sodium hydroxide solution. The basic solution was boiled to remove ether and then acidified and extracted with benzene. Distillation of the benzene solution gave 10.5 g. (71%) of 3-benzylbutyric acid, b.p. 166° at 11 mm., $n^{25}D$ 1.5109, d^{25} 1.042, $[\alpha]^{26}D$ +2.46°.

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

The Synthesis of Alkylhydrazines. I. The Reaction of Lithium Aluminum Hydride with Mono- and Diacylhydrazines[1]

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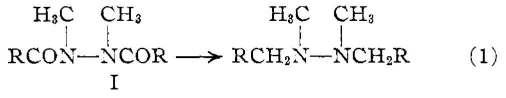
Lithium aluminum hydride in refluxing ether or tetrahydrofuran reduces 1,2-diacyl-1,2-dimethylhydrazines $(RCO\overset{|}{N}CH_3)_2$ rapidly and in fair yields to the corresponding tetraalkylhydrazines $(RCH_2\overset{|}{N}CH_3)_2$. Acylhydrazines, such as RCONH-NHCOR and $RCONHN(CH_3)_2$, which have hydrogens on the acyl-substituted nitrogens, are reduced much more slowly under similar conditions.

As one phase of a search for new and flexible methods for the preparation of alkylhydrazines the reactions of mono- and diacylhydrazines with lithium aluminum hydride are being investigated. Since acylhydrazines have a formal and in many respects an actual resemblance to amides, many of which have been reduced to amines by lithium aluminum hydride,[2] this approach appeared attractive. However, the results of the only two previously reported experiments of this type stand in marked contrast to each other. 1,2-Diacetylhydrazine is not reduced by lithium aluminum hydride, presumably because of the low solubility of the acylhydrazine in the solvents used.[3] However, 1,2-diformyl-1,2-dimethylhydrazine, which is but slightly soluble in ether, is rapidly reduced in that solvent to tetramethylhydrazine.[4,5]

In the present study it has been found that several mono- and diacylhydrazines can be converted to the corresponding alkylhydrazines by an excess of lithium aluminum hydride in refluxing ether or tetrahydrofuran. The reactions are summarized in equations 1–3.



$$RCO\overset{H_3C}{\overset{|}{N}}-\overset{CH_3}{\overset{|}{N}}COR \longrightarrow RCH_2\overset{H_3C}{\overset{|}{N}}-\overset{CH_3}{\overset{|}{N}}CH_2R \qquad (1)$$

I

$$RCONHNHCOR \longrightarrow RCH_2NHNHCH_2R \qquad (2)$$

II

$$RCONHN(CH_3)_2 \longrightarrow RCH_2NHN(CH_3)_2 \qquad (3)$$

III

That the ease of reduction varies greatly with the type of structure of the acylhydrazine is evident from the data in Table I. 1,2-Diacyl-1,2-dimethylhydrazines (I) are reduced to the corresponding tetraalkylhydrazines in two to four hours. (The experiment described in ref. 4 is included for comparison.)

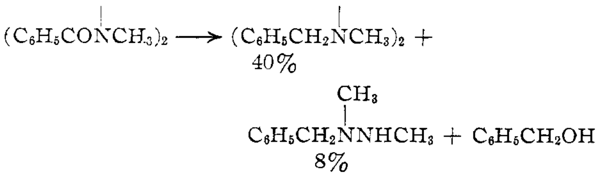
TABLE I

REACTIONS OF LITHIUM ALUMINUM HYDRIDE WITH DIACYLHYDRAZINES OF TYPES I AND II: $RCO\underset{R'}{\underset{|}{N}}-\underset{R'}{\underset{|}{N}}COR$

R	R′	Reaction time, hr.	Yield of alkylhydrazine, %	Excess of LiAlH$_4$, %	Solvent[a]	Solubility of acylhydrazine[b]	Homogeneity[c]
C_6H_5	CH_3	4	48[d]	80	T	S	H
CH_3	CH_3	2	57	30	T	S	H
H[e]	CH_3	1	15[f]	20	E	PS	P[g]
C_6H_5	H	24	0[h]	70	T	PS	P
CH_3	H	68	26	80	T	PS	P
H	H	30	0[i]	100	T	I	P
C_2H_5O	H	24 70	49 72	60	T	S	H

[a] T = tetrahydrofuran; E = ether. [b] S = completely soluble; PS = partly soluble; I = effectively insoluble. [c] H = homogeneous reaction mixture throughout reaction period (aside from a small amount of gray insoluble matter from the lithium aluminum hydride); P = precipitate because of the low solubility of the acylhydrazine. [d] This is the over-all yield of reduction products, composed of 40% of tetraalkylhydrazine and 8% of 1-benzyl-1,2-dimethylhydrazine, the latter from reductive cleavage. [e] This experiment is reported in ref. 4. [f] Considerable product was lost during isolation. [g] Although not stated explicitly in the paper, it is assumed from the concentrations of reactants and the low solubility of 1,2-diformyl-1,2-dimethylhydrazine in ether that the reaction mixture was heterogeneous. [h] 88% of starting material recovered. [i] 75% of starting material recovered.

