from the cooled filtrate. A single recrystallization from ethanol raised the melting point to 143.5–144.0°. The weight of derivative so obtained generally corresponded to an additional 3–5% recovery of cyclopentanone. A summary of two experiments carried out in this way is found in Table I.

W. LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Reductions at Metal Surfaces. III. Clemmensen Reduction of Some Sterically-hindered Ketones

BY JAMES H. BREWSTER, JOAN PATTERSON AND DELMER A. FIDLER

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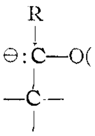
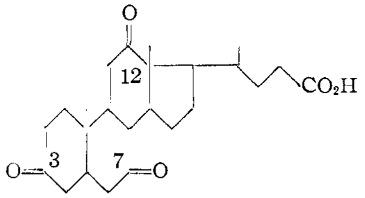
Pinacolone is reduced slowly and with difficulty to neohexane; tetramethylethylene could not be detected in the reaction product. Under the same conditions pinacolyl alcohol is converted to tetramethylethylene. Nearly equivalent amounts of neopentylbenzene and 2-methyl-3-phenyl-2-butene are formed in the reduction of pivalophenone; no 2-methyl-3-phenylbutane is produced under these conditions. Phenyl-*t*-butylcarbinol also forms neopentylbenzene and 2-methyl-3-phenyl-2-butene; in this case the latter predominates. The olefin is not reduced under these conditions. Benzopinacolone is reduced to tetraphenylethylene; no *unsym*-tetraphenylethane could be detected in the product. These results lend support to some of the conclusions of parts I and II. They also indicate that a phenyl ketone can be reduced by way of the corresponding alcohol, without intervention of the chloride or of a carbonium ion.

Reductions of carbonyl compounds by means of active metals appear to involve coördination of a metal surface with the carbonyl group to form I in neutral or alkaline medium or II in acidic medium.[1] In the presence of proton donors I reacts to form an alcohol; II can react to form a pinacol or be reduced to a hydrocarbon, as in the Clemmensen reduction.[2] Hindrance to the formation of II should make normal Clemmensen reduction difficult and might permit other reactions, involving alcohols as intermediates, to become important.

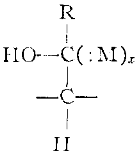


$$\ominus{:}\underset{\substack{|\\ -\mathrm{C}-\\ |}}{\overset{\substack{\mathrm{R}\\ |}}{\mathrm{C}}}-\mathrm{O}(:\mathrm{M})_x^{\oplus}$$

I

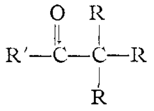


IV



$$\mathrm{HO}-\underset{\substack{|\\ -\mathrm{C}-\\ |}}{\overset{\substack{\mathrm{R}\\ |}}{\mathrm{C}}}(:\mathrm{M})_x^{\oplus}$$

II



$$\mathrm{R'}-\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{C}}-\underset{\substack{|\\ \mathrm{R}}}{\overset{\substack{\mathrm{R}\\ |}}{\mathrm{C}}}-\mathrm{R}$$

IIIa, R′ = R = $-CH_3$
b, R′ = R = $-C_6H_5$
c, R′ = $-C_6H_5$; R = $-CH_3$

Substituents *alpha* to the carbonyl group should hinder the formation of II. It is reported, without details, that pinacolone (IIIa) is reduced to only a small extent under "Clemmensen conditions."[3] The carbonyl group at the 3-position of dehydrocholic acid (IV) is reduced more easily than are the keto groups at the more highly hindered 7- and 12-positions.[4] In the present work, the reduction of pinacolone with excess 10% zinc amalgam in aqueous hydrochloric acid was found, qualitatively, to be much more difficult than the reduction of unbranched aliphatic ketones.[2] Neohexane (usually about 14%) was the only hydrocarbon product formed at the end of eight hours[5]; about 50% of the starting ketone usually was recovered. The nature of the zinc, the extent of amalgamation and the presence of impurities in the acid had no effect on these results. Pinacolyl alcohol was not reduced under these conditions but was dehydrated to tetramethylethylene. These findings constitute further evidence that neither the alcohol nor the chloride derived from it are intermediates in Clemmensen reductions in the aliphatic series[2]; in this case, at least, the chloride would have had a rearranged carbon skeleton. The absence of olefin in the reaction product is evidence that the formation of an alcohol from IIIa is difficult under these conditions.

