(0°), opened, and sealed with a rubber septum cap, and a known amount of n-hexane was introduced as an internal standard.

Decompositions carried out in solvents other than carbon tetrachloride were performed in solutions prepared by diluting a concentrated solution (2–3 M) of the hypochlorite in carbon tetrachloride with a carbon tetrachloride solution of the second solvent component. Chloroacetic acids required acetonitrile as a third solvent component to maintain solution of the acid component.

Quantitative analyses of reaction mixtures were carried out by g.l.p.c. techniques. The columns used for analyses of the alkyl halides were calibrated with standard solutions at the same time and under the same conditions as the unknown. The peak areas on the chromatogram for each component of both the calibration and reaction solutions were determined with a planimeter.

From the ratio of peak areas (alkyl chloride to hexane) of the calibration mixture and the amount of each component in the calibration mixture, the constant m could be determined for the following simple proportionality.

$$\frac{\text{weight of RCl}}{\text{weight of hexane}} = m\frac{\text{area of RCl}}{\text{area of hexane}}$$

The values of m, the areas from the unknown mixtures, and the amount of hexane added to the unknown were then used to calculate the amount of each component present. Reproducibility was 2–3% and experimental errors represent the spread between two or more duplicate analyses. Results are reported as average values.

The gas chromatographic columns are described below. Relative retention times for alkyl chlorides are reported in Table VIII as are the calibration factors. Product ketones were not eluted from columns A, B, and D and were much later than the alkyl chlorides from column C.

Gas Chromatographic Columns and Conditions.—The following columns were used: A, 20-ft. α-chloronaphthalene (7%), Bentone 34 (5%) on Chromosorb P (35–80 mesh) at 18° and 10 p.s.i. of N_2 carrier gas; B, same as above at 0° and 16 p.s.i. of N_2 pressure; C, 12-ft. didecylphthalate (15%), Bentone 34 (5%) on Chromosorb W-HMDS (60–80 mesh) at 70° and 10 p.s.i. of N_2 carrier gas; and D, 12-ft. α-chloronaphthalene (7%), Bentone 34 (5%) on Chromosorb P (35–80 mesh) at 25° and 10 p.s.i. of N_2 carrier gas.

Chloride Determination *via* Solvolysis and Volhard Titration.—The CCl_4 solution resulting from the hypochlorite photolysis was rinsed into a 100-ml. round-bottom flask with acetone. The CCl_4 and alkyl chlorides were removed *via* a rotary vacuum evaporator with benzene added as chaser; complete removal of carbon tetrachloride was checked by g.l.p.c. A 2 M sodium hydroxide–50% aqueous ethanol solution (10 ml.) and a magnetic stirring bar were added; the flask was capped (rubber septum) and heated (oil bath) at 80° for 48 hr. with stirring. The resulting solution was titrated for chloride after acidification (HNO_3) with a $AgNO_3$–NaSCN system (ferric ammonium sulfate indicator). The sum of the chloride titer and amount of alkyl chlorides (by g.l.p.c.) consistently resulted in a 98–100% accounting of chloride based on the amount of t-alkyl hypochlorite initially present. No ionic chloride or hydrogen chloride was formed in detectable amounts during photolysis.

TABLE IX

EFFECT OF HYPOCHLORITE CONCENTRATION ON CLEAVAGE RATES AND YIELDS[a]

Alkyl hypochlorite $R_a(R_b)(R_c)COCl$					
R_a	R_b	R_c	$ROCl$,[b] M	Relative rates,[c] R_c/R_b	Total RCl,[d] %
CH_3	C_2H_5	n-C_3H_7	1.01	0.635	36.2
			0.726	0.629	35.3
			0.507	0.632	34.6
			0.338	0.631	34.0
n-C_4H_9	C_2H_5	n-C_3H_7	1.21	0.726	31.1
			0.764	0.724	28.9
			0.382	0.727	25.0
CH_3	C_2H_5	n-C_4H_9	1.08	0.587	15.4
			0.539	0.577	13.5

[a] Decomposition temperature, 25 ± 0.3°. [b] Molarity of alkyl hypochlorite in CCl_4. [c] Molar ratio of alkyl chloride products. [d] Total β-scission products observed.

Acknowledgment.—We wish to thank the Petroleum Research Fund of the American Chemical Society for a generous grant for support of this research and Dr. G. R. McMillan for helpful discussions.

Synthesis of Unsymmetrical Azoalkanes from Acylalkylhydrazones and 1,2-Dialkylhydrazines[1]

LEONARD SPIALTER, DANIEL H. O'BRIEN,[2] GERALD L. UNTEREINER,[3] AND WILLIAM A. RUSH[3]

Chemistry Research Laboratory, Aerospace Research Laboratories, Wright-Patterson Air Force Base, Ohio

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The syntheses of various unsymmetrical azoalkanes by oxidation of 1,2-dialkylhydrazines, obtained from the lithium aluminum hydride reduction of acylalkylhydrazones, are described. The boiling points are related to those of the analogous hydrocarbons. The azoalkanes, unlike dialkylhydrazines, show no additional structure-dependent interactions. Infrared and ultraviolet absorption data are presented and the *trans*-azo stretching frequency is assigned to 1562 cm.$^{-1}$ (6.40 μ).

Azoalkanes have recently attracted renewed interest as progenitors of alkyl radicals by photolytic,[4] radiolytic,[5] and pyrolytic[6] reactions. For related studies in this laboratory it became of interest to have available azoalkanes containing differing alkyl groups in the same molecule, corresponding to the general formula, $R_aN{=\!=}NR_b$, where R_a and R_b are not identical.[7] A search of the literature showed prior reporting of two such compounds: isopropylazo-*sec*-butane, $(CH_3)_2$-

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[1] Presented in part before the Division of Organic Chemistry, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963.

