrrolidines, indolines, hydrocarbazoles and piperidines. A summary of the results obtained in the dehydrogenation of nineteen compounds over the nickel-on-nickel chromite catalyst (Ni·NiCrO) is given in Table I. The temperatures and time intervals required for reaction are less for the heterocyclic compounds than for the carboxylic compounds studied earlier. Several dehydrogenations were accomplished at 250–300°.

TABLE I

DEHYDROGENATION OF PYRROLIDINES AND PIPERIDINES[a]

Compound	°C.	Hours	Yield, %	
1-(*n*-Amyl)-pyrrolidine[5]	300	1.5	79	1-(*n*-Amyl)-pyrrole
	250	3	88	1-(*n*-Amyl)-pyrrole
1-Ethyl-2,3,4,5,-tetramethyl-pyrrolidine[3]	300	1.5	70	1-Ethyl-2,3,4,5-tetramethylpyrrole
2-Ethyl-3,4,5-trimethylpyrrolidine[3]	300	1.5	56	2-Ethyl-3,4,5-trimethylpyrrole
1-Cyclohexylpyrrolidine[4]	350	5	56	1-Cyclohexylpyrrole
1-Phenylpyrrolidine[4]	350	5	53	1-Phenylpyrrole
Indoline[4,6]	200	1	75	Indole[4]
1,2,3,4-Tetrahydrocarbazole[9]	300	3	95	Carbazole[4]
Perhydrocarbazole[4]	350	4	82	Carbazole[4]
9-Ethylperhydrocarbazole[4]	250	1.5	98	9-Ethylcarbazole[4]
2-Phenylpyrrolidine[4]	300	1.5	46	2-Phenylpyrrole[4]
2-Cyclohexylpyrrolidine[4]	300	3	16	2-Phenylpyrrole[4]
Piperidine	350	5	48	Pyridine
α-Pipecoline	350	5	62	α-Picoline
β-Pipecoline	350	5	53	β-Picoline
γ-Pipecoline	350	5	64	γ-Picoline
2,6-Lupetidine	250	5	45	2,6-Lutidine
trans-Decahydroquinoline[8]	350	5	42	Quinoline
cis-Decahydroquinoline[8]	350	5	47	Quinoline
N-Benzoyl-*cis*-decahydroquinoline[8]	350	5	57	Quinoline

[a] Three to 10 g. of the compound in 20–30 ml. of benzene with 1 to 2 g. of the Ni·NiCrO catalyst was held in a 180 ml. chrome vanadium steel vessel.

There is more tendency for the heterocyclic compounds, especially the piperidines, to go to compounds of higher molecular weight during dehydrogenations. Nevertheless the yields with eight compounds containing the pyridine nucleus averaged about 50% of the theoretical. The yields of ten compounds containing the pyrrole nucleus averaged 73%. The yields for compounds having the carbazole nucleus were almost quantitative. The yields of 1-(*n*-amyl)-pyrrole (88%), 1-ethyl-2,3,4,5-tetramethylpyrrole (74%) and 2-ethyl-3,4,5-trimethylpyrrole (69%) appear particularly attractive from a preparational standpoint since these compounds have not been available. Successful dehydrogenations were not accomplished on 1-benzoylpyrrolidene, 1-carbethoxypyrolidine, nicotine or 4-phenylpiperidine. The yield of 2-phenylpyrrole from 2-phenylpyrrolidine was 46% and from 2-cyclohexylpyrrolidine was only 16%.

The nickel-on-nickel chromite catalyst was prepared as described.[2] The compounds submitted to hydrogenation were available through methods used by others in this Laboratory.[3,4,5,6,7,8] The pipecolines and 2,6-lupetidine were made by the hydrogenation of the corresponding pyridine derivatives from commerical sources, over W-4 Raney nickel at 150–175° during an hour or two. 1,2,3,4-Tetrahydrocarbazole m. p. 118–120° was made by the Fischer indole synthesis[9] from the phenylhydrazone of cyclohexanone in a yield of 86%.

The products of reaction indicated in Table I were isolated by conventional methods of distilla-

TABLE II

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR VARIOUS COMPOUNDS

Compound		B. p.				Nitrogen, %		M_D	
Formula	Name	°C.	Mm.	d^{25}_{4}	n^{25}_{D}	Calcd.	Found	Calcd.	Found
$C_{10}H_{15}N$	1-Cyclohexylpyrrole	114	19	0.953[a]	1.5140	9.39	9.29		
$C_9H_{15}N$	1-*n*-Amylpyrrole	80–82	15	.859[a]	1.4694[a]	10.20	10.12	44.33	44.52
$C_{10}H_{17}N$	1-Ethyl-2,3,4,5-tetramethylpyrrole	84–90	9	.899	1.4930	9.26	9.55	49.15	48.77
$C_9H_{15}N$	2-Ethyl-3,4,5-trimethylpyrrole	81–86	10	.895	1.4890	10.20	10.24	44.18	44.04

[a] Determined at 20°.

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[1] References to earlier papers in this series are given by Adkins and Hager, THIS JOURNAL, **71**, 2962 (1949).

(2) Adkins, Richards and Davis, *ibid.*, **63**, 1320 (1941).

(3) Signaigo and Adkins, *ibid.*, **58**, 709 (1936).

(4) Coonradt and Adkins, *ibid.*, **63**, 1563 (1941).

