used as an analytical probe in the identification of the products. Also, an estimate of the relative amounts of monoacetylamine and diacetylamine was made for those amines which gave both products. This estimate was made by comparison of the intensities of the two carbonyl bands.

The nuclear magnetic resonance data clearly show the difference between *N*-monoacetylamines and *N*,*N*-diacetylamines. The *N*-monoacetylamines show resonance at *ca.* τ 2.10 as a doublet due to the N–H proton, which is coupled with the C–H proton of the neighboring alkyl group. The methyl groups of the acetamido function provide a convenient method of estimating the relative amounts of monoacetylamine and diacetylamine in a given reaction. The methyl protons appear at τ 8.09 ± 0.03 for the *N*-monoacetylamines and at τ 7.70 ± 0.10 for the *N*,*N*-diacetylamines.

Experimental Section[2]

All melting points were obtained on a Fisher-Johns apparatus and are uncorrected. All boiling points were obtained using standard vacuum distillation techniques and are uncorrected. All nuclear magnetic resonance spectra were taken on a Varian A-60A instrument as 50% CCl_4 solutions, using 1% TMS as internal standard, except in those cases where solubility considerations required $CDCl_3$ as solvent. All infrared spectra were taken as neat smears (for liquids) or as KBr pellets (for solids) and were performed on a Beckman IR-5A spectrophotometer. All gas chromatogaphy work was done with a 4-ft SE-30 column on an Aerograph gc instrument. Elemental analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Acetylation of Amines.—The acetylation procedures were nearly the same for all the compounds studied. Therefore, the reactions of the amines examined are divided into two categories: those reactions which gave only a *N*,*N*-diacetylamine, and those reactions which gave a mixture of a *N*-monoacetylamine and a *N*,*N*-diacetylamine.

The Preparation and Isolation of a *N*,*N*-Diacetylamine.—(The acetylation of cyclopropylamine which is given below is typical.) Cyclopropylamine (4.80 g, 0.084 mol) was added dropwise to a mixture of acetic anhydride (125 ml) and anhydrous sodium acetate (0.5 g) contained in a 250-ml three-neck round-bottom flask equipped with reflux condenser, dropping funnel, thermometer, and magnetic stirring. The temperature was maintained at 25° by use of an ice bath since the exothermic reaction involved the addition of the volatile cyclopropylamine (bp 50°). The total time of addition was 10 min. The reaction mixture was then heated at reflux for 20 hr and cooled to room temperature. The reaction mixture, which was clear and yellow, was then rotary evaporated at approximately 70° and 10 mm for 2 hr, leaving a thick yellow sludge. Water (50 ml) was added, forming a yellow solution, which was then stirred at room temperature for 1 hr in order to hydrolyze any remaining acetic anhydride. This water solution was then extracted twice with ether (75 ml per extraction) and the combined ether layer was dried ($MgSO_4$), filtered, and concentrated on the rotary evaporator at reduced pressure, leaving 8.0 g (69%) of yellow *N*,*N*-diacetylcyclopropylamine. The yellow liquid was then distilled through a 6-in. Vigreux column at reduced pressure. After a small forerun (0.5 ml), the major fraction distilled at 94.5° (10.0 mm): $n^{25}D$ 1.4686; $d^{27.5}$ 1.11; ir (neat) 2980, 1692, 1368, 1250, 1035, and 970 cm^{-1}; nmr (CCl_4) τ 8.80–9.30 (m, 4), 7.78 (s, 6), and 7.40 (m, 1).

The Preparation, Isolation, and Separation of a Mixture of a *N*-Monoacetylamine and a *N*,*N*-Diacetylamine.—(The acetylation of *sec*-butylamine given below is typical.) *sec*-Butylamine (14.6 g, 20.0 ml, 0.20 mol) was added dropwise to a mixture of acetic anhydride (140 ml) and anhydrous sodium acetate (0.5 g). The procedure was identical with that of cyclopropylamine until the crude product was isolated. This crude product was submitted for infrared and nuclear magnetic resonance analysis. Comparison of the relative intensities of the carbonyl absorptions in the ir spectrum indicated a mixture of *N*-acetyl-*sec*-butylamine and *N*,*N*-diacetyl-*sec*-butylamine in the ratio of 7:8. Comparison of the relative areas under the singlet methyl peaks of the acetamido functions in the nmr spectrum corroborated the infrared findings. The crude liquid was then fractionally distilled through a 6-in. Vigreux column at reduced pressure. After a small forerun, 5 ml of clear colorless liquid was collected at 86–91° (8.75 mm). A small intermediate fraction was then distilled, and finally a 10-ml collection of clear colorless liquid was made at 101–101.5° (8.75 mm). The infrared spectral data clearly indicated that the 86–91° fraction was the *N*,*N*-diacetyl-*sec*-butylamine, and that the 101–101.5° fraction was the *N*-acetyl-*sec*-butylamine.[3] The identifications were made based on the conclusions set forth in the spectral discussion section of this paper: that the carbonyl absorption at 1692 cm^{-1} indicates diacetylamine, whereas the carbonyl absorption at 1640 cm^{-1} indicates monoacetylamine. The nmr spectra also clearly designate the high-boiling fraction to be pure monoacetylamine while the lower boiling fraction is seen to be nearly pure diacetylamine. The total yield, based on a 7:8 monoacetyl to diacetyl ratio, was 75%, or 35% *N*-acetyl-*sec*-butylamine and 40% *N*,*N*-diacetyl-*sec*-butylamine. The *N*,*N*-diacetyl-*sec*-butylamine was purified by preparative gc from an SE-30 column and analyzed: $n^{25}D$ 1.4361; $d^{27.5}$ 0.96; ir (neat) 2950, 1692, 1450, 1370, and 1240 cm^{-1}; nmr (CCl_4) τ 9.17 (m, 3), 8.67 (d, 3), 8.20 (m, 2), 6.18 (m, 1).

