[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DEPAUW UNIVERSITY AND THE RESEARCH DIVISION OF COMMERCIAL SOLVENTS CORPORATION]

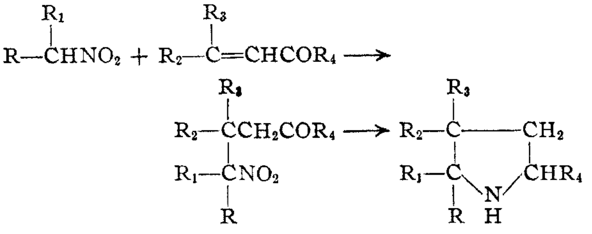
Reactions of Nitroparaffins. I. Synthesis and Reduction of Some γ-Nitroketones

BY MILTON C. KLOETZEL[1]

Catalytic reduction of γ-nitroketones over platinum at atmospheric pressure has been found by Kohler and Drake[2] to yield a variety of products depending upon the nature of the nitroketone. 5-Nitro-4-phenyl-2-pentanone (I) yielded primarily 2-methyl-4-phenylpyrrolidine (VI); 4-nitro-1,3-diphenyl-1-butanone (II) and 3-(3′,4′-methylenedioxyphenyl)-4-nitro-1-phenyl-1-butanone, however, yielded but small quantities of pyrrolidine derivatives.

In the course of the present investigation a number of γ-nitroketones were subjected to catalytic reduction over Raney nickel, both in the presence and absence of ammonia. Substituted pyrrolidines were invariably the principal products.

The requisite nitroketones (Type I–V) were prepared by condensation of nitroparaffins with appropriate α,β-unsaturated ketones. Several Michael condensations of this type, involving the addition of nitromethane to benzalacetone, benzalpinacolone and benzalacetophenones, and of nitroethane and 2-nitropropane to benzalacetophenone have been reported by Kohler, *et al.*,[2–6] who recommended the use of sodium methoxide as catalyst.[7] Nitromethane has also yielded trimolecular condensation products with benzalacetophenone in the presence of diethylamine, and with benzalacetophenone and some of its substitution derivatives in the presence of alcoholic ammonia.[8]



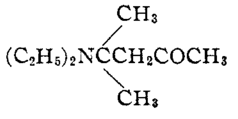
I–V VI–X

I and VI, R = R$_1$ = R$_3$ = H; R$_2$ = C$_6$H$_5$; R$_4$ = CH$_3$
II and VII, R = R$_1$ = R$_3$ = H; R$_2$ = R$_4$ = C$_6$H$_5$
III and VIII, R = C$_2$H$_5$; R$_1$ = R$_3$ = H; R$_2$ = C$_6$H$_5$; R$_4$ = CH$_3$
IV and IX, R = R$_1$ = CH$_3$; R$_2$ = R$_4$ = C$_6$H$_5$; R$_3$ = H
V and X, R = C$_2$H$_5$; R$_1$ = R$_3$ = H; R$_2$ = R$_4$ = C$_6$H$_5$

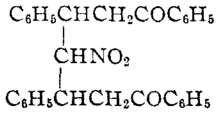
It has now been found that diethylamine is generally a suitable catalyst for the addition of nitroparaffins to unsaturated ketones. Representative condensations were carried out in anhydrous methanol, employing a catalyst concentration of one-tenth mole per mole of nitroparaffin. Side reactions were suppressed by operating at room temperature. Under these conditions 1-nitropropane or 2-nitropropane afforded 78–98% yields of nitroketones with benzalacetone, furfuralacetone, benzalacetophenone and furfuralacetophenone within six to forty days, and nitroethane yielded 95% of nitroketone with benzalacetophenone within six days.

An equilibrium relatively unfavorable to Michael condensation obtained in the reaction of mesityl oxide with nitromethane. Neither prolonged standing at 30° nor prolonged heating was effective in driving the reaction beyond 65% completion. This behavior of mesityl oxide is in accord with previous observations concerning the hindering effect of two substituents on the β-carbon of the acceptor.[9] In addition, mesityl oxide was the only ketone investigated which gave evidence of significant reaction with the catalyst. Formation, in 10–17% yields, of a basic substance which showed the proper analysis for 4-diethylamino-4-methyl-2-pentanone (XI) accompanied the production of the expected nitroketone.

