appearing. Subsequent chromatographic isolation and purification of the individual compounds showed them to have the correct boiling points and refractive indices for vinylcyclopropane[4] and dicyclopropyl.[5] During the identification work, products in addition to vinyl cyclopropane and dicyclopropyl that might also arise from the reaction[6] or subsequent work-up were carefully looked for, but none was found.

The results of five runs made at several conditions are listed in Table II. It is to be noted that the ratio of dicyclopropyl to vinylcyclopropane increased with an increase in the ratio of methylene iodide to butadiene.

TABLE II

REACTION OF BUTADIENE WITH METHYLENE IODIDE

Reactants	I-21[a]	I-25	I-31	I-35	I-50
Butadiene, moles	0.11	0.17	0.20	0.20	0.21
CH_2I_2	0.100	0.100	0.100	0.102	0.165
Zn(Cu), moles	0.15	0.15	0.15	0.15	0.25
Dioxane, ml.	90	90	90	90	90
Temperature, °C.	37	60	60	60	60
Time, hr.	5	72	72	48	42
Conversion, mole % based on CH_2I_2					
Vinylcyclopropane	0	[b]	[b]	26	26
Dicyclopropyl	0	[b]	[b]	7	23

[a] Run at atmospheric pressure in a 500-ml. round-bottomed flask fitted with a Dry Ice condenser and drying tube. [b] Not worked up quantitatively; both products formed at a total conversion of <30%, but the numerical ratios are not certain.

Experimental

Instrumental Analysis.—Gas phase chromatograms for analyses were carried out isothermally on a Perkin-Elmer Model 154 vapor fractometer using a 6-ft. column of polypropylene glycol packed on Haloport F support.

Chromatographic separations were run on an F and M-500 linear programmed gas chromatograph using a 6-ft. column of β,β'-oxydipropionitrile packed on Haloport F and an 8-ft. column of Dow-Corning silicone grease packed on Haloport F.

Infrared analyses were performed on a Perkin-Elmer Model 21 double beam instrument with a sodium chloride prism and a 0.1-mm. microcell of 0.005-ml. capacity.

Mass spectrometry was carried out in a Bendix Time of Flight spectrometer, Model 12-101.

Boiling points were measured by the Emich capillary technique on 2-3 μl. of sample. A National Bureau of Standards calibrated thermometer that could be read to the nearest 0.1° was used.

Refractive indices were read on a 5-decimal place Bausch and Lomb refractometer that would accept a 0.025-ml. sample.

Reaction of Butadiene with Methylene Iodide-Zinc (Cu) Couple.—The zinc-copper couple was prepared by the method of Shank and Shechter[7] from 2-mesh zinc shot (Matheson Coleman and Bell reagent).

To 90 ml. of *p*-dioxane (distilled and dried over Linde 5A sieves) in a 11 in. × 1.5 in. borosilicate glass reaction tube was added 10.8 g. (0.2 mole) of butadiene (MC and B instrument grade). An iodine crystal was added, followed by 26.8 g. (0.1 mole) of reagent grade methylene iodide. Then 9.6 g. (0.15 mole) of the zinc-copper couple was added and the tube was sealed with a metal bottle cap lined with Neoprene rubber and a Teflon gasket. The reaction tube was tumbled in a 60° oil bath for 48 hr. It was opened and its contents were decanted through glass wool. The sludge of zinc-copper and zinc iodide was washed twice with 10 ml. of dioxane and the washes were added to the filtrate which now amounted to 110 g. Analysis o a portion by gas chromatography (column of polypropylene glycol 40°, helium flow of 46 ml./min. at 10 p.s.i.g.) showed five peaks a the following retention times (minutes past the air peak) and percentages by weight: 0.70 (7.7%), 2.00 (0.22%), 2.52 (1.61%), 8.15 (0.26%), 11.36 (90.2%). The 0.70 and 11.36 retention time peaks were shown to be butadiene and *p*-dioxane by comparison with the original reagents employed. Subsequent identification work described below showed that the 2.00 peak was methyl iodide and that the 2.52-min. peak material was vinylcyclopropane and the 8.15-min. peak material was dicyclopropyl.