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[2] The amines in this research were used as received without further purification. The following sources supplied the amines: Aldrich Chemicals, Milwaukee, Wis., Reilly Tar and Chemicals, Indianapolis, Ind., Eastman Kodak, Rochester, N. Y. Additionally, we thank Professor Harvey Posvic of our department for supplying us with generous samples from his amine collection.

[3] *N-sec*-Butylacetamide has a reported boiling point of 87° (3 mm). See Table I, footnote a.

Hydrogenolysis of Carbonyl Derivatives as a Route to Pure Aliphatic–Aromatic Hydrocarbons

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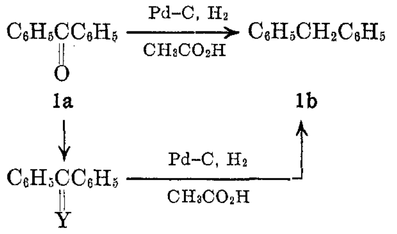
Hydrogenolysis of ketones such as acetophenone, benzophenone (Scheme I), and 1-tetralone to the corresponding hydrocarbons is readily accomplished in good yield[2a–d] and has become an important synthesis route

SCHEME I



1c, Y = $NNHC_6H_3(NO_2)_2$
d, Y = $NNHCONH_2$
e, Y = $NNHC_6H_5$
f, Y = NOH

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[1] (a) American Petroleum Institute Research Assistant (undergraduate, 1968–1969; graduate, 1969–present).

[2] (a) P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967. (b) Presented before the Southwest Regional Meeting of the American Chemical Society, Tulsa, Okla., Dec 4–6, 1969. (c) R. G. Melton, E. J. Eisenbraun, P. W. K. Flanagan, and M. C. Hamming, *Org. Prep. Proced.*, **2**, 37 (1970). (d) Aromatic aldehydes also may be hydrogenolyzed. (e) Correspondence regarding samples of hydrocarbons related to this and earlier[2c] work should be addressed to A. J. Streiff, American Petroleum Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213.

Table I

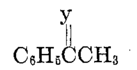
Hydrogenolysis of Carbonyl Derivatives

Compd[a]	Reaction hr	% yield[b]
1a	1.5	95
1c	7	92[c]
1d	6	93[c]
1e	6	96[c]
1f	4	96[c]
2a	1.5	95
2c	6	81
2d	5	97
2e	5	94
2f	3	82
3a[d]	2.5	92
3c[d]	21	84
3d[e]	10	75
4a	1	87
4c	3	71
5a	1	94
5c[f]	4	95

[a] For preparation and melting points of these derivatives except as noted, see R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed, Wiley, New York, N. Y., 1964, pp 147, 253, 289, 363, and 364. The melting points of these derivatives agreed with literature values. [b] Glc comparison with standards. [c] Gravimetrically determined as well. [d] Cl. Ferrero and R. Helg, *Helv. Chim. Acta*, **42**, 2111 (1959). [e] M. G. J. Beets, H. Van Essen and W. Meerburg, *Recl. Trav. Chim. Pays-Bas*, **77**, 854 (1958). [f] F. Ramirez and A. F. Kirby, *J. Amer. Chem. Soc.*, **74**, 4331 (1952).

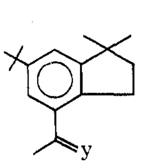
to pure hydrocarbons.[2e] However, in some cases, the available ketone and/or the resulting hydrocarbon could not be brought to the required purity, and it became necessary to resort to preparation of carbonyl derivatives for purification,[3] but, since the hydrocarbon was the desired product and the purified ketone was not required, we decided to investigate direct hydrogenolysis of carbonyl derivatives to hydrocarbons.

As applied to benzophenone (**1a**) or acetophenone (**2a**), which were used to screen for the most suitable derivative, the 2,4-dinitrophenylhydrazone appears to be the most effective derivative for hydrogenolysis to pure **1b** and **2b**. The results of hydrogenolysis experiments applied to several carbonyl derivatives are shown in Table I.

