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

Catalytic Dehydrogenation of Hydroaromatic Compounds in Benzene. IV. Aromatization of Compounds Containing an Angular Alkyl Group

BY HOMER ADKINS AND GLENN F. HAGER[1]

The feasibility of the aromatization of a number of naphthalene, phenanthrene and chrysene derivatives containing angular alkyl groups, under conditions used for simple dehydrogenation, has been investigated, in conjunction with James W. Davis and David C. England.[2,3,4]

A summary of the experimental results obtained in the aromatization of a variety of compounds is given in Table I. The per cent. conversions, based upon the amount of compound undergoing reaction, were considerably higher than those given in the table. Except for one or two cases the amount of recovered starting material was such that 80–90% of the compound reacting went to the indicated product. 1-Methyl-1,2-cyclopentanodecalin and 2-methyl-1,2-cyclopentanoperhydrophenanthrene gave 10% yields of naphthalene and phenanthrene, respectively, in addition to 1,2-cyclopentenonaphthalene and 1,2-cyclopentenophenanthrene. No doubt small quantities of compounds not characterized were present in the various reaction mixtures.

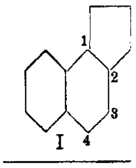
TABLE I

AROMATIZATION IN BENZENE

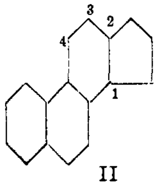
Compound	G. of catalyst	Yield of product, %
1,2-Cyclopentenonaphthalene		
1,2-Cyclopentanodecalin	1 Pd(C)[a]	55
	0.5 Pt(C)	76
	2 Ni·NiCrO	66
1,2-Cyclopentano-1,2,3,4-tetrahydronaphthalene	1 Pd(C)	55
	0.5 Pt(C)	67
	2 Ni·NiCrO	52
1-Methyl-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene	0.5 Pt	52
	2 Ni·NiCrO	40
1-Methyl-1,2-cyclopentano-decalin	2 Ni·NiCrO	45
	0.5 Pt(C)	42
1-(*n*-Butyl)-1,2-cyclopentano-1,2,3,4-tetrahydronaphthalene	2 Ni·NiCrO	22
	0.5 Pt (C)	51
2-Methyl-1,2-cyclopentano-decalin	2 Ni·NiCrO	72
	0.5 Pt (C)	72
2-Carbethoxy-3,4-dihydro-1,2-cyclopentenonaphthalene	0.5 Pt (C)	82
2-Carbethoxy-1,2-cyclopentano-decalin	0.5 Pt (C)	69
1,2-Cyclopentanophenanthrene		
2-Methyl-1,2-cyclopentanoperhydrophenanthrene	0.5 Pt (C)	61
	2 Ni·NiCrO	30
1-Methyl-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene	0.5 Pt (C)	67
	2 Ni·NiCrO	18
1-Methyl-1,2-cyclopentanoperhydrophenanthrene	0.5 Pt (C)	62
	1 Pd (C)	37
	2 Ni·NiCrO	24
1-Ethyl-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene	0.5 Pt	68
	2 Ni·NiCrO	43
1-(*n*-Butyl)-1,2-cyclopentano-1,2,3,4-tetrahydrophenanthrene	0.5 Pt	60
	2 Ni·NiCrO	35
Chrysene		
4a-Methyl-1,2,3,4,4a,11,12,12a-octahydrochrysene	2 Ni·NiCrO	74
	0.5 Pt (C)	64
	1 Pd (C)	65
	2 Ni (k)	53
4a-Methylperhydrochrysene	0.5 Pt (C)	40
	2 Ni·NiCrO	40

[a] The dehydrogenations were on 3-4 g. of compound in a 270-ml. chrome vanadium steel vessel with 20–40 ml. of benzene at 350° for 8–12 hours. A glass liner was used with the palladium catalyst.

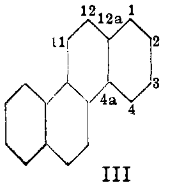
The aromatizations were conducted under rather arbitrarily chosen conditions which were certainly not the optimum, especially from the standpoint of completeness of conversion. The aromatization of 1-methyl-1,2-cyclopentanodecalin was studied under a variety of conditions. The effect of the void in the steel vessel, of various amounts and qualities of benzene, of the addition of thiophene,[5] of ratio of catalyst to compound, of periods of reaction varying from two to twelve hours and of temperatures from 350 to 450°, were determined. The optimum conditions for yield of 1,2-cyclopentanonaphthalene over a Ni·NiCrO catalyst was found to be with equal weights (4 g.) of catalyst and organic compound, 20 ml. of pure benzene containing 40 mg. of thiophene, shaken in a 270-ml. steel vessel at 375° for eight hours. Under these conditions the yield of 1,2-cyclopentenonaphthalene was about 63% of the theoretical as compared with 45% as given in Table I. However, at the lower temperature referred to in the table, 50% of the starting material did not react so that the efficiency of conversion was better at the lower temperature.



I



II



III

A series of eight compounds, related to 1,2-cyclopentenonaphthalene (I), were aromatized to that compound in good yield. These compounds listed in Table I differed from each other in their degree of hydrogenation varying from di to tetra

---

(1) Monsanto Co. Fellow 1942-1943.