Isolation of Vinylcyclopropane and Dicyclopropyl.—The bulk of the butadiene was removed from the reaction solution by fractionation through a 3″×1/2″ Heli-Pak packed micro column and the methyl iodide, vinylcyclopropane and dicyclopropyl distilled along with some *p*-dioxane. Gas chromatography analysis of the distillate showed its composition was 3% butadiene, 6% methyl iodide, 24% vinyl cyclopropane, 5% dicyclopropyl, and 62% *p*-dioxane.

The *p*-dioxane was removed by preparative gas chromatography on a 6 ft × 1/4 in. β,β'-oxydipropionitrile column maintained at 75° and using a helium flow of 40 ml./min. at 35 p.s.i.g., and a block and injection port temperature of 125°. The mixture was injected in 0.5-ml. slugs and the lower boiling materials collected in a 3-in. tapered test tube maintained at −20°. The exhaust from the column was led into and out of the collector by two 20-gauge hypo needles inserted through a rubber serum cap. The collected mixture of butadiene, methyl iodide, vinylcyclopropane, and dicyclopropyl was next separated as individual components by reinjection through a silicone grease column maintained at 25° (helium flow 30 ml./min. at 35 p.s.i.g., block and injection port maintained at 80°). Gas chromatography of these fractions showed only one peak.

Identification of Methyl Iodide, Vinylcyclopropane, and Dicyclopropyl.—A 10-microliter portion of a three-component mixture isolated from the β,β'-oxydipropionitrile column, consisting of 7% methyl iodide, 65% vinylcyclopropane, and 28% dicyclopropyl, was injected into an 8-ft. silicone grease column at 25° as described above. The individual pure components eluting from the column were fed into a Bendix Time of Flight mass spectrometer and analyzed (electron energy, 70 volts; trap current, 0.1 μamp.) The methyl iodide was identified by comparison with the mass spectrum of authentic methyl iodide. The mass spectra of known vinyl cyclopropane and dicyclopropyl were not available from any source so an identification could not be made by a comparison. However, the suspected vinylcyclopropane showed a molecular weight of 68 and the suspected dicyclopropyl showed a molecular weight of 82. The confirmation of the identity of these two compounds was accomplished on the basis of their infrared spectra, boiling points, and refractive indices.

A portion of distillate containing 88% vinylcyclopropane, 9% methyl iodide, and 2% butadiene was purified in the 8-ft silicone grease column at 25°. Gas chromatography of the collected vinylcyclopropane fraction showed only one peak; b.p. 40.2-40.6° (760) and $n^{25}\text{D}$ 1.41133 [vinyl cyclopropane, b.p. 40.19° (760) $n^{20}\text{D}$ 1.4138].[4] Another portion of distillate containing 92% dicyclopropyl, 4% vinylcyclopropane, and 4% dioxane was purified to give only one peak; b.p. 76.0° (760), $n^{23.6}\text{D}$ 1.42201 [dicyclopropyl, b.p., 76.1° (760) and $n^{20}\text{D}$ 1.4239][5]. An infrared spectrum of the two compounds in carbon tetrachloride was identical in every way with those published by Slabey[4,5] for vinylcyclopropane and dicyclopropyl.

Alkyl-(alkoxyalkyl-)hydrazones

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A recent report from this laboratory described the synthesis of methylhydrazine by the thermal decom-

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[4] V. A. Slabey, *J. Am. Chem. Soc.*, **74**, 4930 (1952).

[5] V. A. Slabey, *ibid.*, **74**, 4928 (1952).

[6] Particularly cyclopentene from 1,4-addition and dicyclo[3.1.0]hexane from subsequent reaction of cyclopentane [V. Franzen, *Ber.*, **95**, 571 (1962)]. W. von E. Doering and P. M. LaFlamme, *Tetrahedron*, **2**, 75 (1958), found pentene and 2-methyl-2-butene among the expected cyclopropane products when methylene iodide and zinc-copper couple was added to *cis*- and to *trans*-butene-2.