In addition to its reduction to 1,2-dibenzyl-1,2-dimethylhydrazine, 1,2-dibenzoyl-1,2-dimethylhydrazine also underwent a small amount of cleavage to 1-benzyl-1,2-dimethylhydrazine, identified as the methiodide, and to benzyl alcohol, identified as the α-naphthylurethan.



$$(C_6H_5CO\overset{|}{N}CH_3)_2 \longrightarrow \underset{40\%}{(C_6H_5CH_2\overset{|}{N}CH_3)_2} + \underset{8\%}{C_6H_5CH_2\overset{CH_3}{\overset{|}{N}}NHCH_3} + C_6H_5CH_2OH$$

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(1) Presented in part at the Minneapolis Meeting of the American Chemical Society, September 16, 1955.

(2) V. M. Mičović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953).

(3) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

(4) J. B. Class, J. G. Aston and T. S. Oakwood, THIS JOURNAL, **75**, 2937 (1953).

(5) The reduction of other functional groups by lithium aluminum hydride has been used in syntheses of alkylhydrazines. Thus N-nitrosamines are reduced to *unsym*-dialkylhydrazines (F. W. Schueler and C. Hanna, THIS JOURNAL, **73**, 4996 (1951); **74**, 3693 (1952); H. Zimmer, L. F. Audrieth, M. Zimmer and R. A. Rowe, *ibid.*, **77**, 790 (1955)). The reduction of a hydrazone to a hydrazine is described in ref. 4; see also S. G. Cohen and C. H. Wang, *ibid.*, **77**, 2457, 3628 (1955). Reductions of azines to *sym*-dialkylhydrazines are described in ref. 3.

Although this was the only example of cleavage observed in the series of compounds examined, similar cleavages have been reported for the reactions of lithium aluminum hydride with amides.[2]

In contrast to the compounds of type I, 1,2-diacylhydrazines of type II, in which the nitrogens bear hydrogens rather than methyl groups, are reduced much more slowly, even though larger excesses of the hydride are employed. The two experiments which had been reported previously[3,4] also conform to this general pattern. 1,2-Diformyl-1,2-dimethylhydrazine, a compound of type I, is reduced rapidly. Difficulties in isolation of the product are primarily responsible for the low yield (15%). On the other hand, 1,2-diacetylhydrazine (II, R = CH_3) can be reduced, but the time required to obtain the product in appreciable yield is very long (68 hours). Presumably the previous workers[3] did not allow ample time for reduction to occur. Of the compounds of type II which were examined, only ethyl hydrazodicarboxylate (II, R = C_2H_5O) underwent reduction to an extent comparable to that of compounds of type I. From this reaction *sym*-dimethylhydrazine was isolated as the dihydrochloride in 72% yield, but a reaction time of 70 hours was required. This reduction affords a convenient method for the small-scale synthesis of *sym*-dimethylhydrazine. Ethyl hydrazodicarboxylate is easy to prepare,[6] need not be recrystallized, and the over-all yield of *sym*-dimethylhydrazine dihydrochloride (50%), calculated on the basis of the hydrazine hydrate used in the preparation of ethyl hydrazodicarboxylate, compares favorably with that (47%) obtained by the only other useful synthesis.[7] The latter employs the methylation of *sym*-dibenzoylhydrazine as the essential step of a sequence of three reactions, also starting with hydrazine. Although the reduction of a urethan to a methylamine by lithium aluminum hydride has been reported,[8] the reductions of the N-carbethoxyhydrazines described in this paper appear to be the first extensions of this reaction to the synthesis of methylhydrazines.

As a possible route to trialkylhydrazines, the reductions of a few 1-acyl-2,2-dimethylhydrazines (type III) by lithium aluminum hydride were also investigated. Like the diacylhydrazines of type II, the acylhydrazines of type III, which also bear hydrogens on the acyl-substituted nitrogens, were reduced slowly or not at all in the allotted reaction time. From the results (Table II) it is apparent that increased yields of product are obtained if long reaction times are used. However, a direct correlation between the yield and the homogeneity of the reaction mixture[9] cannot be established. Voluminous precipitates, which sometimes stopped the stirrer, were formed in all the reaction mixtures except that which contained 1-benzoyl-2,2-dimethylhydrazine (III, R = C_6H_5). Despite the homogeneity of the latter reaction, no detectable quantity of alkylhydrazine was obtained, and 70% of the acylhydrazine was recovered. That the low yields are truly indicative of slow reaction rates and are not merely the consequence of incomplete isolation of the products is demonstrated by the recovery of some of the acylhydrazine from each of the reductions of compounds of class III. In addition, the inorganic precipitate, which formed during the decomposition of the hydride at the end of each reaction, was removed by filtration and extracted thoroughly in a Soxhlet extractor. Both starting material (acylhydrazine) and product (alkylhydrazine) were obtained from the extract, but the additional quantity of product never augmented the recorded yield by more than 10%.