(5) Wojcik and Adkins, *ibid.*, **56**, 2419 (1934).

(6) Adkins and Burks, *ibid.*, **70**, 4174 (1948).

(7) Paden and Adkins, *ibid.*, **58**, 2487 (1936).

(8) Bailey and McElvain, *ibid.*, **52**, 4015 (1930).

(9) Sidgwick, "The Organic Chemistry of Nitrogen," Clarendon Press, 1937, p. 498.

tion, steam distillation, crystallization and use of solid derivatives, as was appropriate to the compounds. The properties and analyses of four pyrroles apparently not reported earlier are given in Table II. Other products were identified through refractive indices, boiling points, melting points and solid derivatives.

Summary

Representative compounds, containing a pyrrolidine or piperidine nucleus, have been dehydrogenated in the liquid phase in benzene over a nickel catalyst, to compounds containing a pyrrole or pyridine nucleus.

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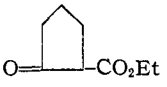
[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Synthesis of Cyclopentanohydronaphthalenes and Hydrophenanthrenes with Substituents in an Angular Position

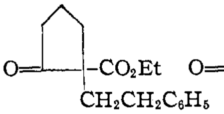
BY HOMER ADKINS AND GLENN F. HAGER[1]

In connection with another investigation,[2] a series of compounds has been made, which have a substituent in an angular position of partially or completely hydrogenated derivatives of 1,2-cyclopentenonaphthalene or 1,2-cyclopentenophenanthrene. The methods used were developments of those described earlier.[3,4,5,6,7,8,9]

The naphthalene derivatives were made through a series of reactions in which 2-carbethoxycyclopentanone (I) was alkylated with β-phenethyl bromide to give the substituted keto ester II. For one group of compounds the keto ester was decarboxylated to the ketone III, and converted to a tertiary alcohol IV, through the use of a Grignard reagent.



I



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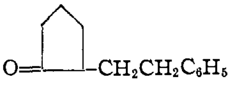

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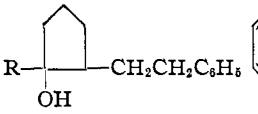
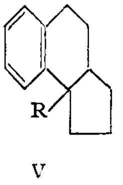
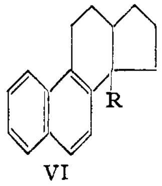


IV



V

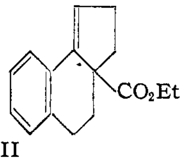


VI

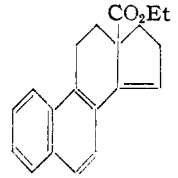
The latter was cyclized to a 1-alkyl-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene (V) where the alkyl group was methyl or *n*-butyl. The parent compound 1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene, where R equals H in formula V, was prepared by reducing the ketone III to an alcohol over copper–chromium oxide, and closing the ring as in converting IV to V.

A group of angular substituted hydrophenanthrenes was prepared, by modifying the synthesis outlined above, through the use of α-$C_{10}H_7$-CH_2CH_2Br instead of $C_6H_5CH_2CH_2Br$ in alkylating the keto ester I. Thus, three 1-alkyl-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrenes (VI) were obtained, where the alkyl group was methyl, ethyl or *n*-butyl.

A modification of the synthesis was made in that the keto ester II was cyclized with liquid hydrogen fluoride to give a 2-carbethoxy-1,2-cyclopenteno-3,4-dihydronaphthalene (VII). The corresponding 2-carbethoxy-1,2-cyclopenteno-3,4-dihydrophenanthrene (VIII) was similarly prepared. In this latter case the cyclization went so rapidly that it was complete within five minutes at 0°. This method of closure gave excellent yields of compounds with a carbethoxy group in an angular position, and seems preferable to that used by Ruzicka and his associates and more recently by Ehmann and Miescher.[10]



VII



VIII

The carbethoxy groups in compounds VII and VIII were hydrogenated to methylol groups and ultimately to the 2-methyl-1,2-cyclopentanodecalin and 2-methyl-1,2-cyclopentanoperhydrophenanthrene. Three catalysts were used in sequence, *i. e.*, copper–chromium oxide, Raney nickel and finally nickel-on-alumina. Several of the dihydro- and tetrahydronaphthalene and phenanthrene derivatives were converted to the corresponding substituted decalins or perhydrophenanthrenes over Raney nickel. The hydrogenated compounds are listed in Table I and the details of hydrogenation are given under the experimental section. Chrysene and 4a-methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene, prepared

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(1) Monsanto Chemical Co. Fellow 1942–1943.

(2) Adkins and Hager, THIS JOURNAL, **71**, 2962 (1949).

(3) Bardhan and Sengupta, *J. Chem. Soc.*, 2520, 2798 (1932).

(4) Kon, *ibid.*, 1081 (1933).

(5) Bougault, *Compt. rend.*, **159**, 745 (1915).

(6) Von Auwers and Möller, *J. prakt. Chem.*, **109**, 124 (1925).

(7) Cook, Haslewood and Robinson, *J. Chem. Soc.*, 667 (1935).

(8) Ruzicka, Ehman, Goldberg and Hosli, *Helv. Chim. Acta*, **16**, 833 (1933).

(9) Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 295 (1936).

(10) Ehmann and Miescher, *Helv. Chim. Acta*, **30**, 413 (1947).