[7] R. S. Shank and H. Shechter, *J. Org. Chem.*, **24**, 1825 (1959).

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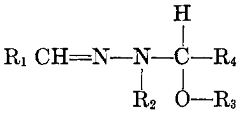
TABLE I

ALKYL-(ALKOXYALKYL-)HYDRAZONES

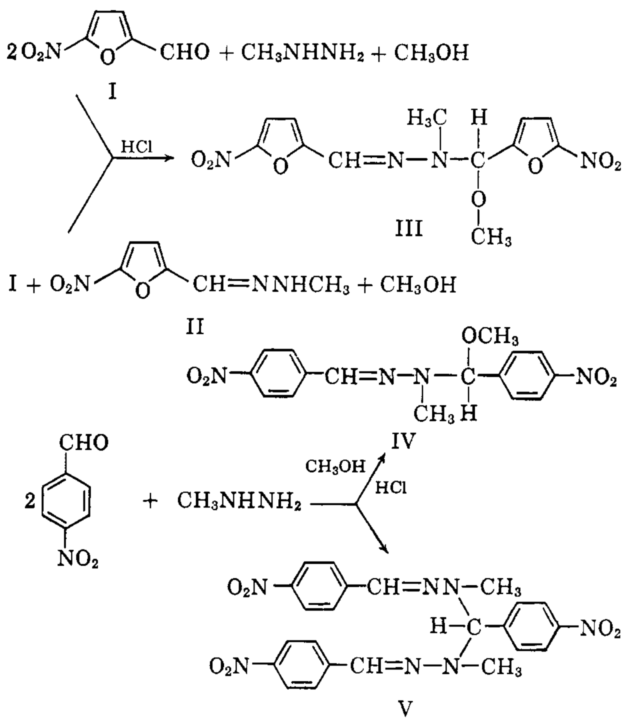


$$R_1\,CH{=}N{-}\underset{R_2}{N}{-}\overset{H}{\underset{O-R_3}{C}}{-}R_4$$

No.	R_1	R_2	R_3	R_4	M.p., °C.	Yield, %	Molecular formula	Analysis: Carbon, %, Calcd. Found	Analysis: Hydrogen, %, Calcd. Found	Analysis: Nitrogen, %, Calcd. Found
III	5-nitro-2-furyl	CH_3	CH_3	5-nitro-2-furyl	131–132	72[b,c]	$C_{12}H_{12}N_4O_7$[a]	44.45	3.73	17.28
								44.41	3.82	16.95
X	5-nitro-2-furyl	CH_3	$CH(CH_3)_2$	5-nitro-2-furyl	102–104	86[b]	$C_{14}H_{16}N_4O_7$	47.73	4.58	15.90
								47.82	4.65	15.70
XI	5-nitro-2-furyl	CH_3	CH_3	C_6H_5	107–108	91[c]	$C_{14}H_{15}N_3O_4$	58.12	5.23	14.53
								58.05	5.34	14.66
VII	5-nitro-2-furyl	$(CH_2)_2COOCH_3$	CH_3	5-nitro-2-furyl	130–131	55[b]	$C_{15}H_{16}N_4O_9$	45.46	4.07	14.14
								45.59	4.20	13.95
XII	5-nitro-2-furyl	$CH_2C_6H_5$	CH_3	5-nitro-2-furyl	159–160	90[b]	$C_{18}H_{16}N_4O_7$	54.00	4.03	14.00
								53.97	4.16	14.21
IV	*p*-nitrophenyl	CH_3	CH_3	*p*-nitrophenyl	121–122.5	59[b]	$C_{16}H_{16}N_4O_5$	55.95	4.79	16.35
								55.81	4.68	16.27

[a] Molecular weight (cryoscopic): Calcd., 324.25. Found: 342 ± 20. [b] Method A (aldehyde + 2 moles of hydrazine). [c] Method B (aldehyde hydrazone + 1 mole of aldehyde).