TABLE II

REACTIONS OF LITHIUM ALUMINUM HYDRIDE WITH 1-ACYL-2,2-DIMETHYLHYDRAZINES: $RCONHN(CH_3)_2$

R	Reaction time, hr.	Yield of alkylhydrazine, %	Excess of $LiAlH_4$, %	Solvent[a]	Solubility of acylhydrazine	Homogeneity[b]	Starting material recovd., %
CH_3	3	19	60	E	S	C	Trace
CH_3	18	35	60	E	S	C	10
C_6H_5	4	0	100	T	S	H	70
C_2H_5O	3	10	100	E	S	C	20

[a] E = ether; T = tetrahydrofuran. [b] H = homogeneous reaction mixture; C = insoluble precipitate formed on mixing the reactants.

As a method for the synthesis of alkylhydrazines, the reduction of acylhydrazines by lithium aluminum hydride is best suited to the preparation of tetralkylhydrazines, most of which have been obtained previously by the reactions of alkyl halides with hydrazine or alkylhydrazines.[10] By the di-N-alkylation of diacylhydrazines of various types,[11] and by the diacylation of various *sym*-dialkylhydrazines, a wide variety of 1,2-diacyl-1,2-dialkylhydrazines and, hence, of tetraalkylhydrazines is accessible.

Two new tetraalkylhydrazines, 1,2-diethyl-1,2-dimethylhydrazine and 1,2-dibenzyl-1,2-dimethylhydrazine were prepared in the course of this study. Each formed a methiodide and a picrate without difficulty. The pure hydrazines remained colorless on standing in contact with air for several days. Stability to mild oxidizing conditions appears to be characteristic of tetraalkylhydrazines.[10a] The trialkylhydrazines prepared in this study rapidly turned color on exposure to air.

1,2-Diethyl-1,2-dimethylhydrazine, which is only partially soluble in water, a fact consistent with its position of intermediate size between tetramethylhydrazine which is soluble in water[4] and tetraethylhydrazine which is not,[12] appears to mark the upper limit of water solubility of the tetraalkylhydrazines. A solution of 1,2-diethyl-1,2-dimethylhydrazine in 0.1 *N* hydrochloric acid can be titrated to a satisfactory end-point with 0.1 *N* sodium hydroxide.

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(6) N. Rabjohn, *Org. Syntheses*, **28**, 58 (1948).

(7) H. H. Hatt, *ibid.*, **II**, 208 (1943).

(8) F. Wessely and W. Swoboda, *Monatsh.*, **82**, 621 (1951).

(9) In all reactions with unfiltered solutions of lithium aluminum hydride, a certain amount of gray insoluble solid is present. The difference between this precipitate and a voluminous one which forms during the reaction with the compound to be reduced is readily apparent. Hence, the gray matter from the hydride is ignored in calling a reaction mixture "homogeneous."

(10) (a) O. Westphal, *Ber.*, **74**, 759 (1941); (b) F. Klages, G. Nober, K. Kircher and M. Bock, *Ann.*, **547**, 1 (1941).

(11) See for example: (a) C. Harries, *Ber.*, **27**, 2276 (1894); (b) C. Harries and T. Haga, *ibid.*, **31**, 56 (1898); (c) H. C. Ramsperger, THIS JOURNAL, **51**, 918 (1929).

(12) O. Westphal and M. Eucken, *Ber.*, **76**, 1137 (1943).

Most of the acylhydrazines used in this investigation were prepared by acylation of the required hydrazines by conventional methods. The synthesis of 1-benzoyl-2,2-dimethylhydrazine from benzoyl chloride and *unsym*-dimethylhydrazine deserves special comment. Regardless of the conditions used—addition of the benzoyl chloride to the dimethylhydrazine in water, with or without sodium carbonate present, or the reverse mode of addition or the use of benzene as a solvent—two products were always obtained. The minor product was the desired 1-benzoyl-2,2-dimethylhydrazine, as established by the analysis and the infrared spectrum of the sample in Nujol mull. The latter contained two bands of about the same intensity in the carbonyl region at 1538 and at 1635 cm.$^{-1}$. This spectral feature which is characteristic of monosubstituted amides (RCONHR), has been observed in the spectra of 1,2-diacetylhydrazine and ethyl carbazate.[13] A band at 3180 cm.$^{-1}$ is attributed to bonded N–H. The major product from the benzoylation of *unsym*-dimethylhydrazine was identified as 1,1-dibenzoyl-2,2-dimethylhydrazine. Behaving like a disubstituted amide, it exhibited only one strong band (1665 cm.$^{-1}$ in Nujol mull) in the carbonyl region of the infrared spectrum. There was no band in the N–H portion of the spectrum.[14]

