essentially negative in 2.5 hours. Excess reducing agent was decomposed by the addition of 10% aqueous acetic acid. Additional chloroform and water were added and the mixture extracted with chloroform. The chloroform extract was washed with dilute potassium bicarbonate and water and dried over magnesium sulfate. Crystallization of the residue from acetone gave 200 mg. of the 20β-acetate-21-ol III, m.p. 237–243°. Chromatography of the mother liquors on 20 g. of neutral alumina gave 270 mg. of the 20β-ol-21-acetate II crystallized from acetone–ether, m.p. 206–210°. Paper chromatography (benzene–cyclohexane 2:1—formamide system) of pertinent fractions indicated the presence of minor amounts of corticosterone acetate (I), a non-ultraviolet absorbing component probably resulting from reduction of the 3 as well as the 20-carbonyl group, and mixed fractions of II and III.

Conversion of the 20β-Ol 21-Acetate II into the 20β-Acetate 21-Ol III.—To a solution of 30 mg. of the 20β-ol-21-acetate II in 0.6 ml. of dimethylformamide was added 0.6 ml. of 2% aqueous potassium bicarbonate. The clear solution was seeded with the 20β-acetate-21-ol III. Within 5 minutes a precipitate of small prisms appeared. The mixture was kept at 0° for 30 minutes, filtered, the precipitate washed with water, 50% aqueous acetone and dried in air; 15 mg., m.p. 240–245° undepressed with authentic 20β-acetate-21-ol III. The respective infrared spectra were identical. An additional 4 mg. of III, m.p. 241–245°, was obtained from the mother liquors on standing overnight.

Similar treatment of 50 mg. of II in 1 ml. of dimethylformamide with 1 ml. of 1% aqueous sodium borohydride led to 38 mg. of III, m.p. 238–243°.

However, when a solution of 50 mg. of II in 2 ml. of 50% aqueous dimethylformamide was seeded with III and permitted to cool slowly, essentially unchanged II (35 mg.) was recovered in 2 crops of long needles, m.p. 208–212° with a trace remaining to 245°. The mixed melting point with authentic II was undepressed and the respective infrared spectra were identical.

Δ^4-Pregnene-11β,17α,20β,21-tetrol-3-one 20-Acetate (Reichstein's Substance E Monoacetate) (XII).—To a stirred solution of 2.00 g. of hydrocortisone 21-acetate (XI) in 80 ml. of dimethylformamide at 20° was added 400 mg. of sodium borohydride in 20 ml. of water. Starting material partly precipitated. Stirring was continued at 20° for four hours at which time all the material was in solution and a blue tetrazolium test on an aliquot was negative. Excess cold 10% aqueous acetic acid was added slowly, water and chloroform were added and the mixture extracted with chloroform. The chloroform extract was washed with potassium bicarbonate solution, water and dried over magnesium sulfate. The crystalline residue was chromatographed on 60 g. of neutral alumina. The fractions from 50% benzene–chloroform to 100% chloroform (1.15 g.) were crystalline and consisted primarily of the monoacetate XII. Crystallization from acetone–ether gave prisms, m.p. 225–235° (233–236° capillary m.p.), $\lambda_{max}^{CH_3OH}$ 242 mμ (15,600); undepressed with an authentic sample of Reichstein's Substance E 21-monoacetate.[13] The respective infrared spectra were identical. Acetylation of 50 mg. of XII in acetic anhydride–pyridine at 25° gave the corresponding 20β,21-diacetate, m.p. 212–220°, likewise identical with authentic material.

Paper chromatography (benzene–chloroform 1:2—formamide system) of the individual chromatogram fractions indicated the total yield of the 20-monoacetate XII formed to be about 70%. Also present were small amounts of a more polar ultraviolet absorbing component (negative blue tetrazolium test) which may be the 20β-monoacetate analogous to III and a very polar non-ultraviolet absorbing component (negative blue tetrazolium test) in which the 3- as well as the 20-carbonyl group has been reduced. These substances were not isolated.