Competition between reactions proceeding through intermediates I and II would be expected to be more pronounced in the series of aryl ketones. Here, the positive charge of the protonated ketone V is delocalized and the resonance of V would be diminished in the formation of II. On the other hand, the unprotonated ketone should form an intermediate such as I more readily since the carbanionic structure VI can be stabilized by resonance. In accord with these conclusions, Clemmensen found that under some conditions (see below) styrene, rather than ethylbenzene, was the chief reduction product of acetophenone.[6] In the case of benzopinacolone (IIIb), the rearranged olefin, tetraphenylethylene, is the only hydrocarbon product formed.[7]

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(1) Part I, THIS JOURNAL, **76**, 6361 (1954).

(2) Part II, *ibid.*, **76**, 6364 (1954).

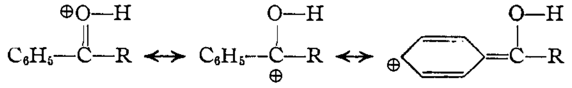
(3) J. P. Wibaut, H. Hoog, S. L. Langendijk, J. Overhoff and J. Smittenberg, *Rec. trav. chim.*, **58**, 329 (1939).

(4) (a) W. Borsche, *Ber.*, **52**, 1353 (1919); (b) H. Wieland and O. Schlichting, *Z. physiol. Chem.*, **150**, 267 (1925).

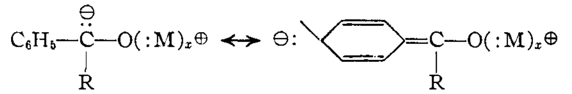
(5) It was originally reported, J. H. Brewster, XIIth Congress of Pure and Applied Chemistry, New York, N. Y., Sept., 1951, that tetramethylethylene was formed as a by-product in this reduction. The pinacolone used in this work was a *redistilled* commercial sample; when this sample was further purified by *rectification* it gave no olefin in numerous attempts to repeat the earlier work. Pinacolone prepared by rearrangement of pinacol hydrate likewise gave no olefin. It has, unfortunately, proved impossible to check the hypothesis that the original sample of ketone contained some pinacolyl alcohol.

(6) E. Clemmensen, *Ber.*, **46**, 1837 (1913).

(7) W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923). We have confirmed this finding; the infrared spectrum of the product contained none of the characteristic peaks of an authentic sample of *unsym*-tetraphenylethane.



V



VI

Clemmensen reduction of pivalophenone (IIIc) in strongly acidic medium and in the presence of an excess of zinc amalgam affords nearly equivalent amounts of neopentylbenzene and 2-methyl-3-phenyl-2-butene. The infrared spectrum of the product showed none of the characteristic peaks of 2-methyl-3-phenylbutane (authentic sample). The olefin was not reduced under these conditions. Phenyl-*t*-butylcarbinol, the alcohol corresponding to IIIc, was, however, reduced to a mixture consisting of about 25% neopentylbenzene and a 75% 2-methyl-3-phenyl-2-butene. These results show that in the aromatic series an alcohol can be formed and further that it can be reduced *directly and without rearrangement* to an alkylbenzene. It seems clear that at least one-third of the neopentylbenzene produced in the reduction of the ketone must have been formed by reduction of the alcohol. Inasmuch as this alcohol is formed slowly and at or near the metal surface, it is possible that all of the neopentylbenzene was formed in this way. Since no rearranged alkyl benzene was found in these studies it seems doubtful that the alcohol is reduced by way of the chloride. This finding is in accord with Martin's[8] postulate that benzyl alcohol is an intermediate in the reduction of benzaldehyde; it renders unnecessary, but does not wholly disprove, his postulate that benzyl chloride is also an intermediate. It further permits a correlation of the Clemmensen reduction with the reduction of *o*-benzylbenzoic acid to benzylbenzoic acid by means of zinc and sodium hydroxide,[8] since here an alcohol would be the expected intermediate. In this case, at least, acid is not needed for reduction of the alcohol.

