

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

THE HYDROGENATION OF CERTAIN BRANCHED COMPOUNDS OVER NICKEL

BY HOMER ADKINS, WALTER H. ZARTMAN AND HOWARD CRAMER

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It has been generally recognized that the catalytic hydrogenation of substituted compounds is usually more difficult than in the case of the simpler compounds. Whether this apparent lowering in reactivity is due to spatial effects or otherwise is uncertain, but it seems worth while to study rather completely and carefully the hydrogenation of compounds which may be considered to fall into this group. Therefore the hydrogenations of triphenylcarbinol, triphenylmethane, dicyclohexylphenylmethane, 1,3,5-triphenylbenzene, triphenylamine, 1,3,5-trimethylbenzene and 2,2',4,4',6,6'-hexamethyldiphenyl have been investigated. The experimental methods and apparatus were essentially the same as those previously described.¹

The significance for the present of most of the results reported in this paper lies in the establishment of experimental conditions under which these hydrogenations may be carried out, so that little need be written in addition to the tabulation. There is recorded in Table I a summary of the experimental conditions and results obtained in typical experiments in the hydrogenation of the above list of compounds. There are reported: (1) the name of the compound, (2) the amount submitted to hydrogenation, (3) the amount of hydrogen absorbed, (4) in the time and (5) at the temperature, (6) and pressure, (7) over the catalyst, (8) and in the amount of solvent indicated; (9) the yield(s) of, (10) product(s) having, (11) the physical constants compared with, (12) the physical constants, (13) previously reported.

The most noteworthy observation made in connection with the hydrogenation of these compounds was that water or ethanol inhibited the reduction of the benzenoid ring in dicyclohexylphenylmethane, while they were without effect upon the hydrogenation of two of the benzenoid rings in triphenylmethane. Dicyclohexylphenylmethane was formed quantitatively by the hydrogenation of triphenylcarbinol in alcohol or methylcyclohexane, and of triphenylmethane in alcohol or in methylcyclohexane containing water. Dicyclohexylphenylmethane in ethanol solution absorbed no hydrogen over an active nickel catalyst at 200° under a pressure of 100 atmospheres of hydrogen.

Tricyclohexylmethane was readily formed by the hydrogenation in methylcyclohexane of triphenylmethane or dicyclohexylphenylmethane.

¹ Adkins and Cramer, *THIS JOURNAL*, **52**, 4349 (1930).

TABLE I
HYDROGENATION OF VARIOUS COMPOUNDS OVER NICKEL

Compound Name	Moles	$\frac{\delta}{\delta_0} \frac{H}{H_0}$	$\frac{\delta}{\delta_0} \frac{H}{H_0}$	$\frac{\delta}{\delta_0} \frac{H}{H_0}$	Pressure, atm.	Catalyst, g.	Solvent, ml.	Yields	Product	Physical constants—	
										Found, °C.	Reported, °C.
Triphenylmethane	.10	0.99	2	175	106 ± 17	3 Z 8	C ₇ H ₁₄ 50	A90 B100	Tricyclohexylmethane	M. p. 58.5–59.5	{ M. p. 48, ^a b. p. 340–345 ^b
Triphenylmethane	.10	.97	6.5	200	110 ± 15	3 Z 5	C ₇ H ₁₄ 75	A88 B100	Tricyclohexylmethane	164–165 (3 mm.)	140 (20 mm.) ^c
Triphenylmethane	.10	.61	9	200	122 ± 20	3 Z 8	C ₂ H ₅ OH 75	A78 B100	Dicyclohexylphenylmethane	161–163 (2 mm.)	196–197 (17 mm.) ^a
Triphenylmethane	.10	.62	9	200	123 ± 21	3 Z 8	C ₇ H ₁₄ 50 + H ₂ O, 1.8 g.	A92 B100	Dicyclohexylphenylmethane	169–171 (3 mm.)	210–212 (20 mm.) ^c
Triphenylcarbinol	.10	.83	9	200	106 ± 15	3 Z 8	C ₇ H ₁₄ 50	A87 B100	Dicyclohexylphenylmethane	169–171 (3 mm.)	
Triphenylcarbinol	.10	.80	12	200	110 ± 16	3 Z 8	C ₂ H ₅ OH 75	A90 B100	Dicyclohexylphenylmethane	166–170 (3 mm.)	
Dicyclohexylphenylmethane	.10	.35	6	200	101 ± 13	3 Z 8	C ₇ H ₁₄ 50	A91 B100	Tricyclohexylmethane	M. p. 58.5–59.5	
Triphenylamine	.05	2.5	200	106 ± 22	3 Z 8		C ₇ H ₁₄ 50	A65 B100	Tricyclohexylamine	{ M. p. 160–161	170–171 (4 mm.) ^d
Triphenylamine	.11	1.00	6	175	220 ± 40	2 H. C. 12	C ₇ H ₁₄ 75	A96	Tricyclohexylamine	{ 188–189 (7 mm.)	
Mesitylene	.50	1.61	6	200	110 ± 35	3 Z 7	None	A90 B100	1,3,5-Trimethylcyclohexane	{ 136–138 (740 mm.)	{ 135.5–136 (743 mm.) ^e
Mesitylene	.50	1.60	4	200	108 ± 40	3 Z 7	None	A92 B100	1,3,5-Trimethylcyclohexane	{ 136–138 (740 mm.)	{ 136–140 (760 mm.) ^f
1,3,5-Triphenylbenzene	.10	1.16	12	200	106 ± 17	3 Z 8	C ₇ H ₁₄ 75	A94 B100	1,3,5-Tricyclohexylcyclohexane	{ M. p. 159–160	
1,3,5-Triphenylbenzene	.10	1.12	12	200	98 ± 9	3 Z 5	C ₇ H ₁₄ 75	A86 B100	1,3,5-Tricyclohexylcyclohexane	{ 228–228.5 (3.5 mm.)	
Dimesityl	.10	0.60	18	200	124 ± 23	3 Z 8	C ₇ H ₁₄ 75	A90 B100	2,2',4,4',6,6'-Hexamethylcyclohexyl	123–126 (3 mm.)	