Δ^4-Pregnene-17α,20β,21-triol-3,11-dione 21-Acetate (Reichstein's Substance U Monoacetate) (XIV).—Reduction of a suspension of 2.00 g. of cortisone 21-acetate XIII with 380 mg. of sodium borohydride in 100 ml. of 80% aqueous dimethylformamide at 15–20° as in the preceding experiment was complete (negative blue tetrazolium test) in 2.5 hours. The mixture was worked up as above and chromatographed on 60 g. of neutral alumina. The fractions from 30% benzene–chloroform through 50% benzene–chloroform (670 mg.) were crystalline and essentially pure monoacetate XIV. Crystallization from acetone–ether gave prismatic needles, m.p. 181–183°,[14] $[\alpha]_D^{CHCl_3}$ +174°; $\lambda_{max}^{CH_3OH}$ 238 mμ (15,300); $\lambda_{max}^{CHCl_3}$ 2.74, 2.80–2.85, 5.74, 5.84, 5.97, 6.14, 8.0 μ.

Anal. Calcd. for $C_{23}H_{32}O_6$: C, 68.29; H, 7.98. Found: C, 68.23; H, 7.96.

Paper chromatography (benzene–chloroform 1:1—formamide system) of representative chromatogram fractions indicated the presence of small quantity of a more polar ultraviolet absorbing component that gave a negative blue tetrazolium test and a very polar component (no ultraviolet; negative tetrazolium test). These materials were not characterized.

Acetylation of a sample of the monoacetate XIV in acetic anhydride–pyridine at 25° led to the 20β,21-diacetate, m.p. 245–249°, identical with authentic Reichstein's Substance U-20,21-diacetate by mixed melting point and infrared criteria.

Chromium trioxide–acetic acid oxidation[14] of a sample of the monoacetate XIV led to a neutral product resolved by paper chromatography (benzene–formamide system) into cortisone acetate (XIII) and adrenosterone.

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(13) This substance was first prepared by partial acetylation of Reichstein's Substance E by Huang-Minlon and R. H. Pettebone, THIS JOURNAL, **74**, 1562 (1952).

(14) The monoacetate XIV was first obtained by partial acetylation of Reichstein's Substance U by L. H. Sarett [*J. Biol. Chem.*, **162**, 601 (1946)] who reported m.p. 172–174°.

RAHWAY, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

The Oxidation of 1,1-Dibenzylhydrazines[1]

BY R. L. HINMAN[2] AND K. L. HAMM[3]

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A series of unsymmetrically substituted dibenzylhydrazines (p-$XC_6H_4CH_2N(NH_2)CH_2C_6H_5$, where X = CH_3O–, $(CH_3)_2N$–, CH_3–, Cl–) have been oxidized with yellow mercuric oxide and in each case the only product identified was the unsymmetrical bibenzyl, p-$XC_6H_4CH_2CH_2C_6H_5$. Similarly, 2-(β-phenylethyl)-furan was obtained from the oxidation of 1-benzyl-1-furfurylhydrazine. The oxidation of 1-benzyl-1-(p-methoxybenzyl)-hydrazine by potassium permanganate, Fehling solution, or air also yielded the unsymmetrical bibenzyl, but oxidation of the same hydrazine with mercuric acetate or quinone produced the corresponding tetrazene. The benzenesulfonyl derivatives of 1-benzyl-1-(p-methoxybenzyl)-hydrazine and of 1-benzyl-1-(p-chlorobenzyl)-hydrazine were converted in good yield to the unsymmetrical bibenzyls by treatment with hot aqueous sodium hydroxide.

A large number of 1,1-disubstituted hydrazines (I) have been oxidized with many commonly used oxidizing agents, including potassium permanganate, bromine, sodium hypochlorite, ferric chloride,

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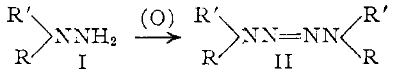
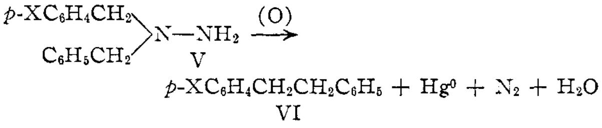
quinone and mercuric oxide, and in general a tetrazene (II) has been obtained as the primary product.[4]


$$\underset{\text{I}}{R'RNNH_2} \xrightarrow{(O)} \underset{\text{II}}{R'RNN{=}NNR'R}$$

