equal weights of the *cis* and *trans* diacetates (VI, 41 g.) were pyrolyzed at 520 ± 5° by the procedure of Bailey and King.[23] Premelted VI was added with dry nitrogen (4 ml./min.) at the rate of 0.2–0.3 g./min. to the reaction chamber which consisted of a 14 × 310 mm. Vycor tube packed with $^3/_{16}$-in. Pyrex helices. By titration of the crude pyrolysate with base, 0.20 mole (63%) of acetic acid was estimated. The pyrolysate was taken up in ether, washed repeatedly with 1% aqueous sodium carbonate, dried over sodium sulfate, and evaporated to a residue which was fractionally distilled to yield 6.0 g. (28%) of crude II, b.p. 130–134° (750 mm.). Fractional vacuum distillation of the residue resulting from the above distillation resulted in the recovery of 4.2 g. (10%) of VI, b.p. 130–138° (6–7 mm.), and 7.0 g. (23%) of a pale yellow liquid, b.p. 88.5–95.0° (6–7 mm.), which was unsaturated to bromine in carbon tetrachloride and had an infrared spectrum consistent with its formulation as 3,3,6,6-tetramethylcyclohexene 4-acetate (peaks at 1740 and 1030 cm.$^{-1}$). Repyrolysis of 5.3 g. of this acetate resulted in 1.5 g. (41%) of II. *p*-Xylene was detected as an impurity in crude II by gas–liquid chromatography and comparison of its infrared spectrum with that of an authentic sample. The gas chromatographic peak area ratio of II to *p*-xylene was found to be 10:1. An analytical sample of II was obtained by gas–liquid chromatography over a 7-ft. column of 30% silicone oil 550 on base-washed Chromosorb P, b.p. 132–133° (750 mm.), n^{25}D 1.4367.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.31; H, 11.68.

Bromination of II in carbon tetrachloride for 45 min. at 27° resulted in a tetrabromide which was crystallized from ethanol to m.p. 69.0–69.5°.

Anal. Calcd. for $C_{10}H_{16}Br_4$: C, 26.35; H, 3.54; Br, 70.12. Found: C, 26.41; H, 3.76; Br, 69.99.

Catalytic hydrogenation of II with Adams catalyst in glacial acetic acid resulted in the absorption of 99.2% of the theoretical volume of hydrogen. 1,1,4,4-Tetramethylcyclohexane was isolated and purified by fractional distillation, b.p. 146–148° (750 mm.), n^{25}D 1.4237, d_{25} 0.7747; lit.[15] b.p. 152.6–153.3°, n^{20}D 1.4258, d_{20} 0.7754.

4-Iodo-3,3,6,6-tetramethylcyclohexene 5-Benzoate (III).—A solution of 2.5 g. of iodine in 20 ml. of dry benzene was added in portions with shaking to 2.3 g. of freshly prepared dry powdered silver benzoate.[24] To this solution was added, all at once, 1.5 g. of II. After 1 hr. at reflux the solution was cooled and filtered; the filtrate was washed with water, 10% sodium bisulfite solution, 10% sodium carbonate solution, and water. After drying over sodium sulfate the solution was evaporated to a clear sirup which crystallized from methanol to yield 2.60 g. (68% based on iodine) of a white crystalline product, m.p. 78–81°. Repeated recrystallization from ligroin (35–60°) raised this to m.p. 80.5–81.5°.

Anal. Calcd. for $C_{17}H_{21}IO_2$: C, 53.17; H, 5.51; I, 33.03; mol. wt. (Rast), 384. Found: C, 53.14; H, 5.48; I, 33.16; mol. wt. (Rast), 374.

This substance failed to decolorize warm (50°) solutions of 3% bromine in carbon tetrachloride, bromine water, or 1% potassium permanganate in acetone over 5-min. periods relative to blank reagents. It also failed to react with a threefold excess of silver benzoate in refluxing dry benzene over an 85-hr. period.

3-Iodotricyclo[2.2.1.0^{2,6}]heptane 5-Benzoate (IV).—The reaction was carried out as described above using 3.0 g. of dry powdered silver benzoate, 3.3 g. of iodine, and 4.6 g. of freshly distilled bicyclo[2.2.1]heptadiene, b.p. 89° (753 mm.). Crystallization of the clear, sirupy product from methanol and then ligroin (35–60°) resulted in 1.25 g. (37% based on iodine) of a white crystalline product, m.p. 65–68°. Repeated recrystallization from ligroin raised the melting point to 67.5–69.0°.

Anal. Calcd. for $C_{14}H_{13}IO_2$: C, 49.45; H, 3.85; I, 37.33. Found: C, 49.54; H, 3.81; I, 37.11.