At present, the only evidence indicating that aryl ketones can be reduced to alkylbenzenes by way of an intermediate such as II is Clemmensen's[6] finding that acetophenone gives styrene on reduction in weakly acidic medium but ethylbenzene in strongly acidic medium. The reduction of an alcohol would not appear to require the presence of acid; the dehydration of an alcohol is, however, acid catalyzed. If, then, an alcohol were an obligatory intermediate in the reduction, more olefin should be formed in strongly acidic medium. The intervention of a mechanism of reduction *via* II, which should be favored in strongly acidic medium, could account for Clemmensen's observations.

Experimental

Pinacolone.—Reproducible results[5] could be obtained by use of pinacolone prepared by rearrangement[9] of pinacol hydrate.[10] The product was purified by rectification through a column packed with glass helices, b.p. 104°, $n^{20}\text{D}$ 1.3963, lit. b.p. 104–106°.[9]

Methyl-*t*-butylcarbinol was prepared by reduction of pinacolone with sodium and wet ether[11]; b.p. 118–120°, $n^{20}\text{D}$ 1.4148; lit. b.p. 120°, $n^{20}\text{D}$ 1.4148.[12]

Benzopinacolone was prepared from benzopinacol[13] by rearrangement with acetic acid[14]; m.p. 179–180°, lit. 179–180°.[14] The infrared spectrum[15a] contained the following important peaks (Nujol): *5.97*, *6.26*, *6.34*, 6.70, 6.93, *8.25*, 8.49, *11.91*, *12.71*, *12.86*, 13.31, 13.45, *14.20*, 14.37, *14.69* μ.[16]

unsym-**Tetraphenylethane** was prepared from benzylmagnesium chloride[17] and triphenylchloromethane by the method of Gomberg and Cone[18]; m.p. 144°, lit. 144°.[18] The infrared spectrum[15a] contained the following important peaks (CS_2): 3.42, *3.52* (sh), *8.12*, *8.50*, *8.72*, 9.33, *9.72*, 10.04, 10.30, *10.70*, *13.05*, *13.21*, 13.51, 14.35 μ.[16]

Pivalophenone was prepared in 71–84% yield from pivalonitrile[19] and phenylmagnesium bromide using the method of Pearson.[20] The product was rectified through a column packed with glass helices. Most of the material distilled at 78–79° (5 mm.), 84–86° (8 mm.), and had $n^{20}\text{D}$ 1.5094; lit. b.p. 97–98° (16 mm.),[21a] $n^{25}\text{D}$ 1.5082,[20] $n^{20}\text{D}$ 1.5102,[21b] $n^{19.2}\text{D}$ 1.5086.[21c] The 2,4-dinitrophenylhydrazone had m.p. 190–190.5° (uncor.); lit. 194–195°.[21b] The infrared spectrum[15b] had the following important peaks (homog.): (3.30, 3.44), *5.95*, (6.26, 6.32), (6.79, 6.86, 6.94), 7.18, 7.34, *7.87*, (*8.43*, 8.55), 9.32, (9.67, 9.78), 10.01, *10.47*, 11.85, 12.27, *12.61* μ.[16]

***t*-Butylphenylcarbinol** was prepared by reduction of pivalophenone with lithium aluminum hydride under dry, oxygen-free nitrogen. Pivalophenone (60 g., 0.37 mole) was added dropwise, over a period of one hour, to a stirred suspension of 5 g. (0.125 mole) of lithium aluminum hydride in 200 ml. of dry ether. After the addition, the reaction mixture was heated under gentle reflux for one hour. At the end of this time the mixture was cooled and sufficient water was added to decompose the unreacted hydride. The reaction mixture was neutralized with 2.5 l. of a saturated solution of ammonium chloride. The ether layer was removed and the aqueous solution was extracted with three 100-ml. portions of ether. The ethereal solutions were combined and washed three times with 200-ml. portions of 5% sodium bicarbonate solution and once with water; the ether layer was dried over magnesium sulfate.