[2] Visiting Research Associate on leave from University of Dayton during the summer of 1962.

[3] A portion of this work is derived from theses submitted by W. A. R. (June 1960) and G. L. U. (July 1963) to the Air Force Institute of Technology in partial fulfillment of the requirements for the M.S. degree.

[4] (a) C. Steel and M. Szwarc, *J. Chem. Phys.*, **33**, 1677 (1960); (b) M. Shanin and K. O. Kutschke, *J. Phys. Chem.*, **65**, 189 (1961); (c) S. Toby, *ibid.*, **64**, 1575 (1960); (d) R. H. Riem and K. O. Kutschke, *Can. J. Chem.*, **38**, 2332 (1960); (e) B. C. Roquitte and J. H. Futrell, *J. Chem. Phys.*, **37**, 378 (1962); (f) J. A. Kerr and J. G. Calvert, *J. Am. Chem. Soc.*, **83**, 3391 (1961); (g) R. K. Lyon, *ibid.*, **83**, 4290 (1961).

[5] L. J. Stief and P. Ausloos, *J. Phys. Chem.*, **65**, 877 (1961).

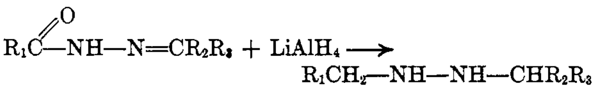
[6] (a) T. A. Whatley, Ph.D. Thesis, University of Oregon, 1961; University Microfilms, Ann Arbor, Mich., L. C. No. Mic 61-2089; *Dissertation Abstr.*, **21**, 3652 (1961); (b) M. B. Neiman, V. Ya. Efremov, and Yu. Ya. Efremov, *Trudy po Khim. i Khim. Tekhnol*, **2**, 500 (1959); (c) J. B. Levy and B. K. W. Copeland, *J. Am. Chem. Soc.*, **82**, 5314 (1960).

[7] These compounds are called "unsymmetrical" azoalkanes by Chemical Abstracts Service [*Chem. Abstr.*, **56**, 44*n* (1962)], although there is a possibility of confusion because they are obtainable by oxidation of "symmetrical" hydrazines rather than unsymmetrical ones. These latter have two alkyl groups on the same nitrogen.

$CHN{=}N{-}CH(CH_3)C_2H_5$, in an unpublished thesis,[8] and isopropylazomethane, $(CH_3)_2CHN{=}NCH_3$.[9]

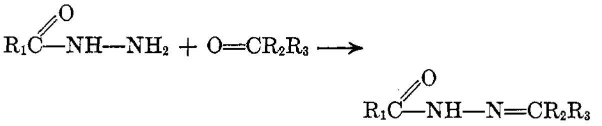
The most convenient precursors for azo compounds of the desired type[10] are the parent hydrazines from which they can be obtained by oxidation. Oxidizing agents reported in the literature have included potassium chromate,[11] copper(II) salts,[12,13] hydrogen peroxide,[8,9a] iodine,[14] and mercuric oxide[15] under a variety of experimental conditions. After preliminary experiments with these, as well as with other oxidizing agents which proved uniformly unsatisfactory (PbO, Pb_3O_4, and PbO_2 were not powerful enough and AgO caused catalytic decomposition of the hydrazine with nitrogen evolution), mercuric oxide was adopted as the reagent of choice.

The heart of the preparative scheme, however, was a suitable synthesis of the parent hydrazine. Methods applicable to symmetrically substituted hydrazines having identical alkyl groups, *e.g.*, those based on the reduction of alkylideneazines, $(R)_2C{=}NN{=}C(R)_2$,[15a,16] the alkylation of 1,2-diacylhydrazides (with subsequent hydrolysis),[17] or the reduction of 1,2-diacylamides, are not convenient for stepwise insertion of differing substituents, although this was essentially the method used by Ramsperger.[9b] The simple Raschig-type synthetic reaction between amines and alkylchloramines gives negligible yield.[18] Recently, Schmitz[19] reported a novel synthesis for mixed 1,2-dialkylhydrazines by acid hydrolysis of trialkyldiaziridines formed from Schiff bases and alkylchloramines. However, the ability of lithium aluminum hydride to reduce hydrazides and hydrazones[20] and the actual obtaining of a mixed hydrazine from a mixed acylhydrazone by means of this reagent[21] (eq. 1) recommended this last-named technique. Unfortunately, it is true that the resulting dialkylhydrazine is limited to those structures where one alkyl group is primary and the other is either primary or secondary.



$$R_1C({=}O){-}NH{-}N{=}CR_2R_3 + LiAlH_4 \longrightarrow R_1CH_2{-}NH{-}NH{-}CHR_2R_3 \quad (1)$$

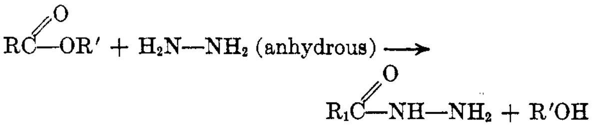
The acylhydrazones were readily prepared by reaction of an acylhydrazide with an aldehyde or ketone.



$$R_1C({=}O){-}NH{-}NH_2 + O{=}CR_2R_3 \longrightarrow R_1C({=}O){-}NH{-}N{=}CR_2R_3 \quad (2)$$

The different functional groups on each end of the hydrazine moiety prevent reshuffling of groups during synthesis and preserve the molecular integrity. Although the completely aliphatic acylhydrazones have not been well studied, the condensation reaction leading to their formation is the basis for the use of the well-known carbonyl extractants, Girard reagents T and P,[22] which are quaternary ammonium derivatives of acethydrazide.