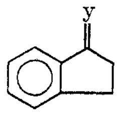


$C_6H_5\overset{\overset{y}{\|}}{C}CH_3$

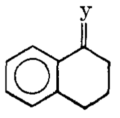
2



3



4



5

y = O	**2a**	**3a**	**4a**	**5a**
y = H_2	**b**	**b**	**b**	**b**
y = $NNHC_6H_3(NO_2)_2$	**c**	**c**	**c**	**c**
y = $NNH\overset{\overset{O}{\|}}{C}NH_2$	**d**	**d**		
y = $NNHC_6H_5$	**e**			
y = NOH	**f**			

Gas–liquid chromatography (glc) studies were used to determine the extent of hydrogenolysis and hydrogenation. For example, acetophenone phenylhydrazone (**2e**) gave some phenethylamine as well as cyclohexylamine. Additional hydrogenolysis converted the former to ethylbenzene, and extraction with aqueous hydrochloric acid removed the latter. Glc studies were also used to identify the hydrocarbon hydrogenolysis products and to determine the yield of **1b**, **2b**, **3b**, **4b**, and **5b**. The nitrogenous hydrogenolysis–hydrogenation products of oximes, semicarbazones, and 2,4-dinitrophenylhydrazones were not investigated.

In general, the hydrogenolyses could be brought to completion in 3–7 hr. However, **3a** and its derivatives **3c** and **3d** were resistant to hydrogenolysis as compared to **1a** and **2a** and their derivatives. As a result of prolonged treatment, "overhydrogenation" was observed for **3a** and **3d** but surprisingly, the 2,4-dinitrophenylhydrazone **3c** cleanly hydrogenolyzed to the corresponding hydrocarbon **3b**.[4] Overhydrogenation may result from prolonged or severe treatment of **1a** or **2a** and their derivatives. This was absent in **4a** and **5a** and their 2,4-dinitrophenylhydrazones.

Experimental Section

General Hydrogenolysis Procedure.—The purified carbonyl derivative (0.03 mol) was introduced into a 300-ml stainless steel hydrogenation vessel containing 50 ml of acetic acid and 0.6 g of 10% Pd/C catalyst.[5a] The vessel was evacuated, hydrogen was introduced, and the vessel was shaken at 30–50 psi at 50–60° until the pressure drop ceased.[5b] Excess hydrogen was vented, and the vessel contents were filtered through Dicalite to remove the catalyst. The filtrate was diluted with 200 ml of water and extracted with ether (two 100-ml portions), and the extract was washed with 10% NaOH (two 100-ml portions), dried ($MgSO_4$), and concentrated by distillation or evaporation under reduced pressure. Other details are given in Table I.

Preparation of Carbonyl Derivatives.—The carbonyl derivatives used were prepared according to published procedures (Table I) and were purified by recrystallization from 95% ethanol except for **3c**, (2,4-DNP), which was best purified by successive recrystallization from nitroethane[6] and isopropyl alcohol.

Glc Studies of Hydrogenolysis Products.—A standard solution of the product hydrocarbon in ether (*ca.* 2%) was prepared, and the glc curve was obtained[7a] with duplicate or more injections (4 μl) onto a 0.25 in. × 11 ft column of 5% UC W-98[7b] coated on 80–100 mesh, acid-washed, DMCS-treated Chromosorb G heated at 190°. The peak areas of average injections were used to compare with peak areas obtained for each hydrogenolysis product. The yields (Table I) were derived from these data and also gravimetrically for benzophenone derivatives.

Acknowledgments.—We are grateful to the American Petroleum Institute for partial support of this work through Research Project 58A. We thank Dr. O. C. Dermer for having read the manuscript and the Research Foundation of Oklahoma State University for some assistance.

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(3) H. R. Harrison and E. J. Eisenbraun, *J. Org. Chem.*, **31**, 1294 (1966).

(4) We are grateful to T. F. Wood, P. Porcaro, and A. Hochstetler of Givaudan Corp. for samples and analytical studies (nmr, mass spectrum, glc) which showed that hydrocarbons giving molecular ions at *m/e* 234 and 236 were present after hydrogenolysis of **3a**, *m/e* 244, to **3b**, *m/e* 230.

(5) (a) The 10% Pd/C catalyst was purchased as a stock item from Engelhard Industries. (b) A Parr Model 3920 hydrogenation apparatus was used.

(6) Nitroethane shows considerable promise as a recrystallizing solvent for otherwise insoluble 2,4-dinitrophenylhydrazones.

(7) (a) A Hewlett-Packard 5750B glc apparatus equipped with dual thermal conductivity filaments was used. (b) A Union Carbide Chemicals Co. methyl vinyl silicone purchased from Applied Science Laboratories, State College, Pa.