The ether solution was filtered and the ether was evaporated. *t*-Butylphenylcarbinol crystallized when the residue was cooled. The product was recrystallized from petroleum ether (35–40°); 54 g. (90%), m.p. 43°, was so obtained. A purer product, m.p. 44.5°, was obtained by sublimation under vacuum; lit. m.p. 45°.[22] The following peaks were prominent in the infrared spectrum of this material (CCl_4)[15a]: *2.90*, 3.39, *6.48*, 6.75, *6.87*, *7.18*, 7.34, 7.76, *8.12*, *8.25*, 8.55, *9.25*, *9.55*, 9.74, *9.95*, 11.17 μ.[16]

α-Phenylneopentyl chloride was prepared from *t*-butylphenylcarbinol by reaction with thionyl chloride[23]; b.p. 89–90° (6–7 mm.), $n^{20}\text{D}$ 1.5161; lit. b.p. 89.5–90.5° (6.7

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[8] E. L. Martin, THIS JOURNAL, **58**, 1438 (1936).

[9] G. A. Hill and E. W. Flosdorf, in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 462.

[10] R. Adams and E. W. Adams, *ibid.*, p. 459.

[11] A. Richard, *Ann. chim.*, [8] **21**, 346 (1910).

[12] F. C. Whitmore and P. L. Meunier, THIS JOURNAL, **55**, 3721 (1933).

[13] M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 236 (1927).

[14] W. E. Bachmann, in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 73.

[15] Infrared spectra by T. R. Riethof, C. Ward and P. Kinsey of this department. The complete spectra are to be found in: (a) D. A. Fidler, M.S. Thesis, Purdue University, 1953; (b) J. Patterson, M.S. Thesis, Purdue University, 1952.

[16] The italicized values refer to peaks thought to be sufficiently strong and characteristic to be used for identification in the mixtures encountered in this work.

[17] H. Gilman and W. E. Catlin, in "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 471.

[18] M. Gomberg and L. H. Cone, *Ber.*, **39**, 1461 (1906).

[19] Generously donated by E. I. du Pont de Nemours & Co., Inc., Electrochemical Division.

[20] D. E. Pearson, THIS JOURNAL, **72**, 4169 (1950).

[21] (a) P. L. de Benneville, *J. Org. Chem.*, **6**, 462 (1941); (b) J. H. Ford, C. D. Thompson and C. S. Marvel, THIS JOURNAL, **57**, 2619 (1935); (c) K. v. Auwers, *Ber.*, **45**, 2764 (1912).

[22] A. Lepin, *J. Russ. Phys. Chem. Soc.*, **44**, 1165 (1912); *Chem. Zentr.*, **83**, II, 2080 (1912).

[23] S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1133 (1952).

mm.), $n^{25}\mathrm{D}$ 1.5142.[23] The infrared spectrum (homog.)[15a] showed prominent peaks at 3.41, (6.25, 6.31), (6.70, 6.76, 6.90), 7.18, 7.33, *8.00*, 8.15, *8.54*, 9.29, 9.76, 11.15, *12.00*, *12.75*, 13.30, 13.76, 14.33 μ.[16]