^a Ipatiev and Dolgov, *Compt. rend.*, **185**, 210 (1927); **183**, 304 (1925). ^b Zelinski and Goverdovskaia, *Ber.*, **60B**, 713 (1927); ^c Godchot, *Compt. rend.*, **147**, 1057 (1909). ^d Adams and Hiers, *This Journal*, **49**, 1099 (1927); ^e Adams and Marshall, *ibid.*, **50**, 1970 (1928). ^f J. Klepper, *Chem. Ind.*, Spec. No. 261 (February, 1929) [*Chem. Abstracts*, **23**, 3897 (1929)].

It was found to be a white crystalline substance melting at 58.5–59.5° rather than a liquid as reported by Zelinski and Goverdovskaia and by Godchot or a solid melting at 48° as observed by Ipatiev and Dolgov.

Tricyclohexylamine was found to be a solid melting at 160–161°. Both the absorption of hydrogen in its formation and the analysis of the product indicated quite definitely that the three phenyl groups in triphenylamine had been converted to cyclohexyl groups. Adams and Hiers obtained a liquid as the result of the hydrogenation of triphenylamine over platinum which they reported on the basis of its nitrogen content as being tricyclohexylamine. Their results have been duplicated in this Laboratory but it is believed that the product is not pure tricyclohexylamine. Analyses for carbon and hydrogen on this material were about 2% from the theoretical values. Analyses for nitrogen are not significant in this case because the presence of rather considerable percentages of impurities such as dicyclohexylphenylamine do not greatly modify the nitrogen content.

Symmetrical tricyclohexylcyclohexane and hexamethyldicyclohexyl have been prepared for the first time.

Experimental Part

Triphenylcarbinol (m. p. 162–162.5°), triphenylmethane (m. p. 92–93°), triphenylamine (m. p. 126–126.5°) and mesitylene (1,3,5-trimethylbenzene) (b. p. 163.5–164.5°) were prepared by standard methods. 2,2',4,4',6,6'-Hexamethyldiphenyl (dimesityl) (m. p. 100–100.5°) and the intermediate bromomesitylene were prepared as by Adams and Moyer, and by Smith and MacDougall.² The 1,3,5-triphenylbenzene (m. p. 172–173°) was prepared as by Fischer, Wille and Vorländer.³ Dicyclohexylphenylmethane was prepared by the hydrogenation, as indicated in Table I, of triphenylcarbinol or of triphenylmethane. Both mesitylene and dimesityl were refluxed for many hours over sodium for the removal of traces of halogen-containing compounds. Dimesityl was further treated five times for three or four hours with reduced nickel (no support) in methylcyclohexane at 200° under 100 atmospheres.

The catalysts referred to as H. C. 12, and Z 5 were made as by Cramer. Catalysts Z 7 and 8 were made similarly except that sodium bicarbonate was used as the precipitant for nickel. Catalysts 7 and 8 were different preparations in which the same method was used.