The first anomalous oxidation of a 1,1-disubstituted hydrazine was reported in 1900 by Busch and Weiss,[5] who oxidized 1,1-dibenzylhydrazine (III) with yellow mercuric oxide and obtained bibenzyl (IV) together with the theoretical quantity of nitrogen gas. Symmetrically disubstituted bibenzyls have also been obtained from the oxidations of 1,1-bis-(*o*-nitrobenzyl)-hydrazine,[5,6] 1,1-bis-(*p*-nitrobenzyl)-hydrazine,[5] and 1,1-bis-(*o*-bromobenzyl)-hydrazine.[7] Recently, interest in the conversion of 1,1-dibenzylhydrazines to bibenzyls has been renewed with studies on both the mechanism and synthetic possibilities of the reaction.[8]

$$\underset{\text{III}}{(C_6H_5CH_2)_2NNH_2} \xrightarrow{HgO} \underset{\text{IV}}{C_6H_5CH_2CH_2C_6H_5} + N_2\uparrow$$

It was the purpose of the work reported here to delineate the scope and limitations of these interesting oxidation reactions more fully. Whereas the previous investigations were carried out with 1,1-dibenzylhydrazines in which both rings were identically substituted, the present study is concerned with the oxidation of 1,1-dibenzylhydrazines in which only one ring bears a substituent (V), in order to ascertain whether this reaction yields "mixed" bibenzyls (VI), a result which would be of value from both the synthetic and the mechanistic points of view.


$$\underset{\text{V}}{(p\text{-}XC_6H_4CH_2)(C_6H_5CH_2)N{-}NH_2} \xrightarrow{(O)} \underset{\text{VI}}{p\text{-}XC_6H_4CH_2CH_2C_6H_5} + Hg^0 + N_2 + H_2O$$

A series of 1,1-dibenzylhydrazines (V) was prepared where X = CH_3O-, CH_3-, Cl- and $(CH_3)_2N-$. A fifth hydrazine, 1-benzyl-1-furfurylhydrazine was also synthesized.[9] Each hydrazine was oxidized by yellow mercuric oxide in 95% ethanol. In each case the "mixed" bibenzyl VI was the only identifiable product. The remainder of the product in each case was a viscous oil, which was not identified. Table I summarizes the results of the oxidations and the methods used to identify the products. Because of the low yields of bibenzyls (Table I) it is impossible to rule out completely the possibility of the formation of more than one bibenzyl in each oxidation. The following facts make it unlikely, however, that more than one bibenzyl was formed: (1) 4-methoxybibenzyl was isolated in 53% yield; (2) in most cases the bibenzyl was isolated by crystallization from the concentrated reaction mixture; if other products of similar structure had been present, it is unlikely that the low-melting bibenzyls would have crystallized so easily; (3) in the case of 2-(β-phenylethyl)-furan, which was isolated by distillation rather than crystallization, after the identified product had been distilled, the residual oil was heated to temperatures far in excess of the expected boiling points of the other possible products of the bibenzyl type, but no additional material distilled.

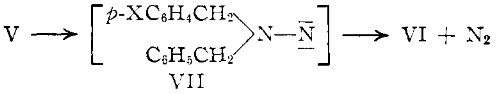
TABLE I

OXIDATION OF 1,1-DIBENZYLHYDRAZINES $(RCH_2\overset{NH_2}{\overset{|}{N}}CH_2C_6H_5)$ BY YELLOW MERCURIC OXIDE

R	Yield of $RCH_2CH_2C_6H_5$, %	Method of identification of $RCH_2CH_2C_6H_5$
p-$CH_3OC_6H_4$–	53	Comparison with authentic specimen[a]
p-$CH_3C_6H_4$–	27	M.p., C, H analysis[b] and oxition to benzoic and terephthalic acids[c]
p-ClC_6H_4–	28	Comparison with authentic specimen[d]
p-$(CH_3)_2NC_6H_4$–	12	Comparison with authentic specimen[a]
2-Furyl	35	Reacn. with maleic anhydride to give known[e] 3-(β-phenylethyl)-3,6-endoxo-Δ^4-tetrahydro-*o*-phthalic anhydride

[a] Prepared by the method of M. Freund and P. Remse, *Ber.*, **23**, 2859 (1890). [b] M.p. found 24–26°; lit. m.p. 27° (W. Mann., *Ber.*, **14**,1645 (1881). Calcd. for $C_{15}H_{16}$: C, 91.77; H, 8.23. Found: C, 92.07; H, 8.43. [c] See Experimental. [d] Prepared by the method of F. Bergmann, J. Weizmann and D. Shapiro, *J. Org. Chem.*, **9**, 408 (1944). [e] R. B. Woodward, THIS JOURNAL, **62**, 1480 (1940).