The acylhydrazides are readily prepared by treating the methyl or ethyl ester of the desired carboxylic acid with anhydrous hydrazine in excess to ensure monohydrazide formation. Previous workers[23] have used the hydrate which required at least 18-hr. refluxing to complete the reaction, but our work has demonstrated that the use of anhydrous hydrazine at ambient temperature reduces reaction time to less than 3 hr.[24]



$$RC({=}O){-}OR' + H_2N{-}NH_2\ (\text{anhydrous}) \longrightarrow R_1C({=}O){-}NH{-}NH_2 + R'OH \quad (3)$$

Essentially, the synthetic scheme leading to the mixed azoalkanes consisted of reactions 3, 2, and 1, in order, then followed by the oxidation step (4).

$$R_1CH_2{-}NH{-}NH{-}CHR_2R_3 \xrightarrow{(O)} R_1CH_2{-}N{=}N{-}CHR_1R_2 \quad (4)$$

Experimental Section

Acethydrazide was obtained from Chemicals Procurement Laboratories and used without further purification, m.p. 64–66°, lit.[25] m.p. 67°.

Formhydrazide, m.p. 54°,[26] and propionhydrazide, m.p. 41°,[27] were prepared by the reaction of anhydrous hydrazine with methyl formate and ethyl propionate, respectively, for 3 hr. at room temperature. All aldehydes were distilled under argon just prior to reaction with the acyl hydrazides. The acetone used was Matheson Coleman and Bell reagent grade material.

1-Acetyl-2-isopropylidenehydrazine.—Acetone (50 g., 0.86 mole) was added to a flask containing acethydrazide (56 g., 0.76 mole) and equipped with a stirrer and a reflux condenser. The mixture warmed appreciably and a homogeneous solution resulted. The solution was cooled and the resulting solid mass was broken up and triturated with 10 ml. of acetone to ensure completeness of reaction. After filtration, the product was recrystallized from isopropyl alcohol and dried in a vacuum oven at 50°.

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(8) G. M. Decherd, Jr., unpublished M.A. Thesis, University of Texas, Austin, Texas, Aug. 1926.

(9) (a) H. C. Ramsperger, *J. Am. Chem. Soc.*, **51**, 918 (1929); (b) R. J. LeFévre, M. F. O'Dwyer, and R. L. Werner, *Australian J. Chem.*, **14**, 315 (1961).

(10) In a paper by H. Esser, K. Rastädter, and G. Reuter [*Chem. Ber.*, **89**, 689 (1956)], describing the direct oxidation of organic isocyanates to symmetric azo compounds by means of hydrogen peroxide, it was stated that the technique would be tested for the synthesis of unsymmetric analogs, but no further publications on this point have appeared. The present authors question the efficiency of application in this direction, but have not studied the feasibility experimentally.

(11) (a) J. Thiele, *Ber.*, **42**, 2575 (1909); (b) H. C. Ramsperger, *J. Am. Chem. Soc.*, **49**, 912 (1927); (c) A. O. Allen and O. K. Rice, *ibid.*, **57**, 310 (1935); (d) O. K. Rice and D. V. Sickman, *J. Chem. Phys.*, **4**, 242 (1936); (e) M. Burton, T. W. Davis, and H. A. Taylor, *J. Am. Chem. Soc.*, **59**, 1038 (1937).

(12) (a) H. L. Lochte, W. A. Noyes, and J. R. Bailey, *ibid.*, **44**, 2556 (1922); (b) L. D. Barrick, G. W. Drake, and H. L. Lochte, *ibid.*, **58**, 160 (1936).

(13) F. P. Jahn, *ibid.*, **59**, 1761 (1937).

(14) G. Fodor and J. Wein, *J. Chem. Soc.*, 890 (1948).

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(16) L. H. Lochte, J. R. Bailey, and W. A. Noyes, *J. Am. Chem. Soc.*, **43**, 2597 (1921).

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(19) E. Schmitz, *Angew. Chem.*, **73**, 23 (1961); German Patent 1,107,238 (May 25, 1961) (to Deutsche Akademie der Wissenschaften zu Berlin).

(20) (a) K. Kratzl and K. P. Berger, *Monatsh.*, **89**, 8487 (1958); (b) R. L. Hinman, *J. Am. Chem. Soc.*, **78**, 1645 (1956).

(21) R. L. Hinman, *ibid.*, **79**, 414 (1957).

(22) A. Girard and G. Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

(23) C. F. H. Allen and A. Bell, *Org. Syn.*, **24**, 12 (1944).

(24) After this technique had been used in our experimentation (see W. A. Rush, M.S. Thesis, Air Force Institute of Technology, June 1960), the analogous observation under slightly modified conditions with acetamide was disclosed by R. D. Twelves, in U. S. Patent 3,023,241 (Feb. 27, 1962).

(25) T. Curtius and T. S. Hoffman, *J. prakt. Chem.*, **53**, 513 (1896).

(26) In agreement with value cited by T. Curtius [*Ber.*, **26**, 404 (1893)].

(27) T. Curtius and H. Hille [*J. prakt. Chem.*, **64**, 401 (1901)] give m.p. 40°.