The lability of two hydrogen atoms in nitromethane was displayed in the reaction of this nitroparaffin with benzalacetophenone. Upon standing at 30°, a methanol solution of benzalacetophenone, nitromethane (1.1 moles) and diethylamine (0.1 mole) slowly deposited a colorless solid which was shown to be a mixture of the anticipated 4-nitro-1,3-diphenyl-1-butanone (II) and two isomeric nitroketones (XII) resulting from the addition of two molecules of benzalacetophenone to one of nitromethane (compare Worrall and Bradway[8]). When a ratio of ten moles of nitromethane to one of benzalacetophenone was employed, the formation of diketones was effectively inhibited and an 84% yield of II was obtained. Utilization of a nitromethane–benzalacetophenone molar ratio of one to two was equally effective in



XI



$$\begin{array}{c}C_6H_5CHCH_2COC_6H_5\\ |\\ CHNO_2\\ |\\ C_6H_5CHCH_2COC_6H_5\end{array}$$

XII

---

[1] Present address: University of Southern California, Los Angeles, California.

[2] Kohler and Drake, THIS JOURNAL, **45**, 2144 (1923).

[3] Kohler, *ibid.*, **38**, 889 (1916).

[4] Kohler and Williams, *ibid.*, **41**, 1644 (1919); Kohler and Rao, *ibid.*, **41**, 1697 (1919).

[5] Kohler and Smith, *ibid.*, **44**, 624 (1922).

[6] Kohler, *ibid.*, **46**, 503 (1924).

[7] Kohler originally stated, without publishing experimental details, that the condensation of nitromethane with benzalacetone or mesityl oxide could be brought about most effectively by the use of a small quantity of diethylamine or piperidine. Kohler and Drake[2] later indicated sodium methoxide to be the best catalyst in the case of benzalacetone. No condensation involving mesityl oxide was ever described.

[8] Worrall and Bradway, THIS JOURNAL, **58**, 1607 (1936).

[9] Connor and McClellan, *J. Org. Chem.*, **3**, 570 (1939).

TABLE I

CATALYTIC REDUCTION OF NITROKETONES OVER RANEY NICKEL

Run	Phenylpyrrolidine		Ketone reduced	Yield, %	B. p. °C.	Mm.	n^{20}_D	d^{20}_{20}	% Nitrogen	
									Calcd.	Found
D	2,4-Di-	(VII)	(II)[a]	82	182.5	3.8	1.5895	1.0664	6.27	6.23
A	2-Ethyl-5-methyl-3-[b]	(VIII)	(III)	78	120	3.3	1.5235	0.9586	7.40	7.36
B	2-Ethyl-5-methyl-3-[b]	(VIII)	(III)[a]	60[c]	125–125.5	3.8	1.5239	.9597	7.40	7.41
C	2-Ethyl-5-methyl-3-	(VIII)	(III)[a]	51.5[c]	90	1.3	1.5250	.9649	7.40	7.41
G	2,2-Dimethyl-3,5-di-	(IX)	(IV)	94	176.5–177	2.3	1.5538	.9995	5.57	5.53
H	2,2-Dimethyl-3,5-di-	(IX)	(IV)[a]	87[d]	171	2.3	....	..	..	..
E	2-Ethyl-3,5-di-	(X)	(V)	72	170–171	2.3	1.5502	.9954	5.57	5.43
F	2-Ethyl-3,5-di-	(X)	(V)[a]	77	173	2.3	1.5742	1.0376	5.57	5.44

[a] Reduction in presence of ammonia. [b] M. p. 69–70°. [c] There was also obtained a fraction boiling at 160–170° at 3.8 mm., approximately half of which was soluble in 10% hydrochloric acid. [d] Product yielded two solid isomers upon fractional crystallization. See Experimental Part.