The mechanism of the oxidation of dibenzylhydrazines has been discussed at some length,[8b,c] and it has been suggested that the reaction proceeds by way of an intermediate (VII), the terminal nitrogen of which lacks the hydrogens of the original hydrazine, and is electron deficient.[10] A closely related reaction is the well-known conversion of hydrazones to diazo compounds by yellow mercuric oxide ($>C{=}NNH_2 \rightarrow >CN_2$). An intermediate such as VII, not as well resonance-stabilized as the aliphatic diazo compound, collapses with simultaneous loss of nitrogen and collision of the benzyl residues. The suggestion[8b] that this is a concerted process is supported by the results reported here.


$$\text{V} \longrightarrow \underset{\text{VII}}{\left[(p\text{-}XC_6H_4CH_2)(C_6H_5CH_2)N{-}\bar{\underline{N}}\right]} \longrightarrow \text{VI} + N_2$$

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[4] See for example: (a) E. Fischer, *Ann.*, **190**, 67 (1877); (b) E. Fischer, *ibid.*, **199**, 281 (1879); (c) E. Renouf, *Ber.*, **13**, 2169 (1880); (d) T. Curtius and H. Franzen, *ibid.*, **34**, 552 (1901); (e) H. Wieland and H. Fressel, *Ann.*, **392**, 133 (1912).

[5] M. Busch and B. Weiss, *Ber.*, **33**, 2701 (1900).

[6] H. Duval, *Bull. soc. chim. France*, [6] **7**, 728 (1910).

[7] J. Kenner and J. Wilson, *J. Chem. Soc.*, 1108 (1927).

[8] (a) C. G. Overberger and B. S. Marks, THIS JOURNAL, **77**, 4104 (1955); (b) C. G. Overberger, J. G. Lombardino and R. G. Hiskey, *ibid.*, **79**, 6430 (1957); (c) *ibid.*, **80**, 3009 (1958); (d) L. A. Carpino, *ibid.*, **79**, 4427 (1957).

[9] The synthesis of these hydrazines is described in a previous paper: R. L. Hinman and K. L. Hamm, *J. Org. Chem.*, **23**, 529 (1958).

[10] This type of intermediate was first proposed by J. Kenner and E. C. Knight, *Ber.*, **69**, 341 (1936), and is similar to that suggested earlier by Goldschmidt (S. Goldschmidt and V. Voeth, *Ann.*, **435**, 265 (1924)) to account for the mode of oxidation of amines by oxidizing agents such as potassium permanganate and lead dioxide. Evidence for the existence of an intermediate such as VII in the oxidations of 1,1-dialkylhydrazines has recently been reported (W. R. McBride and H. W. Kruse, THIS JOURNAL, **79**, 572 (1957)).

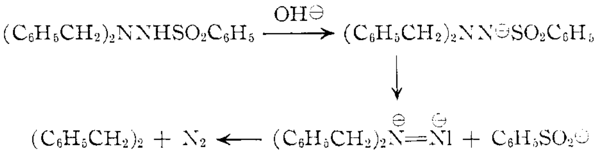
From the experiments described in this paper and in the literature, certain limitations can be cited with regard to the number and nature of the substituents on the hydrazine molecule which will permit a successful oxidation with loss of nitrogen and coupling of the substituent residues. In the first place, one nitrogen of the hydrazine must be unsubstituted. Thus, the oxidation of 1,1-dibenzyl-2-(2,4,6-trinitrophenyl)-hydrazine with lead dioxide yielded 1-benzylidene-2-(2,4,6-trinitrophenyl)-hydrazine.[11] Only starting material was obtained from the oxidation of 1,1-dibenzyl-2-*t*-butylhydrazine.[11] Goldschmidt also reported[10] that benzoyltribenzylhydrazine was obtained from the oxidation of tetrabenzylhydrazine with potassium permanganate.[12]