TABLE I

PREPARATION OF 1-ACYL-2-ALKYLIDENEHYDRAZINES

$$\underset{A}{R_1CONH{-}NH_2} + \underset{B}{O{=}CR_2R_3} \longrightarrow \underset{C}{R_1CONH{-}N{=}CR_2R_3}$$

R_1	R_2	R_3	Mole ratio, A/B	Yield, %	M.p., °C.	Calcd., % C	Calcd., % H	Calcd., % N	Calcd., % O	Found, % C	Found, % H	Found, % N	Found, % O
H	CH_3	CH_3	1.08	58.3	75–75.5[a]	47.98	8.05	27.98	15.98	47.85	8.21	28.05	16.03
H	H	C_2H_5	1.04	*ca.* 87	Oil[b]								
CH_3	H	C_2H_5	1.11	75.3	76–77	52.61	8.83	24.54	14.02	52.72	8.82	24.38	14.00
CH_3	H	n-C_3H_7	1.12	67.0	75.5–76.5	56.22	9.44	21.86	12.48	56.02	9.45	21.71	12.27
CH_3	H	i-C_3H_7	1.04	73.4	57–58	56.22	9.44	21.86	12.48	55.99	9.36	21.92	12.31
CH_3	CH_3	CH_3	1.13	82.0	134–135[c]	52.61	8.83	24.54	14.02	52.42	8.81	24.54	13.92
C_2H_5	CH_3	CH_3	1.04	95.6	105–106[d]	56.22	9.44	21.86	12.48	56.10	9.50	21.72	12.38

[a] R. D. Twelves [U. S. Patent 3,023,241 (Feb. 27, 1962)] reports white needles, m.p. 35–35.5°, from the same reaction. Our results are reproducible and we cannot account for the discrepancy with this citation. [b] Product could not be distilled or crystallized. The oily residue remaining after evaporation of water and unreacted excess hydrazine was used directly in the next step, reduction with $LiAlH_4$. [c] A. N. Kurtz and C. Niemann [*J. Org. Chem.*, **26**, 1843 (1961)] report m.p. 136.5–138°; T. Curtius and T. S. Hofmann [*J. prakt. Chem.*, **53**, 513 (1896)] give m.p. 133°; L. Horner and H. Fernekess [*Chem. Ber.*, **94**, 712 (1961)] cited m.p. 134°. [d] T. Curtius and H. Hille [*J. prakt. Chem.*, **64**, 401 (1901)] report m.p. 101°.

TABLE II

PREPARATION AND PROPERTIES OF ALKYLHYDRAZINES

$$\underset{D}{R_1{-}COHN{-}N{=}CR_2R_3} + \underset{E}{LiAlH_4} \longrightarrow R_1{-}CH_2NH{-}NH{-}CHR_2R_3$$

R_1CH_2	CHR_2R_3	Mole ratio, D/E	Method	Yield, %	B.p., °C. (740 mm.)	$n^{25}D$	d^{25}_4	d^0_4	Molar refractivity Calcd.	Molar refractivity Found
CH_3CH_2	$CH_2CH_2CH_3$	0.34	B	61	134–135	1.4310	0.8151	0.8411	32.49	32.48
CH_3CH_2	$CH(CH_3)_2$	0.45	B	61	114–115[a]	1.4215	0.8024	0.8272	32.49	32.33
CH_3CH_2	$CH_2CH_2CH_2CH_3$	0.33	A, B	61	152–154	1.4332	0.8136	0.8389	37.04	37.02
CH_3CH_2	$CH_2CH(CH_3)_2$	0.43	C	61	148–148.5	1.4397	0.8236	0.8479	37.14	37.16
$CH_3CH_2CH_2$	$CH(CH_3)_2$	0.43	B	74	140–141	1.4229	0.7971	0.8199	37.17	37.11
CH_3	$CH(CH_3)_2$	0.38	C	63	99–100[b]	1.4148	0.7947[b]	0.8190	27.85	27.84
CH_3	$CH_2CH_2CH_3$	0.25	A	24[c]	122–124	1.4301	0.8224	0.8498	27.84	27.80

[a] K. Kratzl and K. P. Berger [*Monatsh.*, **89**, 83 (1958)] report b.p. 116–118° at 760 mm. [b] H. C. Ramsperger [*J. Am. Chem. Soc.*, **51**, 918 (1929)] reports b.p. 100.2° at 760 mm., *d* 0.7959 (temperature unspecified). [c] Based on propiohydrazide used.

TABLE III

PREPARATION OF MIXED AZOALKANES

$$R_1NHNHR_2 \xrightarrow{HgO} R_1N{=}NR_2$$

R_1	R_2	Yield, %	Formula	Calcd., % C	Calcd., % H	Calcd., % N	Found, % C	Found, % H	Found, % N
CH_3CH_2	$CH_2CH_2CH_3$	23	$C_5H_{12}N_2$	59.95	12.08	27.97	60.22	12.07	28.23
CH_3CH_2	$CH(CH_3)_2$	59	$C_5H_{12}N_2$	59.95	12.08	27.97	59.99	11.96	28.20
CH_3CH_2	$CH_2CH_2CH_2CH_3$	36	$C_6H_{14}N_2$	63.11	12.36	24.53	63.05	12.25	24.76
CH_3CH_2	$CH_2CH(CH_3)_2$	40	$C_6H_{14}N_2$	63.11	12.36	24.53	63.08	12.42	24.26
$CH_3CH_2CH_2$	$CH(CH_3)_2$	46	$C_6H_{14}N_2$	63.11	12.36	24.53	63.24	12.28	24.83

TABLE IV

PHYSICAL PROPERTIES OF MIXED AZOALKANES

$$R_1N{=}NR_2$$

R_1	R_2	B.p., °C. (741 mm.)	$n^{25}D$	d^{25}_4	d^0_4	Molar refractivity Calcd.	Molar refractivity Found
CH_3CH_2	$CH_2CH_2CH_3$	86–87	1.3946	0.7603	0.7876	31.46	31.52
CH_3CH_2	$CH(CH_3)_2$	74–75	1.3856	0.7410	0.7703	31.47	31.63
CH_3CH_2	$CH_2CH_2CH_2CH_3$	119–120	1.4048	0.7755	0.8015	36.08	36.07
CH_3CH_2	$CH_2CH(CH_3)_2$	105–107	1.3996	0.7643	0.7911	36.11	36.01
$CH_3CH_2CH_2$	$CH(CH_3)_2$	101–102	1.3958	0.7549	0.7803	36.08	36.14

The other 1-acyl-2-alkylidenehydrazines were synthesized in a procedure analogous to that above, by reaction of the appropriate carbonyl compound and the acylhydrazide. Preparative and analytical data appear in Table I.