TABLE II

SOLID DERIVATIVES OF PYRROLIDINES, P = PYRROLIDINES

Run[a]	P	Benzenesulfonamide				Benzamide				Phenylthiourea			
		M. p., °C.	Crystals	% Nitrogen Calcd.	% Nitrogen Found	M. p., °C.	Crystals	Nitrogen, % Calcd.	Nitrogen, % Found	M. p., °C.	Crystals	Nitrogen, % Calcd.	Nitrogen, % Found
D	(VII)[b]	123–124	Needles	3.85	3.93	122–124	Rect. pr.	4.28	4.27	189–190[c]	Plates	7.82	7.80
B	(VIII)	86–87	Hex. pl.	4.25	4.09	.....	......	..	..	......	......	..	..
C	(VIII)[d]	....	......	..	..	.....	......	..	..	128–129	Rect. pl.	8.63	8.65
G	(IX)	106–107	Prisms	3.58	3.53	127–128	Hex. pr.	3.94	3.89	......	......	..	..
H	(IX)[e]	153–154	Stout N.	3.58	3.55	160–161	Prisms	3.94	3.91	165–167	Prisms	7.25	7.13
H	(IX)[f]	....	......	..	..	.....	......	..	..	194–195	Needles	7.25	7.28
E	(X)	....	......	..	..	143–144	Needles	3.94	3.84	......	......	..	..
F	(X)	155–156.5	Hex. pr.	3.58	3.55	137–138	Needles	3.94	3.88	139–141	Leaflets	7.25	7.17

[a] See Table I. [b] Yields a hydrochloride; colorless prisms from methanol–ether, m. p. 168–170°. *Anal.* Calcd. for $C_{16}H_{18}NCl$: Cl, 13.65. Found: Cl, 13.64. This m. p. is in substantial agreement with that reported by Kohler and Drake (ref. 2) (171–172°); Rupe and Gisiger, *Helv. Chim. Acta.*, **8**, 338 (1925), reported a m. p. of 154° for this hydrochloride. [c] Rupe and Gisiger, *ibid.*, **8**, 338 (1925), reported 188°. [d] Yields a picrate; flat yellow needles from ethanol, m. p. 141–143°. *Anal.* Calcd. for $C_{19}H_{22}O_7N_4$: N, 13.39. Found: N, 13.17. [e] M. p. 60–61°. [f] M. p. 66–70°.

promoting the double addition, and afforded an 89% yield of mixed nitrodiketones (XII).

Reduction of the γ-nitroketones was effected over Raney nickel in methanol at 100° under a pressure of 1000 lb. per sq. in., both in the presence and absence of ammonia. A smooth conversion to the corresponding substituted pyrrolidine (Type VI–X) was the invariable result (see Table I). The pyrrolidines were characterized by means of solid phenylthioureas, benzamides and benzenesulfonamides (Table II). In each instance the Hinsberg test indicated the absence of any primary amine in the pyrrolidine fraction. Only in the reduction of 5-nitro-4-phenyl-2-heptanone (III) in the presence of ammonia were obtained appreciable quantities of products other than pyrrolidines. These products, some basic and some neutral, were viscous, unstable oils, and were not identified.

When 4-methyl-4-nitro-1,3-diphenyl-1-pentanone (IV) was reduced in the presence of ammonia the product proved to be a mixture of two solid isomeric 2,2-dimethyl-3,5-diphenylpyrrolidines (IX) which were separated by fractional crystallization. It is not unlikely that mixtures of isomeric pyrrolidines were obtained from the reduction of the other nitroketones as well, and that the identity of the predominating isomer depended upon whether or not ammonia was present during reduction.

Reduction of 4-nitro-1,3-diphenyl-1-butanone (II) over Raney nickel in the presence of ammonia yielded 82% of 2,4-diphenylpyrrolidine (VII). This is of particular interest, for Kohler and Drake[2] found that reduction of the same ketone (II) over platinum at atmospheric pressure yielded but small quantities of the pyrrolidine derivative.

Experimental[10]

Condensation of Unsaturated Ketones with Nitroparaffins. Mesityl Oxide with Nitromethane.—A mixture of mesityl oxide, nitromethane (10 moles) and diethylamine (1 mole) was allowed to stand at 30° for thirty days. After distillation of unreacted reagents (to 55° at 20 mm.) fractionation of the residue yielded 10% of 4-diethylamino-4-methyl-2-pentanone (XI), b. p. 84–87° at 14 mm., and 65% of **4,4-dimethyl-5-nitro-2-pentanone**, b. p. 112–113.5° at 14 mm.

After two more distillations the aminoketone was obtained as a colorless oil with a camphoraceous odor; b. p. 84.3–84.8° at 14 mm.

Anal. Calcd. for $C_{10}H_{21}ON$: N, 8.17. Found: N, 8.02.

The nitroketone was shaken with 10% hydrochloric acid to remove traces of basic substances and was then twice distilled; yield, 58% of colorless oil with a camphoraceous odor; b. p. 128–129° at 22 mm.; n^{20}_D 1.4456; d^{20}_{20} 1.0546.