Attempted Diels–Alder Reactions of II.—Maleic anhydride tetracyanoethylene, and ethyl acetylene dicarboxylate were added to equal weights of II with and without solvent at temperatures from 37 to 150° and for periods of 1–24 hr. Thin layer chromatography and infrared analysis failed to indicate adduction.

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Acknowledgment.—F. W. G. and C. H. B. gratefully acknowledge partial support from the Petroleum Research Fund of the American Chemical Society, Grant 528-B.

Alkylations of Ketone and Aldehyde Phenylhydrazones by Means of Alkali Amides in Liquid Ammonia to Form N-Alkyl Derivatives

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Received August 20, 1964

Alkylations of benzaldehyde phenylhydrazone to form N-alkyl derivatives have previously been effected with alkyl halides by means of sodamide in benzene, but the details were not given.[2]

We have effected alkylations of this phenylhydrazone and of certain ketone phenylhydrazones (I) by means of sodamide or potassium amide in liquid ammonia to form the N-alkyl derivatives II (eq. 1, Table I).

$$\underset{\text{I}}{C_6H_5\overset{R}{\overset{|}{C}}{=}NNHC_6H_5} \xrightarrow[2.\ R'X]{1.\ MNH_2\ (liq.\ NH_3)} \underset{\text{II}}{C_6H_5\overset{R}{\overset{|}{C}}{=}NN\overset{R'}{\overset{|}{C}}C_6H_5} \quad (1)$$

Interestingly, the color of the intermediate anion of benzophenone phenylhydrazone was dark red, similar to that of the diphenylmethide ion. This suggests that resonance form IIIb makes some contribution to the structure of the anion, though the contribution of IIIa may be more important.

$$\underset{\text{IIIa}}{(C_6H_5)_2C{=}N{-}\bar{N}C_6H_5} \longleftrightarrow \underset{\text{IIIb}}{(C_6H_5)_2\bar{C}{-}N{=}NC_6H_5}$$

That the products were the N-alkyl derivatives, not the possible C-alkyl derivatives, was supported by the essential agreement of their melting points with the reported values, analysis in certain cases, and by independent syntheses of the N-benzyl derivatives of benzaldehyde and benzophenone phenylhydrazones (eq. 2).

$$C_6H_5\overset{R}{\overset{|}{C}}{=}O + H_2N\overset{CH_2C_6H_5}{\overset{|}{N}}C_6H_5 \longrightarrow \text{II} \quad (2)$$

R = H or C_6H_5; R′ = $C_6H_5CH_2$

Table I shows that the alkylations of the phenylhydrazones I to form the N-alkyl derivatives II (eq. 1) were realized in good to excellent yields (69–92%). This method appears more convenient than that represented by eq. 2, which has been reported difficult to effect.[2,3] Only the condensation of benzophenone with N-methylphenylhydrazine seems to have been realized previously in good yield (71%) and this required a

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TABLE I

ALKYLATIONS OF PHENYLHYDRAZONES I[a] TO FORM II

I, R	R'X	M	II, R	II, R'	Yield, %	M.p., °C. Found	M.p., °C. Lit.
H	$C_6H_5CH_2Cl$	Na	H	$C_6H_5CH_2$	92[b,c]	109–110	111[d]
CH_3	$C_6H_5CH_2Cl$	K	CH_3	$C_6H_5CH_2$	69[e]	57–58	58[f]
C_6H_5	CH_3I	K	C_6H_5	CH_3	77[g]	76–79	81[h]
C_6H_5	n-C_4H_9Br	K	C_6H_5	n-C_4H_9Br	93[i,c]	52–54[j]	...
C_6H	$C_6H_5CH_2Cl$	Na	C_6H_5	$C_6H_5CH_2$	85[b]	108–109	105–106[k]
C_6H_5	$C_6H_5CH_2Cl$	K	C_6H_5	$C_6H_5CH_2$	90[b]	108–109[l]	105–106[k]

[a] According to eq. 1. [b] 90-min. reaction period. [c] Combined yield from two crops. [d] Ref. 2. [e] 30-min. reaction period. [f] M. Busch and K. Schmidt, *J. prakt. Chem.*, **129**, 151 (1931). [g] 1-hr. reaction period. [h] Ref. 4. [i] 3-hr. reaction period. [j] *Anal.* Calcd. for $C_{23}H_{24}N_2$: C, 84.10; H, 7.37; N, 8.53. Found: C, 84.03; H, 7.42; N, 8.66. [k] Ref. 3. [l] *Anal.* Calcd. for $C_{26}H_{22}N_2$: C, 86.15; H, 6.12; N, 7.73. Found: C, 86.45; H, 6.24; N, 8.15.