Neopentylbenzene was prepared from benzylmagnesium chloride[17] and *t*-butyl bromide essentially by the method of Bygden.[24] The crude product was purified by rectification through a column packed with glass helices; b.p. 75–76° (20 mm.), $n^{20}\mathrm{D}$ 1.4890; lit. $n^{25}\mathrm{D}$ 1.4885.[25] The infrared spectrum of this material[15a] had the following prominent peaks (homog.): 3.34 (sh), 3.42, (6.25, 6.32), (6.70, 6.79, 6.90), *7.20*, *7.35*, *8.10*, *8.36*, 8.78, 9.31, *9.71*, *11.15*, 13.00, 14.00, 14.35 μ.[16]

2-Methyl-3-phenyl-2-butene was prepared by oxalic acid dehydration of the alcohol formed by reaction of acetophenone with isopropylmagnesium bromide.[26] The alcohol underwent dehydration on attempted rectification and was therefore treated directly with oxalic acid. The product obtained in this way contained considerable acetophenone, as shown by its infrared spectrum. The ketone was removed by use of 2,4-dinitrophenylhydrazine in methanol containing a little sulfuric acid. The recovered olefin was twice distilled through a modified Widmer column; b.p. 63–64° (6–8 mm.), $n^{20}\mathrm{D}$ 1.5221; lit. b.p. 70° (8 mm.), $n^{20}\mathrm{D}$ 1.51635,[22] $n^{19.8}\mathrm{D}$ 1.5200.[26] The infrared spectrum[15b] of this material showed the following major peaks (homog.): 3.30–3.50, 6.23, 6.35, 6.72, *6.94*, *7.28*, *7.75*, *8.31*, *8.84*, 9.33, *9.76*, *11.01*, 13.15, 14.32 μ.[16]

2-Methyl-3-phenylbutane was prepared by catalytic hydrogenation of the olefin in ethanol over Raney nickel at 2–3 atm. (one week required for theoretical consumption of hydrogen). The product was distilled through a 50-cm. modified Widmer column, the middle cuts, b.p. 56–58° (5–8 mm.), $n^{20}\mathrm{D}$ 1.4913–1.4919 being taken; lit. b.p. 184° (760 mm.), $n^{20}\mathrm{D}$ 1.4882,[25] $n^{16}\mathrm{D}$ 1.4972.[27] Although the product reacted to a slight extent with permanganate in acetone, the infrared spectrum[15b] showed it to be free of the olefin. The following were the principal absorption peaks observed (homog.): 3.42, 6.25, 6.70, 6.90, 7.29, *7.95*, *8.57*, *9.25*, *9.50*, *9.87*, 11.07, 13.02, 13.36, *13.89*, 14.35 μ.[16]

Zinc amalgams were prepared as described in part II.[2]

Clemmensen Reduction of Pinacolone.—A 10% amalgam of zinc was prepared from 130 g. (2.0 atom) of zinc (Mallinckrodt, Analytical Reagent, 20 mesh, granular) and covered with 250 ml. of water. To this was added 25 g. (0.25 mole) of pinacolone (above) and 250 ml. of 37% hydrochloric acid (Baker and Adamson, C.P.). The mixture was heated for eight hours under reflux, during which time a Dry Ice trap was connected to the condenser. About 10 ml. of liquid collected in the trap; this was taken up in cumene (b.p. 150–152°) and the solution was washed with 5% sodium bicarbonate solution and then with water. The cumene solution was dried over magnesium sulfate and rectified through a column packed with glass helices under a reflux ratio of 20:1. There was obtained 3 g. (13.6%) of neohexane in four fractions, b.p. 48–50°, $n^{20}\mathrm{D}$ 1.3685; lit. b.p. 49.82° (760 mm.),[28a] $n^{20}\mathrm{D}$ 1.3692,[28a] $n^{20}\mathrm{D}$ 1.3675,[28b] $n^{20}\mathrm{D}$ 1.3688.[3] No tetramethylethylene (b.p. 73°, $n^{20}\mathrm{D}$ 1.4115[29]) could be detected by distillation or tests for unsaturation.