Reduction of Acylhydrazones to Hydrazines.—The general procedure for the reduction of the acylhydrazones was as follows. $LiAlH_4$ was dissolved in anhydrous ether in a previously dried three-necked flask equipped with a reflux condenser, magnetic stirrer, and drying tube. The acylhydrazone was added either simply in ether solution (method A) or, where solubility was too low, by continual extraction by refluxing ether solvent over the hydrazone in the thimble of a Soxhlet apparatus (method B) or packed into a liquid–liquid extractor (method C). After the addition of the acyl hydrazone was complete and no further reaction was noted, enough water was carefully added to hydrolyze the excess hydride. The resulting solution was filtered and the precipitate was washed with a large quantity of anhydrous ether. The ether washings were concentrated and the hydrazines were isolated by fractional distillation. Despite numerous attempts by the microanalytical laboratory, the hydrazines failed to give consistent analytical results. Similar difficulties have been noted before.[16,28] However, other data such as mode of syn-

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(28) A. Franke, *Monatsh.*, **19**, 524 (1898).

thesis, the infrared absorption spectra, physical properties, convertibility to the azoalkanes, and the molar refractivity are compatible with the assigned structures and acceptable purity. Preparative yields are given in Table II.

Oxidation of 1,2-Dialkylhydrazines to Azoalkanes.—The general oxidative procedure was as follows. The hydrazine sample, approximately 15 g., was added slowly to a well-agitated suspension of 40 g. of mercuric oxide in 100 ml. of water. The mixture was stirred for an additional 0.5 hr. at room temperature. Usually the product was isolated by filtering the mercury and mercury salts, washing the precipitate with ether, extracting the aqueous phase with ether, drying the combined washings and extracts with $MgSO_4$, and distilling. In one case (ethylisopropyl) the product was obtained by distillation directly from the reaction mixture, but frothing proved troublesome. The low yields (less than 60%) observed may be due to several factors. Incomplete oxidation was noted in the case of ethyl-*n*-propyl when a fraction was collected at the approximate boiling point of the hydrazine. Some side reaction, occurring either during the oxidation or in the subsequent distillation, probably caused some lowering of yield in the case of methylisopropyl (4 g. of high-boiling residue was obtained), ethyl-*n*-propyl (2.1 g. of a fraction boiling at 132–144° plus a residue of 1.3 g. was obtained), ethylisobutyl (when the original product was redistilled for physical constant measurements, an appreciable high-boiling residue remained), and ethyl-*n*-butyl (a high-boiling residue was obtained). Decomposition of the sensitive azoalkane is also a distinct possibility, as well as adsorption or complexing by the mercury salts of either nitrogen compound. The preparative results are shown in Table III.

Physical Properties of the Hydrazines and Azoalkanes.—All of these compounds were clear liquids. The hydrazines were colorless with an earthy ammoniacal odor. The azoalkanes possessed a straw yellow color and a sickeningly sweet odor. The boiling point of these substances was taken as the point at which the principal fraction of the liquid boiled upon distillation through a 5-cm. distilling column packed with glass helices. The physical data appear in Tables II and IV. Ultraviolet and infrared spectra were obtained on the Cary Model 11 and Perkin-Elmer Model 21 spectrophotometers, respectively.

Discussion

Hydrogen Bonding and Steric Hindrance.—The comparison between the boiling points of the azoalkanes, 1,2- and 1,1-dialkylhydrazines, respectively, with those of their hydrocarbon analogs, wherein the nitrogen atoms are replaced by C–H groups, is shown in Tables V–VII. The azoalkane data of Table V yield, as is shown in Figure 1, an excellent linear plot with an inclination of 45°. This suggests that there are no significant additional structural-dependent intermolecular bonding forces beyond those present also in the reference olefin. In support of this conclusion is the uniform difference of about −10 ± 2° observed between the boiling points of each azoalkane and its olefin analog.[29]

On the other hand, the 1,2-dialkylhydrazine data depicted in Figure 2 are more scattered and, as is seen in Table VI, the boiling point increment between the nitrogen compound and its carbon analog becomes consistently less as the alkyl groups on the nitrogen increase in size and/or extent of branching. The most reasonable and generally accepted interpretation is that enhancement of boiling point is due to hydrogen bonding in the hydrazines, and the larger and more branched substituents, in the present case, present steric hindrance to such bonding. Further qualitative support for this interpretation is drawn from progressive sharpening of the N–H stretching vibration at 3.07–3.12 μ in the infrared absorption spectra as the boiling-point increment diminishes.

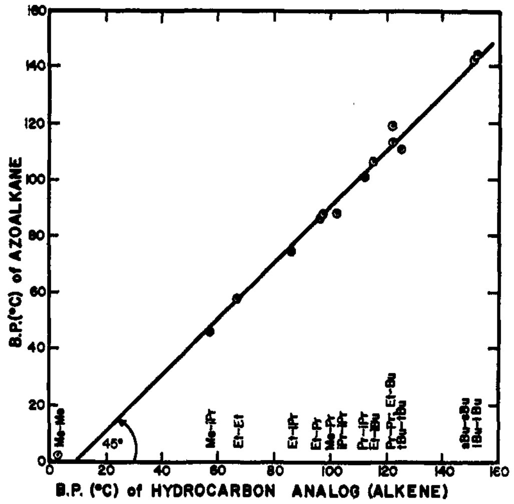

Figure 1.—The effect of molecular structure on the boiling points of azoalkanes. Points represent *cis–trans* averages.

