ion is catalyzed by manganic ion. The reactions of the oxidizing agents iodine and persulfate under the same conditions are not appreciably catalyzed.

The rate of the catalyzed bromine–oxalic acid reaction has been studied over a wide range of the concentration of the substances (except H^+) which affect the rate.

The initial rates in 2 *M* hydrochloric acid agree closely with those observed in the corresponding reaction of chlorine and oxalic acid; this agreement substantiates important conclusions about the mechanism of the changes.

Data obtained for a medium 2 *M* in perchloric acid have led to conclusions about the affinity of manganic ion and oxalate. By adding various complex forming substances—Cl^-, hydrofluoric acid and pyrophosphate—to the medium, it has been possible to reach conclusions also about the affinity of the corresponding anions and manganic ion.

Under certain conditions the kinetics of the catalyst disappearance reaction are identical, and even the rates nearly the same as in the catalyzed chlorine–oxalic acid reaction. At high values of the ratio $(Br^-)^2(H^+)^2/(Mn^{++})(H_2C_2O_4)$, however, the rate of catalyst disappearance is greatly enhanced. Analysis of the data for this concentration region has led to some conclusions about equilibria involving Br_2.

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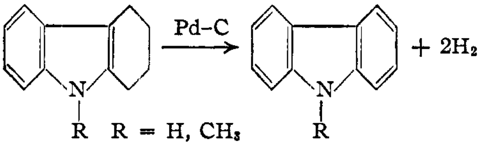
[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF THE UNIVERSITY OF PENNSYLVANIA]

Aromatization Studies. VII. Alkylcarbazoles

BY E. C. HORNING, M. G. HORNING AND G. N. WALKER[1]

Carbazoles are generally prepared by the Graebe–Ullmann method,[2] or by the distillation of tetrahydrocarbazoles over heated lead oxide according to the procedure of Borsche.[3] The thermal decomposition of phenylbenzotriazoles gives good yields of carbazoles in a few cases,[2] but neither method is particularly satisfactory from a preparative point of view. It has now been found that a variety of alkylcarbazoles can be obtained easily by a method involving the aromatization of 1,2,3,4-tetrahydrocarbazoles with a palladium–carbon catalyst. The dehydrogenation reaction is best carried out in a solvent (trimethylbenzene), and the yields are usually nearly quantitative. The necessary 1,2,3,4-tetrahydrocarbazoles were prepared according to the recently published method of Rogers and Corson.[4] This one-step modified indole-type of synthesis provides an excellent way of obtaining alkyl (including N-alkyl) substituted tetrahydrocarbazoles in good yield. The usefulness of this procedure is apparently limited chiefly by the availability of the substituted cyclohexanones and phenylhydrazines which are combined to provide tetrahydrocarbazoles.



Although there is a considerable difference in the ease of hydrogenation of carbazoles and N-alkylcarbazoles, both 1,2,3,4-tetrahydrocarbazole and N-methyl-1,2,3,4-tetrahydrocarbazole undergo dehydrogenation with comparative ease. For all of the compounds investigated here, dehydrogenation occurred readily and there was no evident disproportionation. There was no need to consider the employment of a hydrogen acceptor, and, although no rate studies were made, it is evident that the aromatization required only a comparatively short time for completion. A previous study[5] described the dehydrogenation of several tetrahydrocarbazoles in molten cinnamic acid with a palladium catalyst, but the use of cinnamic acid as a solvent as well as a hydrogen acceptor has not found wide use in aromatization work.

In one case, that of 2,4-dimethyl-3-carboxy-1,2,3,4-tetrahydrocarbazole, the aromatization was accompanied by decarboxylation to give 2,4-dimethylcarbazole as the product. This carbazole was also obtained directly by the aromatization of 2,4-dimethyl-1,2,3,4-tetrahydrocarbazole.

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Experimental

All melting points are corrected.

Catalyst.—A 5% palladium–carbon catalyst was prepared according to Hartung's method.[6]

Dehydrogenation Procedure.—The general procedure is illustrated by the following example. To 5.00 g. of 1,2,3,4-tetrahydrocarbazole in 15 ml. of trimethylbenzene (Eastman Kodak Co. technical grade, redistilled, b. p. 168–172°) was added 1.5 g. of 5% palladium–carbon cata-

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[1] Research Corporation Research Assistant.

[2] Graebe and Ullmann, *Ann.*, **291**, 16 (1896).

[3] Borsche, *Ann.*, **359**, 74 (1908).

[4] Rogers and Corson, THIS JOURNAL, **69**, 2910 (1947).

[5] Hoshino and Takiura, *Bull. Chem. Soc. Japan*, **11**, 218 (1936).

[6] "Organic Syntheses," **26**, 77 (1946).

lyst. The mixture was heated under vigorous reflux for two hours. After cooling to about 50°, the catalyst and crystallized carbazole were removed by filtration. The catalyst was washed free of carbazole with a total of 400 ml. of hot ethyl acetate. The original filtrate was added to the ethyl acetate solution, and the total volume was reduced to about 50 ml. by distillation of the ethyl acetate. After cooling, 100 ml. of pentane was added. The crystalline product separated immediately; it was removed by filtration, washed well with pentane, and air-dried. The yield was 4.67 g. (95%) of colorless leaflets of carbazole, m. p. 244–245°.