A second limitation appears in the nature of the two substituents attached to the substituted nitrogen. Although the work of Overberger[13] has shown that the successful oxidation of 1,1-disubstituted hydrazines with elimination of nitrogen is not limited to molecules containing benzyl substituents, it appears that the nature of the substituent must be such that the intermediate fragment produced during the oxidation is well stabilized.[14] The successful oxidation of 1-benzyl-1-furfurylhydrazine to 2-(*β*-phenylethyl)-furan in the present work indicates that a benzyl-like structure with a heterocyclic nucleus can be substituted for a benzyl residue in VII. Similar resonance stabilization of the intermediate fragment would be anticipated.[15]

In an effort to improve the yield of the unsymmetrical bibenzyl the effects of a number of oxidizing agents were compared using 1-benzyl-1-(*p*-methoxybenzyl)-hydrazine as the substrate. When potassium permanganate, Fehling solution or air was used, 4-methoxybibenzyl was the product, although the yields varied considerably. Fehling solution gave yields roughly equal to those obtained with yellow mercuric oxide.[16,17] It is noteworthy that when quinone or mercuric acetate was employed as the oxidizing agent the tetrazene was obtained.[18]

Other attempts to increase the yield of the bibenzyl included varying the reaction temperature and the *p*H. Thus, the reaction was complete after 1.5 hr. in refluxing ethanol, but required 6–8 hr. at room temperature. When a still higher boiling solvent, 1-butanol, was used, the yield of the bibenzyl decreased. The yield also decreased when the *p*H of the ethanolic reaction mixture was raised by the addition of sodium hydroxide, an experiment suggested by the different products obtained from the oxidation of 1,1-dibenzylhydrazine and from its hydrochloride.[12]

It is known that bibenzyl is a major product from the alkaline decomposition of 1,1-dibenzyl-2-benzenesulfonylhydrazine,[8d] which presumably occurs as shown in the equation[14]



$$(\mathrm{C_6H_5CH_2})_2\mathrm{NNHSO_2C_6H_5} \xrightarrow{\mathrm{OH}^\ominus} (\mathrm{C_6H_5CH_2})_2\mathrm{NN}^\ominus\mathrm{SO_2C_6H_5}$$
$$\downarrow$$
$$(\mathrm{C_6H_5CH_2})_2 + \mathrm{N_2} \longleftarrow (\mathrm{C_6H_5CH_2})_2\overset{\ominus}{\mathrm{N}}{=}\overset{\ominus}{\mathrm{N}}\mathrm{l} + \mathrm{C_6H_5SO_2}^\ominus$$

In the present investigation this reaction was extended to the benzenesulfonyl derivatives of two of the unsymmetrically substituted 1,1-dibenzylhydrazines which have been described. In each case the unsymmetrical bibenzyl VI was isolated. The yield of 4-methoxybibenzyl was 93%. Thus it would appear that this reaction is also of the intramolecular type. The results are given in Table II. A third compound assumed to be the benzenesulfonyl derivative of 1-benzyl-1-(*p*-dimethylaminobenzyl)-hydrazine resisted the alkaline decomposition and was recovered intact. This may have been due to the insolubility of the starting material in the aqueous alkaline solution. However, the identity of the starting material was not established conclusively. The bibenzyls obtained directly from alkaline decomposition were purer than those obtained by oxidation and the yields were better.

TABLE II

ALKALINE DECOMPOSITION OF 1,1-DIBENZYL-2-BENZENESULFONYLHYDRAZINES $(p\text{-XC}_6\text{H}_4\text{CH}_2\underset{\substack{|\\ \text{CH}_2\text{C}_6\text{H}_5}}{\text{N}}\text{NHSO}_2\text{C}_6\text{H}_5)$

X	M.p., °C.	Yield of benzenesulfonylhydrazine, %	Decomposition product	Yield, of bibenzyl, %
CH_3O–[a]	131–132.5	46	$p\text{-CH}_3\text{OC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$[c]	93
$(\text{CH}_3)_2\text{N}$–	145–146.5	5	Starting material recovered	
Cl–[b]	105–106	5	$p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$[c]	49

[a] Calcd. for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{SO}_3$: C, 65.95; H, 5.81; N, 7.33. Found: C, 65.77; H, 6.10; N, 7.51. [b] Calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}_2\text{ClS}$: C, 62.08; H, 4.96. Found: C, 62.55; H, 4.98. [c] Identified by comparison with an authentic specimen.