In an attempt to prepare the pure monobenzoyl derivative, the reaction of methyl benzoate and *unsym*-dimethylhydrazine was investigated. Only starting materials were recovered after they had refluxed together for 20 hours. The use of ethanol as a solvent and/or hydrochloric acid as a catalyst had no effect. In view of the rapid and essentially complete reaction between esters and hydrazine hydrate, this result is surprising. Although it is known that phenylhydrazine does not react readily with esters without a catalyst,[15] it might be expected that *unsym*-dimethylhydrazine would be more akin to hydrazine itself. To what factors the failure to react can be attributed and whether the phenomenon is a general one for alkylhydrazines are questions now under investigation.

Experimental[16]

1,2-Diacetyl-1,2-dimethylhydrazine.—A mixture of 5 g. of *sym*-dimethylhydrazine dihydrochloride[7] and 20 ml. of acetic anhydride was refluxed until the solid had dissolved (about 10 minutes). The solution was poured into 200 ml. of ice-water. The aqueous mixture was made basic with solid sodium carbonate, and extracted three times with 20-ml. portions of chloroform. After the combined extracts had been dried over potassium carbonate, the solvent was removed, leaving an oil which crystallized on standing. Recrystallization from a mixture of ethyl acetate and petroleum ether, b.p. 30–60°, yielded 3.5 g. (60%) of white crystals, m.p. 61–62°. The product was readily soluble in water and insoluble in ether.

An analytical sample, m.p. 61–62°, was prepared by two further crystallizations from the same solvents.

Anal. Calcd. for $C_6H_{12}N_2O_2$: C, 49.97; H, 8.39; N, 19.43. Found: C, 50.19; H, 8.25; N, 19.48.

1-Acetyl-2,2-dimethylhydrazine.—To a solution of 20 g. (25 ml., 0.33 mole) of *unsym*-dimethylhydrazine[17] in 50 ml. of benzene was added with swirling, 41 g. (38 ml., 0.4 mole) of acetic anhydride in 5-ml. portions over a period of 15 minutes. The temperature rose rapidly to the boiling point and the reaction was controlled by cooling in ice. The pale yellow solution was boiled under reflux for 15 minutes, after which the volatile materials were removed under reduced pressure. The residual yellow oil was distilled through a 24-cm. Vigreux column, yielding 21 g. (62%) of a colorless liquid, b.p. 98–99° (16 mm.), $n^{25}{}_D$ 1.4494. The product was soluble in water and in ether. An analytical sample was prepared by redistillation.

Anal. Calcd. for $C_4H_{10}N_2O$: C, 47.03; H, 9.87. Found: C, 46.74; H, 9.48.

Ethyl 2,2-Dimethylcarbazate.—To a stirred, cooled solution of 30 g. (38 ml., 0.5 mole) of *unsym*-dimethylhydrazine in 50 ml. of water was added dropwise 33 g. (24 ml., 0.3 mole) of ethyl chloroformate at such a rate that the temperature was maintained at 30–35° during the addition and for 3 hours longer. The yellow solution, which was basic to *p*H paper, was then extracted three times with 50-ml. portions of chloroform and the combined extracts dried over sodium sulfate. Distillation of the solvent under reduced pressure left a yellow oil which was distilled through a short Vigreux column. After a few drops of forerun had been discarded, the main fraction of colorless liquid, b.p. 83–84° (14 mm.), was collected. The yield was 12.0 g. (30%). A small portion, redistilled for analysis, crystallized on standing. It was hygroscopic.

Anal. Calcd. for $C_5H_{12}N_2O_2$: C, 45.43; H, 9.15. Found: C, 45.19; H, 9.23.

The methiodide, crystallized three times from absolute ethanol, consisted of white crystals, m.p. 150–151° dec.

Anal. Calcd. for $C_6H_{15}N_2O_2I$: C, 26.29; H, 5.53. Found: C, 26.34; H, 5.60.