---

(10) Nitroparaffins used in this investigation were obtained from Commercial Solvents Corporation and, unless otherwise stated, were employed without further purification. Melting points are uncorrected. Nitrogen analyses and physical constants are by the Analytical Department of Commercial Solvents Corporation, Terre Haute, Indiana; carbon and hydrogen analyses by T. S. Ma, Chicago, Illinois. Catalytic hydrogenations were carried out by Dr. E. F. Smith at the High Pressure Laboratory, Commercial Solvents Corporation, Terre Haute, Indiana.

Anal. Calcd. for $C_7H_{13}O_3N$: N, 8.80. Found: N, 9.03.

A 55–60% yield of nitroketone was obtained in forty-eight hours when the reaction mixture was refluxed. Further heating did not increase the yield.

The **semicarbazone of 4,4-dimethyl-5-nitro-2-pentanone** was prepared[11] at room temperature; colorless needles from ethanol, m. p. 164–165° dec.

Anal. Calcd. for $C_8H_{16}O_3N_4$: N, 25.91. Found: N, 25.81.

Benzalacetone with Nitromethane.—Molar quantities of benzalacetone and diethylamine were allowed to react with ten moles of nitromethane in anhydrous methanol (2 cc. per g. of ketone) at 30° for twelve days and the reaction mixture was then allowed to evaporate spontaneously. The dark residue was extracted with ice-cold methanol and finally crystallized from methanol; yield, 58% of **5-nitro-4-phenyl-2-pentanone** (I), m. p. 96–100°. Recrystallization from methanol brought the m. p. to 99–100°, the m. p. reported by Kohler and Drake.[2]

An attempt to substitute piperidine for diethylamine as catalyst yielded only a dark tar.

The **semicarbazone of 5-nitro-4-phenyl-2-pentanone** was prepared in 96% yield at room temperature; colorless leaflets from ethanol, m. p. 153–154°.

Anal. Calcd. for $C_{12}H_{16}O_3N_4$: N, 21.20. Found: N, 20.58.

Benzalacetone with 1-Nitropropane.—Upon distillation, the reaction mixture from 29.2 g. of benzalacetone, 53.4 g. (3 moles) of 1-nitropropane, 4.38 g. (0.3 mole) of diethylamine and 20 cc. of anhydrous methanol which had been allowed to stand for thirty days at 30° yielded 42.4 g. (90%) of **5-nitro-4-phenyl-2-heptanone** (III) as a yellow oil (mixture of solid and liquid isomers), b. p. 162–167° at 3 mm. Crystallization from ethanol–petroleum ether yielded 11.3 g. (24%) of the solid isomer; colorless needles, m. p. 69–70°.

Anal. Calcd. for $C_{13}H_{17}O_3N$: N, 5.95.. Found: N, 5.84.

Evaporation of the mother liquor from crystallization of the solid isomer, and subsequent distillation of the residue yielded the isomeric liquid nitroketone as a yellow oil; b. p. 155–157° at 2.5 mm.

Anal. Calcd. for $C_{13}H_{17}O_3N$: C, 66.36; H, 7.28. Found: C, 66.24; H, 7.02.

Refluxing benzalacetone with five moles of 1-nitropropane and one-half mole of diethylamine in methanol for five days yielded 83% of mixed isomers.

Liquid 5-nitro-4-phenyl-2-heptanone gave a 94.5% yield of **2,4-dinitrophenylhydrazone**[12]; orange cubes from chloroform–ethanol, m. p. 150–152°.

Anal. Calcd. for $C_{19}H_{21}O_6N_5$: C, 54.93; H, 5.10. Found: C, 55.05; H, 5.12.

The **phenylhydrazone of solid 5-nitro-4-phenyl-2-heptanone** separated quickly when a solution containing 1.5 g. of the nitroketone, 0.7 g. of phenylhydrazine, 25 drops of glacial acetic acid, 20 cc. of ethanol and 7 cc. of water was swirled at room temperature. After standing at 30° for fifteen minutes the reaction mixture was cooled to 5° for two hours, the solid product was filtered and recrystallized four times in rapid succession from ethanol; thick yellow needles, m. p. 112–112.5° dec. The phenylhydrazone decomposes upon standing at room temperature.

Anal. Calcd. for $C_{19}H_{23}O_2N_3$: C, 70.12; H, 7.12. Found: C, 69.43; H, 7.16.

The **2,4-dinitrophenylhydrazone of solid 5-nitro-4-phenyl-2-heptanone** crystallizes from chloroform–ethanol in orange needles, m. p. 125–125.5°.

