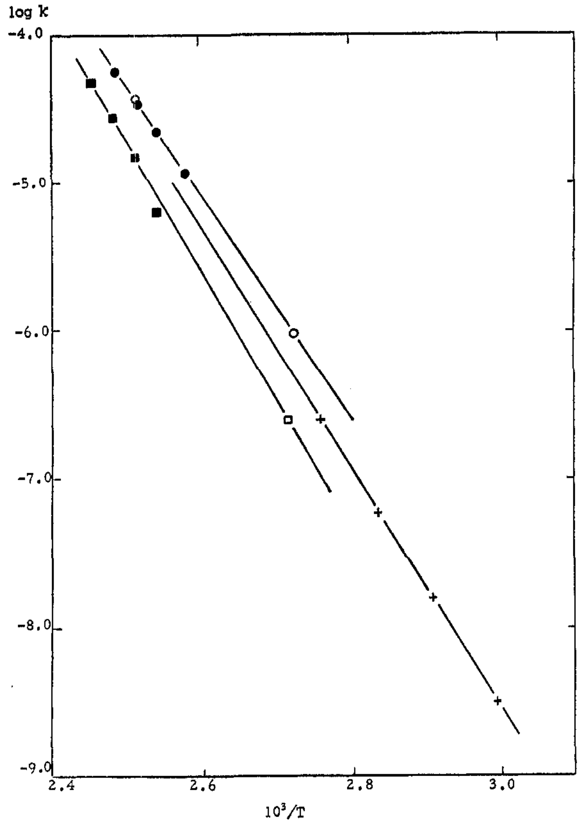

Figure 1.—Solvent effects on temperature dependence of *tert*-butyl peroxide decomposition: circles, acetonitrile; squares, cyclohexane; crosses, styrene; solid symbols, Huyser and Van Scoy; open symbols, this paper.

From Table II we conclude that, while the rate and activation parameters for the decomposition of *tert*-butyl peroxide do vary measurably with solvent, the magnitude of the effect is considerably less than reported by Huyser and Van Scoy. We also believe that our results point up the importance of determining activation parameters from data gathered over as wide a temperature range as possible. To place the matter in perspective, variations in rate of decomposition of *tert*-butyl peroixde with solvent and attributable to variations in reactant and transition-state solvation are comparable to or smaller than those previously observed with simple diacyl peroxides and peresters which decompose by single-bond scission and far smaller than the effects observed in those peroxides which decompose rapidly by concerted multibond scission.[16]

Experimental Section

Materials.—Peroxide and solvents were commercial materials, purified as necessary by conventional means and checked by gas-liquid chromatography (glc).

Decompositions.—Were carried out in sealed, degassed tubes in suitable thermostats, and products and decomposition rates were determined by glc analysis, using suitable internal standards added after reaction. Reaction rates were determined by monitoring either undercomposed peroxide or the appearance of products (*tert*-butyl alcohol plus acetone). Data on columns and conditions found effective for the different systems investigated appear in Table III.

Analysis of Data.—Rate constants were calculated from points from individual runs (usually 9), distributed in time over approximately 0.5–2 half-lives. Runs in both solvents at 95% were run concurrently to compensate for any drift in thermostat temperature over the 1–2 weeks required to achieve adequate reaction.

Table III

Gas Chromatographic Data

Analytical column[a]	Column temp, °C[b]	Compounds analyzed[c]	Solvent
12 ft, 15% diisodecylphthalate	40	Acetone, isobutylene oxide, *tert*-butyl peroxide, 2-pentanone	Acetonitrile, cyclohexene, cyclohexane, *tert*-butyl alcohol, benzene, nitrobenzene
12 ft, 20% DEGS in tandem with 15 ft, 20% FFAP	68	*tert*-Butyl peroxide, acetone, *tert*-butyl alcohol, benzene[d]	Acetonitrile
12 ft, 10% silicone gum rubber UCC-W982	40	*tert*-Butyl alcohol, methylcyclohexane,[d] *tert*-butyl peroxide	Cyclohexane

[a] Stationary phase, 80–100 mesh VarAport 30. [b] Injector temp, 70–80°. [c] In order of elution. [d] Internal standard.

Registry No.—*tert*-Butyl peroxide, 110-05-4.

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(16) For a recent discussion of such systems, *cf.* C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnov, *J. Amer. Chem. Soc.*, **92**, 4927 (1970).

Diacetylation of Amines

R. P. Mariella* and K. H. Brown[1]

Department of Chemistry, Loyola University, Chicago, Illinois 60626

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Several representative primary amines were acetylated under reflux conditions Table I shows the results of the treatment of these amines with boiling acetic anhydride. Those primary amines of the type RCH_2NH_2 gave reasonably good yields of only *N*,*N*-diacetylamines, $RCH_2N(COCH_3)_2$. Primary amines of the type $RR'CHNH_2$ gave *N*-monoacetylamines, $RR'CHNHCOCH_3$, and *N*,*N*-diacetylamines depending on the nature of R and R'. $RR'R''CNH_2$ gave only *N*-monoacetylamine. Mono- or diacetylation is clearly a function of the steric requirements about the amino group. The reaction provides a useful route for obtaining *N*,*N*-diacetylamines in reasonably good yields, as shown in Table I.