Reaction of *unsym*-Dimethylhydrazine with Benzoyl Chloride. (a) In Aqueous Solution.—Into a cold stirred solution of 20 g. (25 ml., 0.33 mole) of *unsym*-dimethylhydrazine in 50 ml. of water was dropped 23.1 g. (19.2 ml., 0.18 mole) of benzoyl chloride. A second equal portion of benzoyl chloride and a saturated aqueous solution of 19.2 g. (0.18 mole) of sodium carbonate were then added dropwise from separate dropping funnels, at such a rate that the addition of benzoyl chloride was completed first. The temperature was kept below 20° throughout the additions and the subsequent one hour of stirring. The resulting solution (*p*H 8), was extracted three times with 50-ml. portions of chloroform, which were combined and dried over potassium carbonate. Removal of the solvent under reduced pressure left a yellow paste, which was extracted several times with water at room temperature. The residual yellow powder was crystallized from 80% ethanol, yielding 12 g. of white flakes, m.p. 152–153°. An analytical sample melted at 152–153° after three additional crystallizations from 80% ethanol. The compound had the composition of 1,1-dibenzoyl-2,2-dimethylhydrazine.

Anal. Calcd. for $C_{16}H_{16}N_2O_2$: C, 71.63; H, 6.01; N, 10.45. Found: C, 71.47; H, 6.08, N, 10.21.

Evaporation of the combined aqueous extracts left a yellowish powder, which yielded 7 g. of white needles, m.p. 106–107° after two crystallizations from carbon tetrachloride.

Anal. Calcd. for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.07. Found: C, 65.92; H, 7.52; N, 16.71.

The results were similar when the sodium carbonate was omitted from a reaction run on the same scale.

(b) In Benzene.—This experiment was carried out on the same scale as the one described above, but with an inverse method of mixing the reactants. To a cold stirred solution of benzoyl chloride in 25 ml. of benzene a solution of *unsym*-dimethylhydrazine in 50 ml. of benzene was added dropwise. A white solid began to precipitate immediately. The reaction mixture was stirred at 15–20° during the addition and for one hour thereafter. To the stirred reaction mixture, which still smelled of benzoyl chloride, 100 ml. of water was added. The layers were separated. The aqueous layer was made basic with a saturated solution of sodium

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(13) H. M. Randall, N. Fuson, R. G. Fowler and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 160.

(14) The author is indebted to Dr. Jack Hummel of the Biochemistry Department, State University of Iowa, for the infrared curves.

(15) T. O. Jones, R. E. Halter and W. T. Myers, THIS JOURNAL, **75**, 6055 (1953).

(16) M.p.'s and b.p.'s are uncorrected.

(17) Used directly as purchased from the Metalectro Corp., Laurel, Md.

carbonate, and extracted with chloroform. Evaporation of the solvent *in vacuo* left a yellow paste, from which the two products were obtained by extraction with water and purified as described above; yields: 15 g. of 1,1-dibenzoyl-2,2-dimethylhydrazine and 5.5 g. of 1-benzoyl-2,2-dimethylhydrazine, both identified by mixed m.p.'s with the analytical samples described above.

Reductions with Lithium Aluminum Hydride.—Except where otherwise noted, the reactions of lithium aluminum hydride with the acylhydrazines were carried out according to the following general directions.

In each experiment the solution of the acylhydrazine in the appropriate dry solvent was added dropwise to a stirred solution of powdered lithium aluminum hydride in the same solvent. At the end of the allowed reaction time the excess lithium aluminum hydride was decomposed by the cautious addition of *n* ml. of water, then *n* ml. of 15% sodium hydroxide, and finally 3*n* ml. of water, where *n* is the number of grams of hydride used.[2] The resulting white granular precipitate was removed by filtration and washed thoroughly with ether and/or tetrahydrofuran. After the filtrate had been dried over sodium sulfate, the solvents were removed by one of the following methods. If the products were volatile, the solvents were removed by distillation through a column packed with glass helices. If the product was relatively high-boiling, the solvents were removed by simple distillation at the water-pump. In either case the residual crude product was then purified by distillation. The quantities of reactants and the properties of the product are described for each experiment.

The procedure used in the isolation and purification of the product from the reaction of the hydride with ethyl hydrazodicarboxylate is described in detail, as it differs markedly from the general directions above.

1,2-Diethyl-1,2-dimethylhydrazine.—1,2-Diacetyl-1,2-dimethylhydrazine,[7] 7 g. (0.05 mole) in 75 ml. of tetrahydrofuran; lithium aluminum hydride, 2.5 g. (0.07 mole) in the same volume of solvent. Two distillations of the product from barium oxide yielded 3.3 g. (57%) of a colorless liquid with b.p. 93–94° (752 mm.), and $n^{27}\mathrm{D}$ 1.4121. The product, which had a distinct amide-like odor, was soluble in ether but only slightly soluble in water. It exploded in the carbon–hydrogen combustion train.