Anal. Calcd. for $C_{19}H_{21}O_6N_5$: C, 54.93; H, 5.10. Found: C, 55.33; H, 5.02.

Benzalacetone with 2-Nitropropane.—A solution of 292 g. of benzalacetone, 1780 g. (10 moles) of 2-nitropropane and 146 g. (1 mole) of diethylamine in 200 cc. of anhydrous methanol was allowed to stand at 30° for thirty days. Distillation under reduced pressure yielded 434 g. of yellow oil, b. p. 159–163° at 2.3 mm., from which 364.3 g. (77.5%) of crystalline **5-methyl-5-nitro-4-phenyl-2-hexanone** was obtained by cooling and scratching. The nitroketone is dimorphic; one sample crystallized from ethanol–water in long colorless needles, m. p. 50–51°, which, upon standing for several days in contact with mother liquor, changed spontaneously to hexagonal prisms, m. p. 63–64°. Further crystallization from ethanol–petroleum ether failed to raise this melting point.

Anal. Calcd. for $C_{13}H_{17}O_3N$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.74; H, 7.03; N, 6.22.

When piperidine was substituted for diethylamine as catalyst, a 61% yield of nitroketone was obtained after reaction at 30° for thirty days.

5-Methyl-5-nitro-4-phenyl-2-hexanone yielded a **semicarbazone** which crystallized from anhydrous ethanol in colorless needles, m. p. 185.5–186°.

Anal. Calcd. for $C_{14}H_{20}O_3N_4$: N, 19.16. Found: N, 19.21.

The **2,4-dinitrophenylhydrazone of 5-methyl-5-nitro-4-phenyl-2-hexanone** crystallized from chloroform–ethanol in orange plates, m. p. 117–118°.

Anal. Calcd. for $C_{19}H_{21}O_6N_5$: N, 16.86. Found: N, 16.43.

Furfuralacetone with 1-Nitropropane.—When a mixture of furfuralacetone, 1-nitropropane (3 moles) with diethylamine (0.3 mole) was allowed to stand at 30° for fourteen days and then distilled, there was obtained 75% of yellow **4-(2′-furyl)-5-nitro-2-heptanone**, b. p. 116–117° at 1 mm.; n^{20}_{D} 1.4859; d^{20}_{20} 1.1414. The yield was raised to 96% when reaction was allowed to continue for forty days. Use of methanol as solvent did not influence the yield materially.

Anal. Calcd. for $C_{11}H_{15}O_4N$: N, 6.21. Found: N, 6.36.

When preparation of the **2,4-dinitrophenylhydrazone** was attempted in the usual manner, a mixture of two compounds was obtained, the lower-melting of which was not purified effectively by fractional crystallization. The higher-melting product separated from ethanol in orange plates, m. p. 146–147°.

Anal. Calcd. for $C_{17}H_{19}O_7N_5$: N, 17.27. Found: N, 16.83.

Furfuralacetone with 2-Nitropropane.—The yellow **4-(2′-furyl)-5-methyl-5-nitro-2-hexanone** obtained in 95% yield from furfuralacetone, 2-nitropropane (10 moles) and diethylamine (1 mole) after thirty days at 30° boiled at 114–115° at 1 mm.; n^{20}_{D} 1.4905; d^{20}_{20} 1.1558. This ketone gave a positive iodoform test.

Anal. Calcd. for $C_{11}H_{15}O_4N$: N, 6.21. Found: N, 6.35.

The **semicarbazone**, prepared at room temperature, separated from ethanol in flat colorless needles, m. p. 157–158°.

Anal. Calcd. for $C_{12}H_{18}O_4N_4$: N, 19.84. Found: N, 19.35.

Benzalacetophenone with Nitromethane: Procedure A.—A solution of 20.8 g. of benzalacetophenone, 6.7 g. (1.1 moles) of nitromethane and 0.73 g. (0.1 mole) of diethylamine in 10 cc. of anhydrous methanol began depositing solid condensation product after standing at 30° for sixty-five hours. After fourteen days the crystalline material was filtered and a second crop was obtained by evaporation of the mother liquor; total yield, 24.4 g. Extraction of this material with 100 cc. of boiling methanol left 5.4 g. (23%) of **4-nitro-1,3,5,7-tetraphenyl-1,7-heptanedione** (XII) which, after crystallization from dioxane–methanol, formed colorless needles, m. p. 223–225° dec (after sintering at 210°).[8]

---

(11) Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, New York, N. Y. 1940, p. 142.