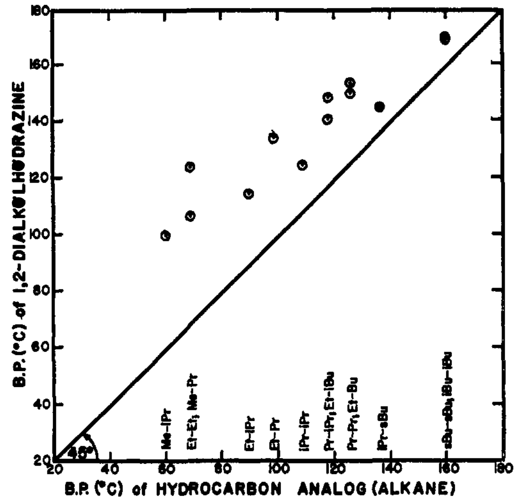

Figure 2.—The effect of molecular structure on the boiling points of 1,2-dialkylhydrazines.

It has been found possible to assign linearly additive values to the seven different kinds of alkyl substituents in the 1,2-dialkylhydrazines which allow calculation of the boiling point increments for such compounds in good agreement (±3°) with the observed quantities. Initially, these values were computed for a given alkyl substituent by taking one-half of the boiling point increment observed in the symmetrical dialkylhydrazine. However, it was subsequently found that the increments for related alkyl-substituent pairs in 1,1-dialkylhydrazines were similar. As a result, the available normal boiling point data for all known 1,1- and 1,2-dialkylhydrazines were combined and analyzed mathematically. Simply taking one-half of the increment observed for the cases of disubstituted hydrazines containing the same alkyl groups yielded the contributions for each such alkyl group to the boiling point increment averaging within ±3° for the 22 compounds on which suitable data are available. Values for this parameter are given in Table VIII. The increments calculated therefrom are compared with the experimental in the last columns of Tables VI and VII and the agreement is considered significantly good and useful within the uncertainties inherent in the data. It is particularly instructive to note that the values

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[29] The first member, azomethane, is anomalous.

TABLE V

BOILING POINT INCREMENTS IN AZOALKANES (AZ) COMPARED WITH THEIR HYDROCARBON ANALOGS (HC)

		B.p., °C. (mm.)[a]		
R_1	R_2	$R_1N{=}NR_2$ (AZ)	$R_1CH{=}CHR_2$ (HC)	B.p.$_{AZ}$ − b.p.$_{HC}$
CH_3	CH_3	2 (758)[b]	2.3[c]	−0.3
CH_3	$CH(CH_3)_2$	46 (760)[d]	57.4[c]	−11
CH_3	$CH_2CH_2CH_3$	88[e]	98.2[c]	−10
C_2H_5	CH_2	58[f]	66.7[c]	−10
C_2H_5	$CH(CH_3)_2$	74–75 (741)[g]		−11
C_2H_5	$CH_2CH_2CH_3$	86–87 (741)[g]	95.7[c]	−9
C_2H_5	$CH_2CH(CH_3)_2$	105–107 (741)[g]	115[c]	−9
C_2H_5	$CH_2CH_2CH_2CH_3$	119–120 (741)[g]	123.1[c]	−13
$(CH_3)_2CH$	$CH(CH_3)_2$	89–89.5 (747)[h]	102[c]	−13
$(CH_3)_2CH$	$CH_2CH_2CH_3$	101–102 (741)[c]	112[c]	−10
$CH_3CH_2CH_2$	$CH_2CH_2CH_3$	113.5[f]	120.5[c]	−7
$(CH_3)_3C$	$C(CH_3)_3$	109–110 (760)[i]	123.5–124 (758)[j]	−14
$(CH_3)_2CHCH_2$	$CH_2CH(CH_3)_2$	143–145 (752)[k]	151 (731)[l]	−6
$CH_3CH_2CH(CH_3)$	$CH(CH_3)CH_2CH_3$	141–142 (747)[h]	149.5–150 (760)[m]	−8

[a] Boiling point values are either the average of *cis* and *trans*, or *syn* and *anti* values, where such have been studied, or that for the normally occurring species or mixture of these isomers. [b] H. C. Ramsperger, *J. Am. Chem. Soc.*, **49**, 912 (1927). [c] R. R. Dreisbach, Ed., "Physical Properties of Chemical Compounds—II," Advances in Chemistry Series No. 22, American Chemical Society, Washington, D. C., 1959. All values are reduced to 760-mm. pressure. [d] H. C. Ramsperger, *J. Am. Chem. Soc.*, **51**, 918 (1929). [e] Data based on other work by L. Spialter and G. L. Untereiner to be published elsewhere. [f] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954). [g] This work. [h] L. D. Barrick, G. W. Drake, and H. L. Lochte, *J. Am. Chem. Soc.*, **58**, 160 (1936). Renaud and Leitch, ref. *f* above, give 88.5° for the boiling point of azoisopropane, the same value reported in an earlier paper by H. L. Lochte, W. A. Noyes, and J. R. Bailey, *J. Am. Chem. Soc.*, **44**, 2556 (1922). [i] E. Farenhorst and E. C. Kooyman, *Rec. trav. chim.*, **72**, 993 (1953). [j] V. R. Skvarchenko, *Uch. Zap. Mosk. Gos. Univ.*, **No. 131**, 167 (1950); *Chem. Abstr.*, **47**, 9893 (1953). [k] K. A. Taipale, *J. Russ. Phys. Chem. Soc.*, **56**, 81 (1925). [l] M. Tuot, *Bull. soc. chim. France*, **9**, 899 (1942). [m] R. Ya. Levina, V. R. Skvarchenko, E. G. Treshchova, and V. M. Tatevskii, *Zh. Obshch. Khim.*, **20**, 419 (1950); also given in ref. *j*.