position of 1-hydrazino-2-propanol.[2] In an effort to determine the yield by a more efficient method than the isolation of pure methylhydrazine, we attempted to prepare 5-nitro-2-furaldehyde methylhydrazone (II) by the addition of methanolic 5-nitro-2-furaldehyde (I) to the crude distilled reaction product, which consisted mainly of methylhydrazine and acetaldehyde methylhydrazone. It was found that in the presence of acid and two moles of the aldehyde a yellow crystalline product was formed which was not the expected methylhydrazone. Consideration of the compound's elemental analysis, molecular weight and infrared spectrum (no NH or OH absorption) led to the assignment of structure III.[3] This was supported by the direct synthesis of III from the methylhydrazone II (prepared from equimolar quantities of 5-nitro-2-furaldehyde and methylhydrazine), methanol, and I. Since this type of hydrazone had not been reported, we prepared several related compounds by varying the aldehyde, alcohol, and hydrazine moieties (Table I). The product from two moles of *p*-nitrobenzaldehyde and one mole of methylhydrazine in acidified methanol was the alkoxyhydrazone IV and not the bishydrazone V which is formed in neutral ethanol.[4]



The preparation of methyl 3-hydrazinopropionate hydrochloride (VI), an intermediate in the synthesis of VII, resulted in the first practical synthesis of 3-pyrazolidinone hydrochloride (VIII). The sodium salt of 3-chloropropionic acid and hydrazine yielded the 3-hydrazinopropionate salt which was converted to the methyl ester hydrochloride. Attempts to prepare an analytical sample of VI by recrystallization from methanol gave VIII,[5] which was also obtained in 85% yield by heating VI in an oven at 110°. Previous methods involved the addition of hydrazine to acrylic acid[6] or methyl acrylate[7] and the bromination of pyrazoline-3-sulfonamides.[5]

The reaction of VIII with I gave a golden crystalline material which melted above 300°. It was assigned the inner salt structure IX by analogy to the product of a similar reaction between 5-phenyl-3-pyrazolidinone and benzaldehyde.[7]

An attempt to extend the series to the aromatic hydrazines by the reaction of I, phenylhydrazine and methanol resulted only in the isolation of 5-nitro-2-furaldehyde phenylhydrazone.

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(2) J. C. Howard, G. Gever, A. B. Neill, and P. H. L. Wei, *J. Org. Chem.*, **26**, 1082 (1961).

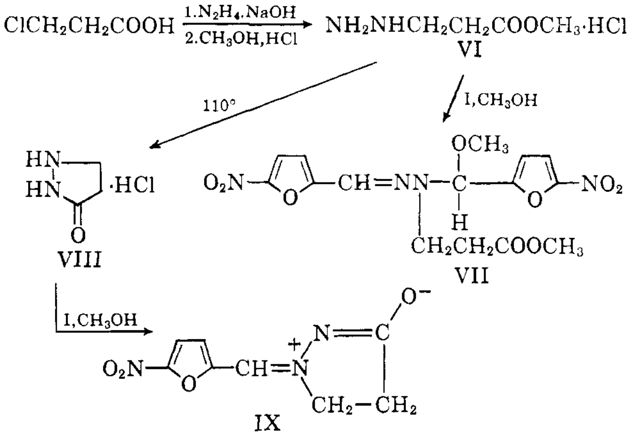
(3) III has been named "5-nitro-2-furaldehyde 2-(α-methoxy-5-nitrofurfuryl)-2-methylhydrazone."

(4) O. L. Brady and G. P. McHugh, *J. Chem. Soc.*, **121**, 1651 (1922).

(5) C. S. Rondestvedt, Jr., and P. K. Chang, *J. Am. Chem. Soc.*, **77**, 6532 (1955).

(6) R. von Rothenberg, *J. prakt. Chem.*, **51**, 72 (1895).