The reaction mixture was cooled and then was extracted with cumene; the cumene solution was washed with 5% sodium bicarbonate solution and then with water and finally dried over magnesium sulfate. The cumene solution was rectified as before. There was obtained 12.5 g. (50% recovery) of pinacolone, b.p. 104–106°, $n^{20}\mathrm{D}$ 1.3963.

The aqueous layer was neutralized with 40% sodium hydroxide, saturated with salt and steam distilled. The distillate was saturated with salt and extracted with ether. No further product was obtained by distillation of the ether.

The same yields of neohexane and pinacolone were obtained when the reaction time was extended to 24 hours. When the reaction time was extended to 170 hours, with 20 ml. of 37% hydrochloric acid added every 24 hours, neohexane (4.5%—probably some loss by volatilization) and pinacolone (52% recovery) were again the only products obtained. These results were not significantly changed when mossy zinc was used, with technical hydrochloric acid (containing iron), or a 2% amalgam.

Clemmensen Reduction of Pinacolyl Alcohol.—Pinacolyl alcohol (above) (10 g., 0.1 mole) was subjected to the conditions used in the reduction of pinacolone for eight hours. The products were isolated in the same manner. There were obtained 3.9 g. (47.5%) of tetramethylethylene, b.p. 72–73°, $n^{20}\mathrm{D}$ 1.4110 (lit. b.p. 73.3°, $n^{20}\mathrm{D}$ 1.4115[29]) and 2 g. (20%) of the carbinol. No neohexane could be isolated by distillation.

Clemmensen Reduction of Benzopinacolone.—Benzopinacolone (5 g., 0.014 mole), 250 ml. of ethanol and 50 g. of a 7% zinc amalgam were placed in a 1-l. flask fitted with an efficient condenser. Then 100 ml. of 37% hydrochloric acid was added and the mixture was heated under reflux for three hours. The solution was cooled and filtered. The precipitate was washed with ethanol and recrystallized from acetic acid to give 3.9 g. (80%) of tetraphenylethylene m.p. 224°; lit. m.p. 220°,[7] 224°.[30] The infrared spectrum of this material[15a] showed the following principal peaks (CS_2): 3.39, *9.38*, *9.77*, *11.75*, *12.95*, 13.30, 13.49, 14.40 μ.[16] The characteristic peaks of benzopinacolone and of *unsym*-tetraphenylethane were absent

This reduction was repeated with 300 g. of calcium chloride added. The infrared spectrum of the low-melting (150–170°) product showed that benzopinacolone and tetraphenylethylene were present, but that *unsym*-tetraphenylethane was absent.

Clemmensen Reduction of Pivalophenone.—An amalgam prepared from 110 g. of mossy zinc and 11.0 g. of mercuric chloride was covered with 160 ml. of water, 150 ml. of 37% hydrochloric acid and 32.2 g. (0.2 mole) of pivalophenone. The mixture was heated under reflux for a total of 172 hours; with additional zinc amalgam (from 55.0 g. of zinc and 5.5 g. of mercuric chloride) at the end of 96 hr. Each day 20 ml. of 37% hydrochloric acid was added with a further 55 ml. of acid and the fresh amalgam for a total of 325 ml. of acid.

At the end of the reaction period the reaction mixture was cooled and the layers were separated. The aqueous layer was extracted with five 75-ml. portions of ether. The organic solutions were combined, washed with sodium bicarbonate solution and dried over magnesium sulfate. The solution was filtered, the ether was distilled and the residue was rectified at 4–6 mm. to give 24.7 g. of hydrocarbon product in 14 fractions. The first fraction had b.p. 51–54° (4–5 mm.), $n^{20}\mathrm{D}$ 1.4909; the last portion had b.p., 59–60° (4–5 mm.), $n^{20}\mathrm{D}$ 1.5222.