TABLE VI

BOILING POINT INCREMENTS IN 1,2-DIALKYLHYDRAZINES (HZ) COMPARED WITH THEIR HYDROCARBON ANALOGS (HC)

		B.p., °C. (mm.)		B.p.$_{HZ}$ − b.p.$_{HC}$	
R_1	R_2	R_1NHNHR_2 (HZ)	$R_1CH_2CH_2R_2$ (HC)	Calcd.	Obsd.
CH_3	CH_3	81 (747)[a]	−0.5[b]	80	81
CH_3	$CH(CH_3)_2$	100.2 (760)[c]	60.3[b]	47	40
CH_3	$CH_2CH_2CH_3$	123–124 (740)[d]	68.7[b]	52	55
C_2H_5	C_2H_5	106–107[e]	68.7[b]	38	38
C_2H_5	$CH(CH_3)_2$	114–115 (740)[f]	90.1[b]	26	25
C_2H_5	$CH_2CH_2CH_3$	134–135 (740)[d]	98.4[b]	31	36
C_2H_5	$CH_2CH(CH_3)_2$	148–148.5 (740)[d]	117.6[b]	24	31
C_2H_5	$CH_2CH_2CH_2CH_3$	152–154 (740)[d]	125.7[b]	23	28
$(CH_3)_2CH$	$CH(CH_3)_2$	124.5 (750)[e,g–i]	109.1[b]	14	15
$(CH_3)_2CH$	$CH_2CH_2CH_3$	140–141 (740)[d]	117.6[b]	19	23
$(CH_3)_2CH$	$CH(CH_3)CH_2CH_3$	145–146[j]	136.0[b]	12	10
$CH_3CH_2CH_2$	$CH_2CH_2CH_3$	149.5–150[e]	125.7[b]	24	24
$(CH_3)_2CHCH_2$	$CH_2CH(CH_3)_2$	169.5–170 (735)[k]	159.9[b]	10	10
$CH_3CH_2CH(CH_3)$	$CH(CH_3)CH_2CH_3$	168–170[g]	160[b]	10	10

[a] L. Knorr and A. Köhler, *Ber.*, **39**, 3257 (1906). Extrapolation from the vapor pressure–temperature equation of J. G. Aston, G. J. Janz, and K. E. Russell [*J. Am. Chem. Soc.*, **73**, 1943 (1951)] gives 82.2° at 760 mm. [b] R. R. Dreisbach, Ed., "Physical Properties of Chemical Compounds—II," Advances in Chemistry Series No. 22, American Chemical Society, Washington, D. C., 1959. All values are reduced to 760-mm. pressure. [c] H. C. Ramsperger, *J. Am. Chem. Soc.*, **51**, 918 (1929). We find a value of 99–100° at 740 mm. [d] This work. [e] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954). [f] This work. K. Kratzl and K. P. Berger [*Monatsh.*, **89**, 83 (1958)] report 116–118° (760 mm.). [g] L. D. Barrick, G. W. Drake, and H. L. Lochte, *J. Am. Chem. Soc.*, **58**, 160 (1936). [h] H. L. Lochte, J. R. Bailey, and W. A. Noyes, *ibid.*, **43**, 2597 (1921). [i] K. A. Taipale, *Ber.*, **56B**, 954 (1923). [j] Estimated from distillation data of G. M. Decherd, Jr., unpublished M.A. Thesis, University of Texas, Aug. 1926. [k] K. A. Taipale, *J. Russ. Phys. Chem. Soc.*, **56**, 81 (1925).

of Table VIII do follow the pattern that the greater the steric hindrance of the substituent the smaller is the boiling point increment. However, it is not clear whether the increments are solely a function of hydrogen bonding. Class, *et al.*,[30] suggest that this is so for various methyl-substituted hydrazines because of comparable increments for ammonia and methylamines, but their parallelisms prove to be invalid when ethyl or other groups replace methyl in their compounds. Another objection difficult to overcome is the fact that tetramethylhydrazine, which has no hydrogen-bonding potential in the neat state, nevertheless boils 15° higher than its hydrocarbon analog.[30] This suggests that other intermolecular effects, possibly dipole–dipole interactions, may also make a significant contribution.

Ultraviolet Absorption Spectra.—The dialkylhydrazines do not absorb in the visible or ultraviolet down to 200 mμ. The ultraviolet spectral data for the azoalkanes prepared in this study are presented in Table IX. The data were obtained for solutions with cyclohexane as the solvent. The observed molar absorp-

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(30) J. B. Class, J. G. Aston, and T. S. Oakwood, *J. Am. Chem. Soc.*, **75**, 2937 (1953).