Anal. Calcd. for $C_6H_{16}N_2$: neut. equiv., 116. Found: neut. equiv., 112, 114 (by potentiometric back titration of the solution of the hydrazine in std. hydrochloric acid).

Attempts to prepare a methiodide yielded white crystals, m.p. 181–182° dec., which turned yellow within a few minutes even in a vacuum desiccator. A satisfactory analysis could not be obtained.

1,2-Diethyl-1,2-dimethylhydrazine picrate, crystallized twice from absolute ethanol, melted at 170–172° dec.

Anal. Calcd. for $C_{12}H_{19}N_5O_7$: C, 41.74; H, 5.55; N, 20.28. Found: C, 41.78; H, 5.60; N, 20.83.

1,2-Dibenzyl-1,2-dimethylhydrazine.—1,2-Dibenzoyl-1,2-dimethylhydrazine,[7] 9.0 g. (0.033 mole) in 75 ml. of hot tetrahydrofuran; lithium aluminum hydride, 2.3 g. (0.06 mole) in 75 ml. of solvent. From the distillation of the crude product three fractions were collected: b.p. 42–44° (0.30 mm.), 0.7 g.; b.p. 95–105° (0.15 mm.), 0.5 g.; b.p. 118–120° (0.15 mm.), 3.6 g. Treatment of a portion of the first fraction with methyl iodide produced a white precipitate. Ether was added, and after several hours the mixture was filtered. The precipitate, recrystallized from absolute ethanol, melted at 135–137° dec.

Anal. Calcd. for $C_{10}H_{17}N_2I$: N, 9.59. Found: N, 9.51.

The addition of α-naphthyl isocyanate to the ethereal filtrate was accompanied by the formation of white crystals. After three recrystallizations from petroleum ether, b.p. 60–70°, the product melted at 131–132° and did not depress the m.p. of an authentic specimen of benzyl N-α-naphthylcarbamate, m.p. 131–132°.

The third fraction from the distillation was redistilled. The main fraction was a colorless liquid of rather sweet odor, b.p. 128–130° (0.80 mm.), $n^{26}\mathrm{D}$ 1.5538, yield 3.1 g. (40%).

Anal. Calcd. for $C_{16}H_{20}N_2$: C, 79.97; H, 8.39; N, 11.66. Found: C, 80.02; H, 8.24; N, 11.94.

The methiodide of 1,2-dibenzyl-1,2-dimethylhydrazine, recrystallized from absolute ethanol, melted at 156–157° dec.

Anal. Calcd. for $C_{17}H_{23}N_2I$: C, 53.41; H, 6.06; N, 7.33. Found: C, 53.63; H, 6.22; N, 7.24.

1,2-Diethylhydrazine Dihydrochloride.—Powdered 1,2-diacetylhydrazine[18] (3.5 g., 0.03 mole) was added in small portions to a vigorously stirred slurry of 3.0 g. (0.08 mole) of lithium aluminum hydride in 150 ml. of dry tetrahydrofuran. After the excess hydride had been decomposed in the usual way, and the white precipitate removed by filtration, 10 ml. of concd. hydrochloric acid was added to the filtrate, which was then evaporated to dryness under reduced pressure. The yellow solid which remained was dissolved in 10 ml. of hot absolute ethanol containing 1 ml. of concd. hydrochloric acid. After cooling to room temperature, 5 ml. of dry ether was added, and the temperature was held at 0° overnight. The white needles which had formed were collected by suction filtration, weighed 1.3 g. (26%) and melted at 164–165°; reported m.p. 160°.[11a]

2,3-Diethylphthalazine-1,4-dione was prepared by the reaction of 0.17 g. of 1,2-diethylhydrazine dihydrochloride and 0.15 g. of phthalic anhydride. A solution of the reactants and 0.5 g. of sodium acetate in 10 ml. of 50% water-acetic acid mixture was refluxed for 1 hour. Concentration to 5 ml. gave a tan precipitate which on recrystallization from water yielded white crystals, m.p. 156–157°.

Anal. Calcd. for $C_{12}H_{14}N_2O_2$: C, 66.02; H, 6.46. Found: C, 65.89; H, 6.30.