(12) Reference 11, p. 143.

Anal. Calcd. for $C_{31}H_{27}O_4N$: C, 77.96; H, 5.70; N, 2.93. Found: C, 77.72; H, 5.98; N, 3.08.

When the aforementioned hot methanol extract was cooled and concentrated there was obtained 3.7 g. (16%) of an **isomeric 4-nitro-1,3,5,7-tetraphenyl-1,7-heptanedione** (XII) which formed colorless needles from ethanol, m. p. 155–156°.

Anal. Calcd. for $C_{31}H_{27}O_4N$: N, 2.93. Found: N, 2.91.

Evaporation of the remaining methanol extract yielded 11.5 g. (43%) of **4-nitro-1,3-diphenyl-1-butanone** (II) which, after crystallization from ethanol, melted at 99–99.5°. This nitroketone yielded a semicarbazone, m. p. 161–163° dec. Kohler[3] reported a m. p. of 103° and 165° for this ketone and semicarbazone, respectively.

Procedure B.—In order to suppress formation of the nitrodiketone, benzalacetophenone was allowed to react with ten moles of nitromethane in anhydrous methanol (3 cc. per g. ketone) at 30° for five and one-half days under the catalytic influence of one mole of diethylamine. Unreacted reagents were removed by steam distillation and the residue crystallized readily upon cooling. Crystallization from ethanol yielded 84% of 4-nitro-1,3-diphenyl-1-butanone (II).

Procedure C.—When a solution of benzalacetophenone, nitromethane (0.5 mole) and diethylamine (0.5 mole) in anhydrous ethanol (10 cc. per g. ketone) was allowed to stand at 30° for twenty-one days and then concentrated, there was obtained 89% of crystalline nitrodiketone (XII). Fractional crystallization from ethanol yielded 35% of high-melting 4-nitro-1,3,5,7-tetraphenyl-1,7-heptanedione and 48% of the lower-melting isomer.

A similar yield of crude nitrodiketones was obtained when the reaction mixture was refluxed for ten days: yields of high- and low-melting isomers were 56 and 26%, respectively.

Benzalacetophenone with Nitroethane.—Evaporation of the mixture of benzalacetophenone, nitroethane (3 moles) and diethylamine (0.3 mole) in anhydrous methanol (0.5 cc. per g. ketone) which had been allowed to stand at 30° for six days, yielded 90–95% of crude solid nitroketones. Fractional crystallization from ethanol or ethanol–petroleum ether (60–75°) yielded 11–33% of **4-nitro-1,3-diphenyl-1-pentanone**, m. p. 69–70°, and 53–78% of the isomeric nitroketone, m. p. 100.5–102°. Kohler[3] reported melting points of 72 and 100° for these respective ketones.

Low-melting (69–70°) 4-nitro-1,3-diphenyl-1-pentanone yielded a **2,4-dinitrophenylhydrazone** which separated from chloroform–ethanol in thin orange plates, m. p. 175.5° dec.

Anal. Calcd. for $C_{23}H_{21}O_6N_5$: N, 15.11. Found: N, 14.97.

High-melting (100.5–102°) 4-nitro-1,3-diphenyl-1-pentanone yielded a **2,4-dinitrophenylhydrazone** which separated from chloroform–ethanol in red prisms, m. p. 174° dec.

Anal. Calcd. for $C_{23}H_{21}O_6N_5$: N, 15.11. Found: N, 14.70.

Benzalacetophenone with 1-Nitropropane.—Benzalacetophenone reacted in the usual manner with 1-nitropropane (3 moles) and diethylamine (0.3 mole) in anhydrous methanol (0.5 cc. per g. of ketone) at 30° to give a 97.5% yield of **4-nitro-1,3-diphenyl-1-hexanone** (V) within six days; colorless needles from chloroform–ethanol, m. p. 156–157°.

Anal. Calcd. for $C_{18}H_{19}O_3N$: N, 4.71. Found: N, 4.71.

Benzalacetophenone with 2-Nitropropane.—The major portion of the **4-methyl-4-nitro-1,3-diphenyl-1-pentanone** (IV) crystallized directly from the reaction mixture of benzalacetophenone, 2-nitropropane (1.5 moles) and diethylamine (0.15 mole) in anhydrous methanol (2.5 cc. per g. ketone) after thirty-five days at 30°; yield, 96% of colorless needles from chloroform–ethanol, m. p. 146–147° (Kohler[3] reported 167°).