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[11] S. Goldschmidt, *Ann.*, **437**, 194 (1924).

[12] The conversion of tribenzylhydrazine hydrochloride to 2-benzylidene-1,1-dibenzylhydrazine by cupric oxide[7] might also be mentioned in connection with the limitation on the number of substituents. This example is rather inconclusive, however, since it is conceivable that the hydrochloride might behave differently from the free base on oxidation. (McBride and Kruse[10] have reported that the oxidation of 1,1-dimethylhydrazine in neutral or basic solution yields the tetrazene, whereas other products are formed in acidic solutions.) To test this point, 1,1-dibenzylhydrazine hydrochloride was oxidized in the usual way with yellow mercuric oxide. The tetrazene was obtained in 19% yield but no bibenzyl was isolated. Although this experiment was repeated with similar results, because of the low yield it is not conclusive. Previous authors[4d,e] have obtained, unpredictably, bibenzyl and/or tetrazene from oxidations of 1,1-dibenzylhydrazine with yellow mercuric oxide.

[13] C. G. Overberger, P. Huang and T. B. Gibbs, THIS JOURNAL, **75**, 2082 (1953).

[14] A reaction whose mechanism is apparently closely related to that described in this work is the conversion of the benzenesulfonyl derivatives of 1,1-disubstituted hydrazines to bibenzyls by alkaline solutions. No non-benzyl derivatives have been encountered which undergo this reaction.[8d]

[15] In dealing with benzyl substituted hydrazines, it should be noted that these compounds commonly give anomalous reactions and that the benzyl group is particularly prone to undergo migration during the oxidation of such hydrazines. For example, Busch (M. Busch and K. Lang, *J. prakt. Chem.*, **144**, 291 (1936)), reported that when 1-benzyl-1-(*o*-tolyl)-hydrazine was oxidized with yellow mercuric oxide, 2-benzylidene-1-(*o*-tolyl)-hydrazine was obtained: $o\text{-CH}_3\text{C}_6\text{H}_4\text{N}(\text{NH}_2)\text{CH}_2\text{C}_6\text{H}_5 \rightarrow o\text{-CH}_3\text{C}_6\text{H}_4\text{NHN{=}CHC}_6\text{H}_5$. It should also be noted that distillation of benzylhydrazine at atmospheric pressure yields some bibenzyl (A. Wohl and C. Oesterlin, *Ber.*, **33**, 2736 (1900)).

[16] It is interesting that Fehling solution effects nitrogen–nitrogen cleavage with other 1,1-disubstituted hydrazines yielding the corresponding disubstituted amine and nitrogen.[4a,b]

[17] Red mercuric oxide was inert under the conditions used in this study.

[18] Quinone has been used previously[4c] to prepare the tetrazene from 1,1-dibenzylhydrazine when other oxidizing agents produced bibenzyl.

Experimental[19]

Oxidations of 1-Benzyl-1-(*p*-methoxybenzyl)-hydrazine· A. With Yellow Mercuric Oxide.—Since the yellow mercuric oxide oxidation of all of the hydrazines was carried out in essentially the same manner, only the detailed description of the oxidation of 1-benzyl-1-(*p*-methoxybenzyl)-hydrazine will be presented here.