1,2-Dimethylhydrazine Dihydrochloride.—A solution of 40 g. (0.23 mole) of ethyl hydrazodicarboxylate[6] in 150 ml. of hot dry tetrahydrofuran was kept near the boiling point in a dropping funnel, which was heated by means of several encircling coils of nichrome wire. The hot solution was added dropwise to a rapidly stirred slurry of 28.5 g. (0.75 mole) of lithium aluminum hydride in the same solvent. After the addition had been completed, the reaction mixture was stirred at the reflux temperature for 70 hours. Water, added to the cold mixture to decompose the excess hydride, was followed by sufficient 20% hydrochloric acid to dissolve the inorganic precipitate. After the organic layer had been separated and discarded, the aqueous layer was concentrated under reduced pressure to about 150 ml. The yellow concentrate, which contained a thick precipitate of salts, was added by means of a dropping funnel with a wide-bore stopcock to a hot solution of 220 g. of sodium hydroxide in 120 ml. of water in a flask equipped for distillation. The distillate from the heated flask was led directly into 50 ml. of concd. hydrochloric acid. Distillate was collected until the temperature reached 100°, and for 30 minutes thereafter. (One-third of the product was obtained from the final 30 minutes of distillation. From further distillation only trace amounts of product were obtained.) The yellow acidic solution of the distillate was evaporated to dryness under reduced pressure, leaving a yellow paste. Purification according to the directions in reference 7 produced fine white needles, m.p. and mixed m.p. with an authentic sample of 1,2-dimethylhydrazine dihydrochloride, 164–166°. The yield was 22 g. (72%). The diacetyl derivative did not depress the m.p. of an authentic specimen of 1,2-diacetyl-1,2-dimethylhydrazine.

1-Ethyl-2,2-dimethylhydrazine.—1-Acetyl-2,2-dimethylhydrazine, 10.2 g. (0.10 mole) in 50 ml. of ether; lithium aluminum hydride, 4.6 g. (0.12 mole) in 50 ml. of ether. After three distillations of the crude product from barium oxide 1.7 g. (19%) of a colorless product, b.p. 74–75° (754 mm.), was collected; reported b.p.[10b] 76–77° (720 mm.). Some higher boiling residual liquid distilled under reduced pressure, b.p. 98° (16 mm.). From its boiling point and index of refraction, $n^{25}\mathrm{D}$ 1.4502, the last fraction was tentatively identified as starting material, of which 0.4 g. was thus recovered. When the reaction time was increased to 18 hours, the yield was 35%, and 16% of the starting material was recovered. The picrate of 1-ethyl-2,2-dimethylhydrazine melted at 93–94° dec.; reported m.p.[10b] 92–93° dec. The methiodide melted at 155–156° dec. after crystallization from absolute ethanol.

Anal. Calcd. for $C_5H_{15}N_2I$: C, 26.11; H, 6.57; N, 12.18. Found: C, 26.09; H, 6.44; N, 12.06.

Ethyl 2,2-Dimethylcarbazate and Lithium Aluminum Hydride.—Ethyl 2,2-dimethylcarbazate, 17 g. (0.13 mole)

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[18] R. Stollé, *Ber.*, **32**, 796 (1899). A dry product, m.p. 137–139°, was obtained by two crystallizations from a mixture of absolute ethanol and cyclohexane.

in 100 ml. of ether; hydride, 9.5 g. (0.25 mole) in 200 ml. of ether. The volatility of the product and the tenacity with which it was adsorbed on the lithium aluminate seriously hindered the isolation and purification of the product. From the final distillation there was obtained 0.92 g. (10%) of clear liquid distilling at 62–63° (753 mm.), n^{24}D 1.4035. The reported b.p. and index of refraction of trimethylhydrazine[4] are 58.8–60.1° (735 mm.) and n^{20}D 1.4039.

Anal. Calcd. for $C_3H_{10}N_2$: neut. equiv., 74. Found: neut. equiv., 76, 77 (potentiometric titration).

Twenty per cent. of the ethyl 2,2-dimethylcarbazate was recovered. It was identified by conversion to the methiodide which did not depress the m.p. of an authentic specimen.

Attempted Reductions of 1,2-Dibenzoylhydrazine, 1,2-Diformylhydrazine and 1-Benzoyl-2,2-dimethylhydrazine.—From the treatment of each of these substances with the hydride only starting material was recovered. No alkylhydrazine could be detected.

Dimethylhydrazine Picrate.—This compound, which has not been reported previously, was prepared for comparison with some of the picrates described above. After one recrystallization from absolute ethanol the golden flakes melted at 145–146° dec.

Anal. Calcd. for $C_8H_{11}N_5O_7$: C, 33.22; H, 3.83. Found: C, 33.60; H, 4.06.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, CAIRO UNIVERSITY]

Reactions with Diazoalkanes. VI. Action of 9-Diazofluorene on 2-Arylideneindane-1,3-diones

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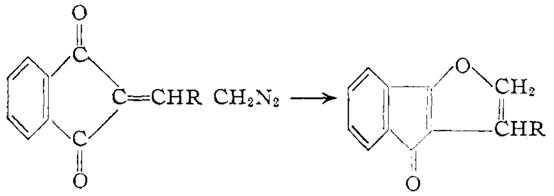
The intensely colored 2-arylideneindane-1,3-diones, listed in Table II, react with 9-diazofluorene to give colorless products believed to have the cyclopropane structure (III).