Tests with bromine and permanganate showed that the high-boiling fractions contained olefin while the low-boiling fractions were nearly olefin-free. Attempts to remove the olefins from the lower-boiling fractions by oxidation with permanganate or by extraction with sulfuric acid failed. The low-boiling fraction was shown to consist mainly of neopentylbenzene by nitration, reduction and acetylation, using the method of Ipatieff and Schmerling.[25,31] The derivative, *p*-acetamidoneopentylbenzene, melted at 163.5–164.5° (cor.), lit. 164°.[25] The four lower-boiling fractions were combined and redistilled. The infrared spectrum[15b] of the product was superimposable on that of an authentic sample of neopentylbenzene[15a] except for two additional small peaks at 13.37 and 13.61 μ found in the spectrum of the reduction product. These peaks are absent in the crude hydrocarbon mixture and appear to be adventitious. The higher boiling fraction was identified as nearly pure 2-methyl-3-phenyl-2-butene by a comparison of its infrared spectrum with that of an authentic sample of the olefin.[15b] A comparison of these spectra with those for the ketone[15b] (above),

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(24) A. Bygden, *Ber.*, **45**, 3479 (1912).

(25) V. N. Ipatieff and L. Schmerling, THIS JOURNAL, **60**, 1476 (1938). A value of $n^{20}\mathrm{D}$ 1.4870 for pure neopentylbenzene is given by E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949), who report that neopentylbenzene prepared by the method of Bygden[24] is contaminated by 4-methyl-*t*-butylbenzene. The infrared spectrum of this substance (A.P.I. Research Project 44, Serial #1421, Carnegie Technical Institute, Pittsburgh, Pa., 1953) has strong peaks at 6.07, 6.59, 7.87, 9.00, 9.80 and 12.26 μ; these peaks are not present at all in the spectra of our samples prepared as described above and by Clemmensen reduction.

(26) K. v. Auwers and F. Eisenlohr, *J. prakt. Chem.*, [2] **82**, 65 (1910).

(27) A. Klages, *Ber.*, **36**, 3688 (1903).

(28) (a) P. L. Cramer and M. J. Mulligan, THIS JOURNAL, **58**, 373 (1936); (b) C. R. Noller, *ibid.*, **51**, 594 (1929).

(29) I. Schurman and C. E. Boord, *ibid.*, **55**, 4930 (1933).

(30) J. Schmidlin, *Ber.*, **39**, 4198 (1907).

(31) (a) E. Berliner and F. Berliner, THIS JOURNAL, **71**, 1195 (1949); (b) V. N. Ipatieff and L. Schmerling, *ibid.*, **59**, 1056 (1937).

alcohol[15a] (above) and chloride[15a] (above) showed these substances to be absent, as was 2-methyl-3-phenylbutane[15b] (above). The crude hydrocarbon product had a spectrum that was a simple composite of that of neopentylbenzene and 2-methyl-3-phenyl-2-butene. For this reason it seemed safe to analyze the rectification fractions by refractive index (below). On this basis, the reduction product in this experiment contained a total of 13.3 g. (45%) of neopentylbenzene and 11.4 g. (39%) of 2-methyl-3-phenyl-2-butene.

In a similar experiment, in which fresh acid was added only when new zinc amalgam was put in, the yields were 30% of neopentylbenzene and 30% of the olefin.

When the reduction was carried out as above, changing only the amount of ketone (8.0 g., 0.5 mole) and using 160 ml. of methanol instead of water, there was obtained 3 g., b.p. 60° (10 mm.), $n^{20}\text{D}$ 1.5079. This value corresponds to 43% neopentylbenzene (17% yield) and 57% of the olefin (23%).

Clemmensen Reduction of *t*-Butylphenylcarbinol.—*t*-Butylphenylcarbinol (8.0 g., 0.05 mole) was reduced in aqueous methanol under the conditions described immediately above. There was obtained 4 g. of hydrocarbon, b.p. 70° (18 mm.), $n^{20}\text{D}$ 1.5141. The infrared spectrum showed the product to consist mainly of the olefin together with a small amount of neopentylbenzene. The refractive index corresponds to 24% (14% yield) neopentylbenzene and 76% (42% yield) of the olefin.