(2) Adkins, Richards and Davis, THIS JOURNAL, 63, 1320 (1941).

(3) Adkins and Davis, *ibid.*, 71, 2955 (1949).

(4) Adkins and England, *ibid.*, 71, 2958 (1949).

(5) Adkins, Rae, Davis, Hager and Hoyle, *ibid.*, 70, 381 (1948)

to complete saturation. They also differed in that two of them did not carry a carbon substituent on the ring, while the others had substituents in the angular 1- or 2-positions. Two had methyl groups in the 1-position, one had a *n*-butyl group in the 1-position, two had carbethoxy groups in the 2-position, and one had a methyl group in the 2-position. There was not much difference in the yields of 1,2-cyclopentenonaphthalene from a tetralin as compared with a decalin, although the former was dehydrogenated more rapidly at 350° and could be dehydrogenated under milder conditions than the decalin. The methyl in the 2-position was more readily removed than when in the 1-position. An angular methyl group in the 1-position was more completely removed under the standard conditions than a *n*-butyl group. A carbethoxy group in the 2-position was quite readily eliminated from either the dihydronaphthalene or from the decalin.

The platinum catalyst gave somewhat better yields in most cases than did the nickel on nickel chromate catalyst. However, this is apparently due to a slower rate of aromatization over the nickel catalyst and not to the catalysis of other reactions. Palladium was also an effective catalyst. The nickel on kieselguhr catalyst was uniformly less useful for these compounds than the other catalysts mentioned so that no data for it are given.

A series of five compounds, related to 1,2-cyclopentenophenanthrene (II), were aromatized to that compound. The yields were rather good but somwhat inferior to those obtained for 1,2-cyclopentenonaphthalene discussed above. All of the compounds aromatized carried an angular methyl or ethyl or *n*-butyl group in the 1- or 2-position. There was little difference in the yield of 1,2-cyclopentenophenanthrene from tetra- as compared with perhydrophenanthrene. This is understandable since the conditions required for the elimination of an angular alkyl group are rather drastic, so that the relative ease of dehydrogenation of a tetrahydro as compared with a perhydro compound is not a significant factor in determining yields. The platinum catalyst gave on the average twice as high yields as did the nickel catalyst.

Chrysene (III) was obtained as a minor product (10%) in the aromatization of 2-methyl-1,2-cyclopentanoperhydrophenanthrene through ring expansion over the platinum catalyst. Chrysene was obtained in better yields by England[4] through ring expansion of another phenanthrene, *i. e.*, 1-spirocyclopentano - 1,2,3,4 - tetrahydrophenanthrene. An octahydro- and a perhydrochrysene, with a methyl group in the angular 4a position, gave good yields of chrysene over four different catalysts.

The methods of synthesis and properties of the compounds aromatized are given in another paper.[6] The catalysts were prepared and used as described in an earlier paper[2] except for palladium-on-carbon. This catalyst, carrying about 8% palladium, was prepared by a standard method,[7] and used in a glass liner.

Separation, Characterization and Estimation of Products

The products of reaction were removed from the reaction vessel and catalyst with ether or benzene. The products containing 1,2-cyclopentenonaphthalene were distilled in a 7-ml. modified Claisen flask at less than 1 mm. pressure. Yields were estimated from the refractive index of the distillate, assuming it to be a binary mixture of starting material and 1,2-cyclopentenonaphthalene. The validity of this assumption was justified by various experiments including the formation of various derivatives. Identification of 1,2-cyclopentenonaphthalene (b. p. 118 (0.5 mm.), $n^{25}\text{D}$ 1.6300) was effected by conversion to its picrate (m. p. 109°) and trinitrobenzene (m. p. 121°) derivatives. The products containing 1,2-cyclopentenophenanthrene or chrysene were washed with two portions of about 7 ml. of petroleum ether, b. p. 40–60°, on a sintered glass funnel at −80° by the "Dry Ice technique"[2] to separate aromatic products from starting material. The solid was then distilled evaporatively in a sublimer tube at a pressure of about 0.1 mm. Yields and purity of product were estimated from the weight and m. p. of this distillate. When the distillate contained both 1,2-cyclopentenophenanthrene (m. p. 135°) and chrysene (m. p. 251°), yields were estimated from the melting point of the mixture. The melting points for mixtures containing various proportions of chrysene are: 12.5%, 158°; 25%, 175°; 37.5%, 191°; 50%, 202°; and 75%, 226°. These aromatics were separated by fractional crystallization and identified by conversion to trinitrobenzene derivatives: 1,2-cyclopentenophenanthrene-TNB, m. p. 165° and chrysene-TNB, m. p. 188°.

Summary

Fifteen compounds, in various stages of hydrogenation, related to 1,2-cyclopentenonaphthalene, 1,2-cyclopentenophenanthrene or chrysene and in thirteen cases containing angular substituents, have been aromatized to one of the three compounds just mentioned. Fairly good yields of the aromatic compound have been obtained in benzene under pressure at 350° over platinum, palladium or nickel catalysts.

MADISON, WISCONSIN RECEIVED DECEMBER 10, 1948

---

[6] Adkins and Hager, THIS JOURNAL, **71**, 2965 (1949).

[7] Zelinsky and Turowa-Pollock, *Ber.*, **58**, 1295 (1925).