The infrared spectra of the *N*-monoacetylamines show bands at 3225–3275 cm^{-1} due to the N–H stretch of amides of the type CH_3CONHR. In all compounds prepared, whether monoacetylamine or diacetylamine, the symmetrical N–H stretch of the methyl group in the acetyl function shows absorption at 1366–1374 cm^{-1}. The carbonyl group of the monoacetylamines show a strong band at *ca.* 1640 cm^{-1}. The carbonyl band of the diacetylamines show up at 1692 cm^{-1}. The difference in the frequency of absorption of the carbonyl group for monoacetylamines and diacetylamines was

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[1] Taken from the Ph.D. Dissertation of K. H. Brown, Loyola University, 1970.

TABLE I

ACETYLATION OF AMINES

$$RNH_2 + Ac_2O \xrightarrow{\text{reflux}} RNHCOCH_3 + RN(COCH_3)_2$$

Starting amine	N-Acetylamine			N,N-Diacetylamine										
									% C		% H		% N	
	% yield	Mp or bp (mm), °C[a]	Registry no.	% yield	Bp, °C (mm)	Mp, °C	$n^{25}\text{D}$	$d^{27.5}$	Calcd	Found	Calcd	Found	Calcd	Found
Cyclopropylamine	0		27179-51-7	69	94.5 (10.0)		1.4686	1.11	59.57	59.76	7.80	7.82	9.93	9.79
Cyclobutylamine	0		27179-52-8	77	107 (10.5)		1.4712	1.06	61.94	61.94	8.39	8.43	9.03	8.96
Cyclopentylamine	74		27179-53-9	23	115–120 (11)			1.09						
Cyclohexylamine[b]	76	104–106		22	125 (10.0)			1.05						
Cycloheptylamine	66	55–56	27179-54-0	32	138 (9.0)									
Cyclooctylamine	66	45–46	27179-55-1	32	150 (9.0)		1.4765	1.01						
n-Propylamine	0		1563-84-4	65	85 (10.0)		1.4476	1.01	58.72	58.83	9.15	9.09	9.78	9.79
Isopropylamine	15	95 (10)	1563-85-5	30	95 (10.5)		1.4307	0.97	58.72	58.81	9.15	9.23	9.78	9.66
n-Butylamine	0		1563-86-6	90	63 (0.3)		1.4492	1.00	61.12	61.36	9.62	9.41	8.91	9.15
sec-Butylamine	35	101 (9)	19264-30-3	40	85 (9.0)		1.4361	0.96	61.12	61.19	9.62	9.64	8.91	9.07
Isobutylamine	0		1787-52-6	70	91 (10.0)		1.4467	0.99	61.12	60.97	9.62	9.72	8.91	8.90
tert-Butylamine	60	95–96		0										
Octadecylamine	0		27179-61-9	51		45–46			74.73	74.94	12.26	12.30	3.96	3.83
Ethylenediamine[e]	0		10543-57-4	25		149–150			52.62	52.77	7.07	6.99	12.28	12.25
Benzylamine[c]	0		3027-02-9	70	160 (30)									
Phenethylamine	0		27179-64-2	80	165 (11)		1.5254	1.16	70.22	70.20	7.37	7.23	6.83	6.86
2-Aminopyridine	0		3027-04-1	53	110 (0.3)									
3-Aminopyridine	0		27179-66-4	20		82–83			60.66	60.61	5.60	5.66	15.73	15.73
4-Aminopyridine	0		27179-67-5	25		150–151								
3-Picolylamine	0		27178-11-6	63	140 (0.4)		1.5370	1.21	62.48	62.64	6.30	6.38	14.58	14.54
4-Picolylamine	0		27178-12-7	51	150 (0.5)		1.5307		62.48	62.38	6.30	6.37	14.58	14.43
2-(2-Aminoethyl)-pyridine	0		27179-68-6	66	140 (0.4)		1.5238	1.21	63.57	63.30	6.84	6.85	13.58	13.50
Aniline[d]	0			50										

[a] The melting points of the N-alkylacetamides (N-acetylamines) prepared were verified with literature values. N-*tert*-Butylacetamide: B. Scholl, *Justus Liebigs Ann. Chem.*, **16**, 338 (1906). N-Isopropylacetamide, N-*sec*-butylacetamide, N-cyclopentylacetamide, N-cyclohexylacetamide, N-cycloheptylacetamide, and N-cyclooctylacetamide; M. Murakami, K. Akagi, and Y. Mori, *Bull. Chem. Soc.*, **35**, 11 (1962). [b] R. A. B. Bannard, *Can. J. Chem.*, **42**, 744 (1964). [c] C. K. Ingold and E. L. Holmes, *J. Chem. Soc.*, **127**, 1800 (1925). [d] P. P. Bedson and A. J. King, *ibid.*, **37**, 752 (1880). [e] Data given are for tetracetyl derivative.

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

J. W. BURNHAM[1] AND E. J. EISENBRAUN*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

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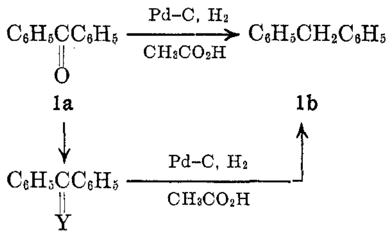
Hydrogenolysis of ketones such as acetophenone, benzophenone (Scheme I), and 1-tetralone to the corresponding hydrocarbons is readily accomplished in good yield[2a–d] and has become an important synthesis route

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.