Anal. Calcd. for $C_{18}H_{19}O_3N$: N, 4.71. Found: N, 4.50.

Furfuralacetophenone with 1-Nitropropane.—Spontaneous evaporation of the solution of freshly-distilled furfuralacetophenone, 1-nitropropane (3 moles) and diethylamine (0.3 mole) in methanol (0.5 cc. per g. ketone) after ten days at 30° left a crystalline residue of 3-(2′-furyl)-4-nitro-1-phenyl-1-hexanone, which was washed with cold methanol to remove colored impurities and was then crystallized from methanol; yield, 79% of colorless needles, m. p. 81–82°.

Anal. Calcd. for $C_{16}H_{17}O_4N$: N, 4.87. Found: N, 4.69.

There was also obtained a lower-melting compound (second isomer?) which was not purified effectively by repeated crystallizations.

3-(2′-Furyl)-4-nitro-1-phenyl-1-hexanone yielded a **2,4-dinitrophenylhydrazone** which separated from chloroform–ethanol in orange blades, m. p. 173–175° dec.

Anal. Calcd. for $C_{22}H_{21}O_7N_5$: N, 14.98. Found: N, 14.70.

Furfuralacetophenone with 2-Nitropropane.—When the dark solution from reaction of furfuralacetophenone, 2-nitropropane (1.5 moles) and diethylamine (0.15 mole) in methanol (1 cc. per g. ketone) at 30° for twenty-eight days was cooled and diluted with water, there was obtained 90.5% of crystalline **3-(2′-furyl)-4-methyl-4-nitro-1-phenyl-1-pentanone**. Crystallization from ethanol yielded colorless prisms, m. p. 82–82.5°.

Anal. Calcd. for $C_{16}H_{17}O_4N$: N, 4.87. Found: N, 4.74.

This nitroketone yielded equal quantities of two distinct ***2,4-dinitrophenylhydrazones***. The *lower-melting isomer* separated from chloroform-ethanol in flat orange needles, m. p. 149–150° dec.

Anal. Calcd. for $C_{22}H_{21}O_7N_5$: N, 14.98. Found: N, 14.80.

The higher-melting isomer formed yellow cubes, m. p. 154–156°.

Anal. Calcd. for $C_{22}H_{21}O_7N_5$: C, 56.52; H, 4.53. Found: C, 56.76; H, 4.62.

Catalytic Reduction of Nitroketones.—A rocking bomb was charged with 0.33–0.5 mole of the nitroketone, 400 cc. of methanol and 10 g. of methanol-washed Raney nickel, and hydrogenation was carried out at 100° under a pressure of 1000 lb. per sq. in. for one to two hours. In some instances 1 mole of liquid ammonia was added to the bomb charge before hydrogenation. After filtration to remove catalyst, the solution was distilled under reduced pressure to remove water, solvents and unreacted materials, and the product was finally distilled in vacuum. In Table I are listed the pyrrolidines which were prepared in this manner.

Reduction of 4-methyl-4-nitro-1,3-diphenyl-1-pentanone (IV) in the presence of ammonia produced an 87% yield of solid secondary amines. Fractional crystallization from 80% ethanol yielded two solid isomeric **2,2-dimethyl-3,5-diphenylpyrrolidines** (IX). The less-soluble isomer separated from aqueous ethanol in long colorless blades, m. p. 60–61°.

Anal. Calcd. for $C_{18}H_{21}N$: N, 5.57. Found: N, 5.51.

The more-soluble isomer was more difficult to purify and was obtained as colorless crystals, m. p. 66–70°. This material was characterized more accurately through the solid phenylthiourea as shown in Table II.

Solid Derivatives of Pyrrolidines.—Benzenesulfonamides, prepared by shaking a mixture of the pyrrolidine, 2.9 moles of benzenesulfonyl chloride and 10% sodium hydroxide solution (22 cc. per g. of sulfonyl chloride), were crystallized from ethanol or chloroform–ethanol. Properties of these derivatives are shown in Table II. The alkaline solution from the preparation of the benzenesulfonamide in every instance failed to give a significant precipitate upon acidification, thereby indicating the absence of any primary amine in the pyrrolidine.