9-Diazofluorene reacts with unsaturated compounds to form cyclopropane derivatives. Thus with acenaphthylene,[1a] ω-nitrostyrenes,[1b] acrylonitrile,[1c] α,β-unsaturated ketones,[1c,1d] α,β-unsaturated esters,[1d,1e] azo compounds, *e.g.* diethylazodicarboxylate[1e] and with *p*-quinonedibenzenesulfonimides,[1f] the corresponding cyclopropane derivatives are obtained.

2-Arylideneindane-1,3-diones (I) have been found to react with ethereal diazomethane solution in the presence of methyl alcohol to yield colorless substances, believed to be furanoindenones (II).[2] We have now found that when the intensely colored compounds Ia-g are allowed to react with 9-diazofluorene in benzene solution at room temperature (except in the case of If-g where the reaction is brought to the boiling point of the benzene solution) the deep color of the reaction mixture faded and colorless or substantially colorless products (III) are obtained.



Ia, R = C_6H_5, b, R = $C_6H_4NO_2$-*o*, II
c, R = $C_6H_4NO_2$-*m*, d, R = $C_6H_4NO_2$-*p*,
e, R = $C_6H_4OCH_3$-*p*, R = $C_6H_3{:}O_2CH_2$-3,4 (piperonyl),
g, R = C_4H_3S (2-thienyl)

In view of the well established mechanism for the addition of 9-diazofluorene to analogous α,β-unsaturated compounds[1] (α,β-unsaturated ketones[1e] and α,β-unsaturated esters),[1e] the addition products of the same reagent to Ia-g have, probably, the cyclopropane structure III. It is improbable that the products IIIa-g are of the furanoindenone structure (*cf.* II), since IIIa, c and d give the corresponding diphenylhydrazone derivatives and IIIa forms phthalic on treatment with chromic acid. IIIa gives the correct molecular weight and analytical values. When an alcoholic solution of IIIa and/or d is treated with hydroxylamine hydrochloride in presence of aqueous potassium hydroxide[3] or in presence of pyridine, 1,3-indandione dioxime is obtained, together with an oily substance which is under further investigation. The behavior of Ia toward hydroxylamine hydrochloride in the presence of pyridine simulates that of IIIa toward the same reagent in the presence of pyridine, yielding 1,3-indandione dioxime. Such a reaction would lend additional support to the theory that the three-membered ring can react in a manner analogous to a carbon–carbon double bond when conjugated with a carbonyl group.[4,5] IIIa is thermolabile and undergoes isomerization by the action of heat at 220° for one hour in a vacuum, to an isomer having the molecular formula $C_{29}H_{18}O_2$; the structure of this isomer is under further investigation.

Evidence for the formation of IIIa in the reaction of Ia and 9-diazofluorene has been obtained from the vibrational spectrum.

The infrared spectra of compounds IIIa and 1,3-indanedione (IV) exhibit a single sharp medium intensity band in the region 1690 to 1550 cm.$^{-1}$.

[1] (a) A. Schönberg, A. Mustafa and N. Latif, THIS JOURNAL, **75**, 2267 (1953); (b) A. Mustafa and A. H. E. Harhash, *ibid.*, **76**, 1383 (1954); (c) L. Horner and E. Lingnau, *Ann.*, **573**, 30 (1951); (d) H. Staudinger and A. Gaule, *Ber.*, **49**, 1956 (1916); (e) L. Horner and E. Lingnau, *Ann.*, **591**, 21 (1955); (f) A. Mustafa and M. Kamel, THIS JOURNAL, **75**, 2939 (1953).

[2] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952).

[3] *Cf.* the ready isomerization of cyclopropane-bis-indandione-1,2,2,2-dispiran by the action of 5% sodium hydroxide solution (*C. A.*, **21**, 3203 (1927)).

[4] *Cf.* the behavior of 2-arylidene-3-phenylindan-1-ones, *e.g.*, 2-benzylidene-3-phenylindan-1-one and of alkylated 2-arylidene-3-phenylidan-1-ones (aryl-radical = $C_6H_4OCH_3$-*p*) toward the action of hydroxylamine hydrochloride in presence of aqueous sodium hydroxide solution (W. S. Johnson and W. S. Shelberg, THIS JOURNAL, **67**, 1758 (1945)).

[5] *Cf.* the behavior of 2-benzylideneindan-1,3-dione (Ia) toward the action of dilute alkali (W. Wislicenus and A. Kötzle, *Ann.*, **252**, 72 (1889)) and toward phenylhydrazine (W. Wislicenus and F. Reitzenstein, *Ann.*, **277**, 362 (1893)).