An alternate isolation procedure was used in some cases. After the catalyst was separated and washed free of product with hot ethyl acetate, the combined organic solutions were steam distilled to remove all solvents. The crystalline carbazole which remained was removed by filtration and air-dried. In all cases the crude products were colorless, crystalline solids. Analytical samples, where required, were obtained by recrystallization from the solvents indicated in Table I. Yields and properties of the products are in Table I.

TABLE I

DEHYDROGENATION TO CARBAZOLES

Carbazole	Yield, %	M. p., °C.
Carbazole	95	244–245
2-Methyl	90	258–260[a]
3-Methyl	99	205–207[b]
2,4-Dimethyl	100	134–136[c,d]
2-Isopropyl-4-methyl	90	119–121[c,e]
N-Methyl	86	86–88[f]

[a] Reported[3] m. p. 259°. [b] Reported[3] m. p. 203°. [c] Recrystallized from cyclohexane. [d] *Anal.* Calcd. for $C_{14}H_{13}N$: C, 86.11; H, 6.71. Found: C, 86.05; H, 6.76. [e] *Anal.* Calcd. for $C_{16}H_{17}N$: C, 86.05; H, 7.67. Found: C, 86.24; H, 7.76. [f] Reported m. p. 87° (Graebe, *Ann.*, **202**, 23 (1880)).

Preparation of Tetrahydrocarbazoles.—The acetic acid method of Rogers and Corson[4] was used for the preparation of tetrahydrocarbazoles. The properties and yields of these compounds have been reported previously[4] with the exception of the following.

2-Isopropyl-4-methyl-1,2,3,4-tetrahydrocarbazole was obtained from 3-methyl-5-isopropylcyclohexanone in 58% yield; b. p. 183–188° (4 mm.). This product was apparently homogeneous; the isopropyl group is assigned to the 2-position for steric reasons.

Anal. Calcd. for $C_{16}H_{21}N$: C, 84.53; H, 9.31. Found: C, 84.62; H, 9.11.

N-Methyl-1,2,3,4-tetrahydrocarbazole was obtained from cyclohexanone and α-methyl-α-phenylhydrazine[7] in 80% yield; m. p. 49–51° (from methanol).

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.28; H, 8.16. Found: C, 84.17; H, 8.40.

2,4-Dimethyl-3-carboxy-1,2,3,4-tetrahydrocarbazole was prepared from 3,5-dimethyl-4-carboxycyclohexanone and phenylhydrazine; the product was purified with difficulty by recrystallization from methanol–water and ether–pentane. The yield was 45%; m. p. 223–224°.

Anal. Calcd. for $C_{15}H_{17}O_2N$: C, 74.04; H, 7.04. Found: C, 73.98; H, 7.14.

3-Methyl-5-isopropylcyclohexanone.—This ketone was obtained from 3-methyl-5-isopropyl-2-cyclohexen-1-one by catalytic reduction with 5% palladium-carbon in a low pressure apparatus without added solvent. After removal of the catalyst, the ketone was used directly. This compound has been reported by Knoevenagel[8]; the steric configuration of the two alkyl groups is unknown.

3,5-Dimethyl-4-carbethoxycyclohexanone.—Using a low-pressure apparatus, 70.0 g. of 3,5-dimethyl-4-carbethoxy-2-cyclohexen-1-one was reduced with 6.0 g. of 5% palladium–carbon catalyst. After removing the catalyst by filtration, there was obtained 64.0 g. (90%) of colorless oil; b. p. 164–166° (45 mm.).

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.63; H, 9.15. Found: C, 66.32; H, 9.15.

3,5-Dimethyl-4-carboxycyclohexanone.—To 40.0 g. of 3,5-dimethyl-4-carbethoxycyclohexanone in 40 ml. of water and 40 ml. of ethanol was added 16.0 g. of sodium hydroxide. The solution was maintained under vigorous reflux for four hours. After pouring into one liter of water, a neutral fraction was extracted with three 80-ml. portions of ether. The aqueous layer was acidified with 150 ml. of 1:1 hydrochloric acid, and the acid fraction extracted with four 100-ml. portions of ether and 80 ml. of ethyl acetate. The combined organic layers were dried with magnesium sulfate and the solvents removed to yield 28.2 g. of crude product. This was distilled with extensive decomposition to yield 13.0 g. of crystalline material; b. p. 208–212° (30 mm.). Recrystallization from ether–pentane gave a colorless crystalline product, m. p. 163–164.5°.

Anal. Calcd. for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.41; H, 8.02.

Summary

The preparation of a number of alkylcarbazoles by aromatization of the corresponding 1,2,3,4-tetrahydrocarbazoles is described.

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(7) "Organic Syntheses," Coll. Vol. II, 418 (1943).

(8) Knoevenagel, *Ann.*, **297**, 172 (1897).