Benzamides, prepared in the customary manner from the pyrrolidine, benzoyl chloride (1 cc. per g. of amine) and 10% sodium hydroxide solution (10 cc. per g. of amine), were recrystallized from 60–80% ethanol and finally from ethanol alone (see Table II).

When equal weights of the pyrrolidine and phenyl isothiocyanate were mixed, considerable heat was evolved and the mixture usually solidified upon cooling. After being washed with 50% ethanol the phenylthioureas were crystallized from chloroform–ethanol. These derivatives are likewise listed in Table II.

Summary

1. It has been found that diethylamine is a suitable catalyst for the addition of nitroparaffins to α,β-unsaturated ketones.

2. Substituted pyrrolidines were the principal products when a number of γ-nitroketones were reduced over Raney nickel, both in the presence and absence of ammonia.

GREENCASTLE, INDIANA RECEIVED MARCH 3, 1947

[CONTRIBUTION NO. 7 FROM THE THERMODYNAMICS LABORATORY OF THE PETROLEUM EXPERIMENT STATION, BUREAU OF MINES, BARTLESVILLE, OKLA.]

Experimental Vapor Heat Capacities and Heats of Vaporization of *n*-Hexane and 2,2-Dimethylbutane[1]

BY GUY WADDINGTON AND DONALD R. DOUSLIN

The current thermodynamic program of the Petroleum and Natural Gas Division of the Bureau of Mines includes the measurement of the heat capacities of hydrocarbon vapors. Incidental to the determination of vapor heat capacities accurate values of the heats of vaporization are obtained. A recent publication[2] describes the flow calorimeter and cycling vaporizer used for determining the above properties.

This paper gives the results of measurements of the vapor heat capacities and heats of vaporization of *n*-hexane and 2,2-dimethylbutane.

Experimental

The Apparatus and Experimental Method.—The flow calorimeter and vapor cycling system have been described recently in considerable detail, hence only a brief account of the method and apparatus will be given here.

A measured constant flow of hydrocarbon vapor is produced in a glass vaporizing vessel thermally isolated from its surroundings. Normally the vapor is passed through the calorimeter, then condensed and returned to the vaporizer as liquid. The boiling temperature is kept constant by carefully controlling the pressure of helium gas in the static portion of the system. The dependence of rate of flow on the power input to the vaporizer heater is determined by diverting the stream of vapor into a suitable collecting vessel for a measured time interval and weighing the condensed sample of hydrocarbon. From properly corrected values of mass, power and time, accurate values of the heat of vaporization are obtained.

To ascertain the heat capacity of the vapor the temperature rise produced in the flowing vapor by the measured power input to the calorimeter heater is determined. Two platinum resistance thermometers situated directly in the vapor stream are used to measure the temperature of the vapor after it has passed the heater. By measuring the resistances of the thermometers before and after supplying energy to the heater a value of the temperature increase, accurate to a few thousandths of a degree, is obtained. From the mass of vapor flowing through the calorimeter per unit of time, the power supplied to the calorimeter heater, and the temperature increase of the vapor, values of the apparent heat capacities are calculated. The apparent heat capacities differ from true heat capacities because of heat losses in the calorimeter. By making measurements at four flow rates, covering the range 0.05 to 0.25 mole per minute, data are obtained by which corrections may be made for heat losses. The design of the calorimeter is such that the relationship $C_{P(\text{obs.})} = C_P + k/F$ accurately represents the experimental data, where C_P is the true heat capacity, F is the flow rate and k a constant for a given set of operating conditions. From this it follows that a plot of $C_{P(\text{obs.})}$ *vs.* $1/F$ extrapolated linearly to zero value of $1/F$ gives the correct value of C_P. To obtain accurate values of C_P^0, the heat capacity of the vapor in the ideal gas state, heat capacities are determined at two or more pressures and the results extrapolated linearly to zero pressure. The validity of the linear extrapolation has been checked experimentally for a number of compounds.

In the case of 2,2-dimethylbutane the mode of carrying out the heat capacity measurements at 1 atmosphere pressure differed from the other measurements reported in this paper and from the work reported earlier.[2] Instead of maintaining a fixed boiling temperature in the vaporizer, for a series of measurements at different flow rates, the helium pressure in the system was maintained constant. Because of the pressure head between the vaporizer and the condensers the boiling temperatures were different at different flow rates. This necessitated a correction for the temperature

---

[1] Approved for publication by the Director of the Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] Guy Waddington, Samuel S. Todd and Hugh M. Huffman, THIS JOURNAL, **69**, 22 (1947).