Yellow mercuric oxide (5 g., 0.02 mole) was added in small portions to a solution of 5 g. (0.02 mole) of 1-benzyl-1-(*p*-methoxybenzyl)-hydrazine in 50 ml. of 95% ethanol. There was an immediate evolution of nitrogen gas. The mixture was heated on a steam-bath for 1.5 hours and then filtered. Small globules of mercury were present in the residue. The solvent was removed from the filtrate under reduced pressure and the residual clear yellow oil was taken up in 100 ml. of ether, washed successively with 20 ml. of dilute hydrochloric acid and 20 ml. of dilute sodium hydroxide and dried over anhydrous potassium carbonate. The mixture was filtered and the ether removed under reduced pressure. The residue was recrystallized from 95% ethanol to yield 2.2 g. (53%) of 4-methoxybibenzyl, m.p. 55–58°. A mixture of this material and an authentic sample (Table I, footnote *a*) (m.p. 59–61°) melted at 56–60°. After the removal of the 4-methoxybibenzyl from the original reaction mixture, and after evaporation of the mother liquor, a clear yellow oil remained which did not solidify upon cooling.

B. With Quinone.—A cold solution of 0.45 g. (0.005 mole) of quinone in 10 ml. of 95% ethanol was added dropwise to a solution of 1 g. (0.005 mole) of 1-benzyl-1-(*p*-methoxybenzyl)-hydrazine in 5 ml. of 95% ethanol. The mixture was stirred and maintained in an ice-bath during the addition. After standing overnight in the refrigerator, dark brown crystals were removed by filtration and recrystallized three times from ethanol and water to yield 0.22 g. (22%) of white crystals of 1,4-dibenzyl-1,4-bis(*p*-methoxybenzyl)-2-tetrazene, m.p. 109–110°.

Anal. Calcd. for $C_{30}H_{32}N_4O_2$: C, 74.96; H, 6.72; N, 11.66. Found: C, 75.96; H, 6.93; N, 11.65.

C. With Potassium Permanganate.[20]—A saturated acetone solution of potassium permanganate was added dropwise to a solution of 1 g. (0.005 mole) of 1-benzyl-1-(*p*-methoxybenzyl)-hydrazine in 10 ml. of acetone. The mixture was stirred and maintained in an ice-bath during the addition which was continued until the color of potassium permanganate persisted. After standing overnight the solution was filtered to remove a brown precipitate of manganese dioxide and the solvent was evaporated until a clear yellow oil remained. The oil was recrystallized from 95% ethanol and water to give 0.32 g. (36%) of light tan crystals, m.p. 50–53°. The material was decolorized with animal charcoal and recrystallized several times to yield white crystals, m.p. 56–58°. A mixture with 4-methoxybibenzyl, m.p. 59.5–60.5°, prepared by an independent synthesis, melted at 56.5–60°.

D. With Mercuric Acetate.—A solution of 1 g. (0.005 mole) of 1-benzyl-1-(*p*-methoxybenzyl)-hydrazine and 1.3 g. (0.005 mole) of mercuric acetate in 50 ml. of 95% ethanol was stirred for one hour. The mixture was filtered and the solvent removed from the filtrate under reduced pressure. To the residue was added 30 ml. of water and this mixture was extracted with two 50-ml. portions of ether. The ether extracts were dried over anhydrous potassium carbonate. The mixture was filtered and the ether removed under reduced pressure, leaving a light yellow oil. This oil was dissolved in 10 ml. of 95% ethanol and upon cooling a white precipitate, m.p. 107–109°, was obtained. The yield was 4%.[21] An authentic sample of 1,4-dibenzyl-1,4-bis-(*p*-methoxybenzyl)-2-tetrazene, m.p. 109–110°, and the above compound, gave a mixed m.p. 107.5–110°.

E. With Fehling Solution.—A mixture of 2.5 g. (0.01 mole) of 1-benzyl-1-(*p*-methoxybenzyl)-hydrazine and a quantity of Fehling solution equivalent to the theoretical amount of cupric oxide necessary to completely oxidize the hydrazine, plus a 20% excess, was heated on a water-bath for 4 hours. The mixture was cooled, decanted from the cuprous oxide and the decant extracted with two 50-ml. portions of ether. The ether was removed under reduced pressure and the residue recrystallized from 95% ethanol. A white precipitate (1.06 g., 48%) of 4-methoxybibenzyl, m.p. 56.5–58.5°, was obtained. When the reaction was carried out using approximately half the calculated quantity of cupric oxide required to oxidize the hydrazine, the yield of 4-methoxybibenzyl was 29%.