When this reduction was carried out using only water as a solvent there was obtained 4 g., b.p. 55–60° (10 mm.), $n^{20}\text{D}$ 1.5171, corresponding to 15% (5% yield) neopentylbenzene and 85% (26% yield) of the olefin.

A sample of 2-methyl-3-phenyl-2-butene was subjected to the conditions described immediately above. The infrared spectrum of the recovered hydrocarbon gave no evidence for the presence of neopentylbenzene.

Analysis of Hydrocarbon Mixtures by Refractive Index.—Mixtures of freshly distilled 2-methyl-3-phenyl-2-butene and neopentylbenzene were prepared. The refractive index *vs. weight* % olefin curve was a straight line.

Olefin, wt. %	$n^{20}\text{D}$	Olefin, wt. %	$n^{20}\text{D}$
0	1.4890	54.22	1.5066
16.94	1.4947	77.40	1.5142
25.84	1.4978	100.00	1.5221

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[CONTRIBUTION FROM DEFENCE RESEARCH CHEMICAL LABORATORIES AND CANADIAN ARMAMENT RESEARCH AND DEVELOPMENT ESTABLISHMENT]

The Structures of Nitroguanidine, 2-nitriminoimidazolidine and 1-Nitro-2-nitriminoimidazolidine[1]

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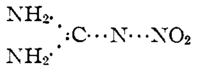
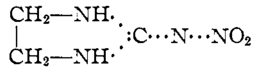
The behavior in alkaline solution of 1-nitro-2-nitriminoimidazolidine and 2-nitriminoimidazolidine has been investigated. It is shown that evidence from potentiometric titrations and methylation studies of these compounds is an unreliable guide to their structure.

Introduction

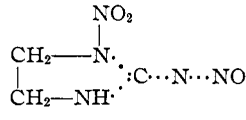
There have been several attempts described in the literature to clarify the structure of nitroguanidine and related compounds. McKay, Picard and Brunet[2] on the basis of ultraviolet spectra regarded nitroguanidine as a resonance hybrid to which forms with charge separation make a considerable contribution. On the other hand, Wright, *et al.*,[3,4] on the evidence of potentiometric titrations and methylation studies of these compounds assigned a simple nitrimine structure to them. Finally, Kumler[5] and Kumler and Sah[6] on the basis of dipole moment and acid strength measurements concluded that the above compounds are probably resonance hybrids with, however, only small contributions from forms with separation of charge. All authors are agreed that the basic nuclear skeleton is the symmetrical one



I, for nitroguanidine



II, for 2-nitriminoimidazolidine



III for 1-nitro-2-nitriminoimidazolidine

In view of this agreement the present authors concede that structures such as II and III should be named nitrimines in the absence of a better term for the actual structures which in their view are resonance hybrids. This reverses the previous stand of McKay, *et al.*,[2] of using the classical names (*e.g.*, 2-nitramino-2-imidazoline for II). The traditional names give an erroneous description of the atomic skeleton and have led to confusion and to some quite undeserved criticism of the authors.[4]

It is realized that the final proof of the structure of nitroguanidine and related compounds will probably be given by crystal structure analysis. However, it is the purpose of the present paper to show that the evidence as to structure obtained from potentiometric titrations and methylation of these compounds is unreliable, and as regards the former to present chemical evidence for the complexity of the behavior of these compounds in alkaline solution.

The discussion concerning the structures of nitroguanidine, 2-nitriminoimidazolidine and 1-nitro-2-nitriminoimidazolidine will be confined to the last two compounds as there is general agreement that the structures of the first two are similar.

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[1] Issued as D.R.C.L. Report No. 118.

[2] A. F. McKay, J. P. Picard and P. E. Brunet, *Can. J. Chem.*, **29**, 746 (1951).

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[5] W. D. Kumler, *ibid.*, **18**, 676 (1953).

[6] W. D. Kumler and P. P. T. Sah, *ibid.*, **18**, 669 (1953).