TABLE VII

BOILING POINT INCREMENTS IN 1,1-DIALKYLHYDRAZINES (HZ) COMPARED WITH THEIR HYDROCARBON ANALOGS (HC)

		B.p., °C. (mm.)		B.p.$_{HZ}$ − b.p.$_{HC}$	
R_1	R_2	$R_1R_2NNH_2$ (HZ)	$R_1R_2CHCH_3$ (HC)	Calcd.	Obsd.
CH_3	CH_3	63.4 (760)[a]	−11.7[b]	80	75
CH_3	$CH(CH_3)_2$	101.3–101.7 (769)[c]	58.0[b]	47	43
CH_3	$CH_2CH_2CH_3$	103.2–103.7 (769)[c]	60.3[b]	52	43
CH_3	$CH_2CH(CH_3)_2$	115.4–115.9 (758)[c]	80.5[b]	45	35
CH_3	$CH_2CH_2CH_2CH_3$	128–128.2 (736)[c]	90.1[b]	44	38
C_2H_5	C_2H_5	98–99.6 (756)[c]	63.3[b]	38	36
$(CH_3)_2CH$	$CH(CH_3)_2$	128–129 (720)[d]	113.5[b]	14	15
$CH_3CH_2CH_2$	$CH_2CH_2CH_3$	141–142.2 (764)[c]	117.7[b]	24	24

[a] Extrapolation from vapor pressure–temperature equation of J. G. Aston, J. L. Wood, and T. P. Zolki, *J. Am. Chem. Soc.*, **75**, 6202 (1953). [b] R. R. Dreisbach, Ed., "Physical Properties of Chemical Compounds—II," Advances in Chemistry Series No. 22, American Chemical Society, Washington, D. C., 1959. All values are reduced to 760-mm. pressure. [c] B. V. Ioffe, *Zh. Obshch. Khim.*, **28**, 1296 (1958). [d] F. Klages, G. Nober, F. Kircher, and M. Bock, *Ann.*, **547**, 1 (1941).

TABLE VIII

CONTRIBUTION PER ALKYL GROUP TO THE BOILING POINT INCREMENT IN DIALKYLHYDRAZINES (RELATIVE TO THE HYDROCARBON ANALOGS)

Group	Value, °C.
Methyl	40
Ethyl	19
Propyl	12
Isopropyl	7
Butyl	4
Isobutyl	5
sec-Butyl	5

tivities (extinction coefficients) are very low and in the range of 15–16. The maxima are quite distinct and only one symmetrical band is observed above 300 mμ. The tail responsible for the yellow color in the visible has $\epsilon < 2.5$ at 400 mμ. There is a trough at about 280 to 300 mμ, below which wave-length absorption gradually rises with $\epsilon > 100$ but no additional peak down to 200 mμ. These observations are quite similar to those made on azoisopropane by Cohen and Zand[31] who reported a symmetrical absorption band with λ_{max} 358 mμ (ϵ 19, falling to zero at 295 mμ and at 485 mμ).

TABLE IX

ULTRAVIOLET ABSORPTION DATA FOR AZOALKANES

Compound	Concn., × 10³, *M*	λ_{max}, mμ	ϵ_{max}	λ_{min}, mμ	ϵ_{min}
$(CH_3)_2CHN{=}NCH_3$	3.260	354.5	15.5	280	1.7
$n\text{-}C_3H_7N{=}NC_2H_5$	3.932	359.5	16.2	290	<1.0
$n\text{-}C_4H_9N{=}NC_2H_5$	4.341	360.0	14.9	300	2.3
$(CH_3)_2CHCH_2N{=}NC_2H_5$	2.853	361.0	14.7	305	2.3
$(CH_3)_2CHN{=}N\text{—}C_3H_7\text{-}n$	4.507	360.0	16.2	280	<1.0

Infrared Absorption Spectra.—The 1,2-dialkylhydrazines show a fairly undistinguished aliphatic hydrocarbon-type spectrum except for the N–H stretching band at 3.09 ± 0.01 μ (3236 ± 10 cm.$^{-1}$) which is quite sharp, but with half-widths ranging from 0.17 μ (170 cm.$^{-1}$) to 0.25 μ (250 cm.$^{-1}$) roughly parallel to increasing boiling point increment.

There has been almost complete uncertainty about the location of the —N=N— stretching frequency in azoalkanes because of the previous lack of suitable nonsymmetrically substituted molecules.[32] LeFévre, O'Dwyer, and Werner,[9b] speculating that the absence of infrared-active absorption for such a vibration in azomethane was due to its centrosymmetry, examined the only well-described previously reported molecule, isopropylazomethane. These workers deduced that the —N=N— stretch is probably between 6.34 μ (1576 cm.$^{-1}$) and 6.39 μ (1565 cm.$^{-1}$). The absorption is very weak, but our compounds in the neat liquid state exhibit two absorption bands of comparable intensity in this vicinity, one at 6.40 ± 0.02 μ (1562 ± 5 cm.$^{-1}$) and the other at 6.17 ± 0.02 μ (1621 ± 5 cm.$^{-1}$). Although LeFévre, *et al.*,[9b] claim to have unpublished measurements which show aliphatic azo derivatives to be nonpolar, *i.e.*, to contain *trans*-azo groups, the possibility exists that the compounds may be *cis–trans* mixtures. However, Hutton and Steel[33] have reported the only substantiated case of a nonring *cis* azoalkane compound and found it unstable with respect to the *trans* isomer. Moreover, there is the possibility of some contamination of azoalkanes by their respective tautomers, the alkylhydrazones, whose strong C=N absorption band would be expected at about 1625 cm.$^{-1}$.[34] Indeed, infrared absorption studies in this laboratory on the hydrazone tautomers[35] have confirmed a strong band at 6.16 ± 0.02 μ (1623 ± 5 cm.$^{-1}$) in such molecules. Hence it is concluded that only the 6.40-μ (1562-cm.$^{-1}$) band is characteristic of the azo compound and probably corresponds to *trans* $\nu_{N=N}$.

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(31) S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).

(32) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 272.

(33) R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964).

(34) This situation was pointed out to the authors by the referee, and thanks are here gratefully acknowledged to this source.

(35) Spectral and tautomerization data to be published elsewhere.