2-day reaction period.[4] The two condensations represented in eq. 2 were accomplished by us after a 20-hr. reaction period in yields of only 40 and 78%, respectively; these yields are appreciably lower than those obtained even after a much shorter reaction period according to eq. 1 (see Table I). Moreover, certain N-alkylphenylhydrazines are not readily available.

Experimental[5]

The benzaldehyde phenylhydrazone,[6] acetophenone phenylhydrazone,[7] and benzophenone phenylhydrazone[8] used in this study were prepared according to literature procedures and were recrystallized. The acetophenone phenylhydrazone should be freshly prepared.

Alkylations of Phenylhydrazones I.—To a stirred suspension of 0.025 mole of sodamide[9] in 500 ml. of commercial, anhydrous, liquid ammonia or to a stirred solution of 0.025–0.1 mole of potassium amide[10] in 250–500 ml. of commercial, anhydrous, liquid ammonia was added 1 mole equiv. of finely ground phenylhydrazone I. The solutions of the resulting alkali salts (see Table I) were colored brownish yellow, orange-tan, and blood red, respectively. After 10–15 min., 1 mole equiv. of the appropriate halide in 15–20 ml. of anhydrous ether was added; the color of the solution changed and a precipitate formed. After stirring for the appropriate length of time (see footnotes *b*, *e*, *g*, and *i* in Table I), a slight excess of 1 mol. equiv. of ammonium chloride was added. The ammonia was allowed to evaporate, and the residue was taken up in ether and water. The layers were separated. The ethereal layer was washed with saturated sodium chloride solution and combined with two ethereal extracts of the aqueous layer treated in the same manner. In the experiment with methyl iodide the ethereal solution was also washed with saturated sodium bisulfate to remove any iodine that might have been formed. The ethereal solution was dried over anhydrous magnesium sulfate and the solvent was removed. The residues were recrystallized from ethanol.

Condensations of N-Benzyl-N-phenylhydrazine Hydrochloride with Carbonyl Compounds to Form II (Eq. 2). A. With Benzaldehyde.—A solution of 1.06 g. (0.01 mole) of benzaldehyde and 2.35 g. (0.01 mole) of N-benzyl-N-phenylhydrazine hydrochloride in 5 ml. of pyridine and 45 ml. of ethanol was refluxed for 20 hr. according to a current method for the preparation of oximes.[11] There was obtained 2.32 g. (78%) of benzaldehyde benzylphenylhydrazone, m.p. 106–108° after recrystallization from ethanol. Upon admixture with the product melting at 109–110° obtained according to eq. 1, the melting point was 108–109°. The infrared spectra of the two samples were identical.

B. With Benzophenone.—The reaction involving 0.91 g. (0.005 mole) of benzophenone, 1.18 g. (0.005 mole) of N-benzyl-N-phenylhydrazine hydrochloride in 5 ml. of pyridine, and 45 ml. of ethanol, refluxed for 20 hr. as described above, yielded 0.72 g. (40%) of benzophenone benzylphenylhydrazone, m.p. and m.m.p 106–108° after recrystallization from ethanol.

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The Asinger Reaction with 1-Methyl-4-piperidone

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Received September 8, 1964

The discovery that β- and γ-mercaptoamines provided some protection against ionizing radiation[2] caused an interest in the synthesis of 3- and 4-mercaptopiperidines. The preparation of these compounds by nucleophilic displacements of halogen from 3- and 4-halopiperidines was complicated by the discovery that the former underwent rearrangement with ring contraction[3] while the latter underwent rupture of the ring[4] during solvolysis reactions. Using a *gem*-dithiol as intermediate, the synthesis of 1-methyl-4-mercaptopiperidine was accomplished,[5] but a similar route to 1-methyl-3-mercaptopiperidine was not successful. The formation of thiazolines by the Asinger reaction[6,6a] seemed to offer an alternate approach to these compounds from 1-methyl-4-piperidone, provided that the intermediate thiazoline could be hydrolyzed to give a derivative of 1-methyl-3-mercapto-4-piperidone.

1-Methyl-4-piperidone (1) gave a mildly exothermic reaction with sulfur and ammonia to form a compound having the properties expected for the thiazoline **2a**.

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(6a) NOTE ADDED IN PROOF.—The Asinger reaction with 1-methyl-4-piperidone (**1**) has been reported by F. Asinger, W. Shäfer, and H. W. Becker, *ibid.*, **674**, 57 (1964).