Properties and Analyses of Products.—Tricyclohexylmethane. *Anal.* Calcd. for C₁₈H₃₄: C, 86.93; H, 13.07. Found: C, 86.50, 86.74; H, 13.23, 13.53. Dicyclohexylphenylmethane. *Anal.* Calcd. for C₁₉H₂₆: C, 88.98; H, 11.02. Found: C, 88.65, 88.65; H, 11.24, 11.05; d_{25}^{25} 0.9724; n_D^{25} 1.5372; MR'_D , calcd. 82.07; found, 82.32. 1,3,5-Tricyclohexylcyclohexane. *Anal.* Calcd. for C₂₄H₄₂: C, 87.18; H, 12.82. Found: C, 86.86, 86.94; H, 12.90, 12.84. 2,2',4,4',6,6'-Hexamethyldicyclohexyl. *Anal.* Calcd. for C₁₈H₃₄: C, 86.31; H, 13.69. Found: C, 86.45, 86.57; H, 13.83, 13.75; d_{25}^{25} 0.8932; n_D^{25} 1.4873; MR'_D , calcd. 80.75; found, 80.62. Tricyclohexylamine. *Anal.* Calcd. for C₁₈H₃₃N: C, 82.04; H, 12.64. Found: C, 82.12, 82.29, 82.32; H, 12.63, 12.68, 12.61. Neutral equivalent. Calcd. 263. Found: 265. Hydrobromide

² Adams and Moyer, *THIS JOURNAL*, **51**, 630 (1929); Smith and MacDougall, *ibid.*, **51**, 3002 (1929).

³ Fischer, Wille and Vorländer, *Ber.*, **62**, 2836 (1929).

of tricyclohexylamine (m. p. 267–268°). *Anal.* Calcd. for $C_{18}H_{34}NBr$: Br, 23.21. Found: Br, 23.15. Hydrochloride of tricyclohexylamine (m. p. 264°). *Anal.* Calcd. for $C_{18}H_{34}NCl$: Cl, 11.63. Found: Cl, 11.89. Picrate of tricyclohexylamine (m. p. 172.5–173°). "Tricyclohexylamine" from hydrogenation over platinum, b. p. 171–173° (4 mm.). *Anal.* Calcd. for $C_{18}H_{34}N$: C, 82.04; H, 12.64. Found: C, 84.48, 84.27; H, 10.69, 10.62.

Summary

Experimental conditions for the successful hydrogenation over nickel of triphenylcarbinol, triphenylmethane, dicyclohexylphenylmethane, 1,3,5-triphenylbenzene, triphenylamine, 1,3,5-trimethylbenzene and 2,2',4,4'-6,6'-hexamethyldiphenyl have been determined. Water and ethanol have been found to inhibit the hydrogenation of dicyclohexylphenylmethane. 1,3,5-Tricyclohexylcyclohexane and 2,2'4,4',6,6'-hexamethyldicyclohexyl have been prepared for the first time. Tricyclohexylmethane and tricyclohexylamine have been found to have physical properties very different from those previously reported.

MADISON, WISCONSIN

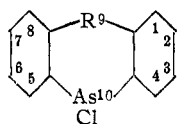
DERIVATIVES OF THE ARSENIC ANALOG OF 9,10-DIHYDROACRIDINE. I¹

BY WILLIAM GUMP AND HUGO STOLTZENBERG

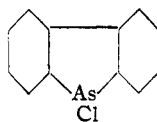
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Compounds of the type represented by the Formula I are known in which R is: NH, (10-chloro-9,10-dihydrophenarsazine);² O, (10-chloro-



I



II

9,10-dihydrophenoxarsine);³ S, (10-chloro-9,10-dihydrophentharsine);⁴ AsCl, (9,10-dichloro-9,10-dihydroarsanthrene).⁵ This series contains the arsenic as a hetero atom in a six-membered ring; an example of a five-membered ring is the *o,o'*-diphenylene arsenious chloride (II).⁶

The synthesis of these compounds can be accomplished in the cases of R=NH and O by heating arsenic trichloride with diphenylamine and with diphenyl ether, but this reaction does not take place with diphenyl,

¹ Read before the Division of Organic Chemistry at the 77th meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

² Bayer and Co., German Patent 281,049 (1913); Wieland and Rheinheimer, *Ann.* **439**, 1 (1921).

³ Lewis, Lowry and Bergeim, *THIS JOURNAL*, **43**, 891 (1921); Turner and Sheppard, *J. Chem. Soc.*, **127**, 544 (1925).

⁴ Roberts and Turner, *ibid.*, **129**, 1207 (1926).

⁵ Kalb, *Ann.*, **423**, 39 (1921).

⁶ Aeschlimann and co-workers, *J. Chem. Soc.*, **127**, 66 (1925).