F. With Air.—Air was passed through an ethanolic solution of 1-benzyl-1-(*p*-methoxybenzyl)-hydrazine (3.2 g., 0.01 mole) for 12 hours. This solution was left standing in a stoppered bottle for approximately 3 months, after which the ethanol was removed under reduced pressure, leaving a clear reddish-brown oil. Ether (70 ml.) was added to the residual oil and the ethereal solution was extracted with two 20-ml. portions of dilute hydrochloric acid. The acid extracts were made basic with dilute sodium hydroxide and cooled. No precipitate or oil was obtained in this manner from the acid extracts. The ether layer was washed with two 20-ml. portions of dilute sodium hydroxide and the ether removed under reduced pressure. The residue, a clear reddish-brown oil, solidified upon cooling. The residue was recrystallized twice from 95% ethanol and decolorized with animal charcoal to yield 0.2 g. (7%) of white crystals, m.p. 60.5–62°. A mixed m.p. 60–62° was obtained with an authentic sample of 4-methoxybibenzyl, m.p. 59.5–60.5°.

Potassium Permanganate Oxidation of 4-Methylbibenzyl.—The procedure employed was essentially that of Shriner and Fuson.[22] A solution of 1 g. of 4-methylbibenzyl, obtained from the mercuric oxide oxidation of 1-benzyl-1-(*p*-methylbenzyl)-hydrazine, 4 g. of potassium permanganate and 1 ml. of 10% sodium hydroxide in 80 ml. of water, was refluxed for 12 hours. The mixture was cooled, acidified with sulfuric acid and refluxed for 30 minutes. The excess manganese dioxide was removed by adding sodium bisulfite. Ether (100 ml.) was added and the resulting mixture filtered to remove a solid believed to be terephthalic acid. The ether layer was separated from the aqueous acid layer, and the ether removed under reduced pressure. The residue was dissolved in dilute sodium hydroxide and extracted with ether. The basic solution was then acidified and a white precipitate obtained. After several recrystallizations from water, white crystals were obtained, m.p. 120–122°. A mixed melting point of 120–122° was obtained with an authentic sample of benzoic acid, m.p. 120–121°. The ether-insoluble solid, believed to be terephthalic acid, was dissolved in dilute sodium hydroxide, heated to boiling and acidified with hydrochloric acid. A slight amount of cream colored precipitate was obtained which sublimed at 320–330° (lit.[23] sublimation at approximately 300°).

Oxidation of 1,1-Dibenzylhydrazine Hydrochloride with Yellow Mercuric Oxide.—A mixture of 2.5 g. (0.01 mole) of dibenzylhydrazine hydrochloride in 50 ml. of 95% ethanol and 3 g. (0.01 mole) of yellow mercuric oxide was heated on a steam-bath for 2 hours. During this time, a gas was evolved and the yellow mercuric oxide became gray in appearance. The mixture was filtered and the excess solvent removed under reduced pressure. The residual oil upon cooling yielded a white precipitate, m.p. 78–82°. This precipitate was recrystallized from 95% ethanol to yield 0.4 g. (19%) of white needles, m.p. 95–96°. A mixed m.p. 95–97° was obtained with an authentic sample of tetrabenzyltetrazene, m.p. 97°, prepared by the procedure of Wieland and Fressel.[4e]

Synthesis and Alkaline Decomposition of 1,1-Dibenzyl-2-benzenesulfonylhydrazines.—The general procedure employed in the preparation of the benzenesulfonyl derivatives of the hydrazines and the alkaline decomposition of these derivatives is similar to that described in reference 8d, except that pyridine was used instead of a mixture of triethylamine and dimethylformamide in the synthesis of the benzenesulfonylhydrazines. The physical properties of the latter and the results observed in the alkaline decomposition are summarized in Table II.

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[19] Melting points and boiling points are uncorrected.

[20] From attempts to oxidize 1-benzyl-1-(*p*-dimethylaminobenzyl)-hydrazine with potassium permanganate and with quinone only tarry, unidentifiable residues were obtained.

[21] From the low yield and the results of others[4e] who have obtained both tetrazene and bibenzyl from one reaction, it seemed likely that 4-methoxybibenzyl would also be a product, but none was isolated.

[22] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 198.

[23] E. H. Huntress and S. P. Mulliken, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 178.