(7) W. O. Godtfredsen and S. Vangedal, *Acta Chem. Scand.*, **9**, 1498 (1955).



Experimental[8]

General Procedure for α-Alkoxyalkylhydrazones. Method A.—To a stirred solution of 0.2–0.3 mole of the aldehyde in 150 ml. of the appropriate alcohol was added slowly 0.1 mole of the hydrazine in 50 ml. of the alcohol. One milliliter of concentrated hydrochloric acid was added and the mixture was stirred at room temperature or on the steam bath until precipitation of the yellow product was judged complete. The crystals were collected, washed with the alcohol, and dried at room temperature. Recrystallization was carried out in the alcohol except with XII (benzene) and IV (benzene and methanol).

Method B. The aldehyde hydrazone was added to 1.5 equivalets of the appropriate aldehyde in an excess of the desired alcohol which contained several drops of concentrated hydrochloric acid. The mixture was warmed at 50° until complete solution occurred, then Darco was added and the mixture was filtered. The crystalline product which precipitated was purified as in Method A.

Methyl 3-Hydrazinopropionate Hydrochloride, VI.—To 164 g. (4.1 moles) of sodium hydroxide dissolved in 824 g. (14 moles) of 85% hydrazine hydrate was added slowly with stirring 220 g. (2.03 moles) of 3-chloropropionic acid in 180 ml. of water. The temperature was kept between 90 and 95° by the rate of addition. Introduction of the acid was completed in 1.5 hr. and the mixture was stirred with heating for 1 hr. longer. Water and excess hydrazine were then removed at reduced pressure and a semisolid residue remained. To this was added 1.5 l. of methanol; the solution was saturated with anhydrous hydrogen chloride, heated on the steam bath for 30 min., then filtered to remove the sodium chloride. The methanolic filtrate gave colorless crystals after cooling and scratching. These were collected and washed with amounts of cold methanol and ether. After drying in a desiccator over sodium hydroxide, the weight was 235 g. (75%). The substance melted slowly over a broad range up to 90° and was extremely hygroscopic. Attempts at recrystallization from methanol and reprecipitation from methanol by ether either failed or gave 3-pyrazolidinone hydrochloride.

3-Pyrazolidinone Hydrochloride, VIII.—The crude methyl 3-hydrazinopropionate hydrochloride, 62 g. (0.40 mole), was heated overnight in an open dish placed in an oven at 110°. The yield was 42 g. (85%), m.p. 230–208°. Recrystallization from methanol raised the m.p. to 209–210° (sealed capillary, uncorrected). This compound was reported by Rondestvedt and Chang[5] to melt at 199–200°. The present sample gave an infrared spectrum essentially identical to theirs.

Anal. Calcd. for $C_3H_7ClN_2O$: C, 29.40; H, 5.75; Cl, 29.01; N, 22.85. Found: C, 29.43; H, 5.71; Cl, 29.15; N, 22.83.

1-(5-Nitro-2-furfurylidene)-3-hydroxy-2-pyrazolinium Hydroxide, Inner Salt, IX.—To 600 mg. (4.92 mmoles) of 3-pyrazolidinone hydrochloride in 5 ml. of water was added 696 mg. (4.94 mmoles) of 5-nitro-2-furaldehyde in 5 ml. of methanol. An orange precipitate rapidly formed. After standing for 30 min. at room temperature the solid was collected and washed with 5 ml. of each of methanol and ether. After drying at 110°, the yield was 930 mg. (91%). An analytical sample was prepared by recrystallization from nitromethane. The compound did not melt below 300°.

Anal. Calcd. for $C_8H_7N_3O_4$: C, 45.93; H, 3.38; N, 20.09. Found: C, 45.68; H, 3.37; N, 19.76.

5-Nitro-2-furaldehyde Methylhydrazone,[9] II.—To 141 g. (1.00 mole) of 5-nitro-2-furaldehyde in 1 l. of absolute ethanol was added dropwise with stirring 50 g. (1.08 moles) of methylhydrazine. The mixture became dark red and the temperature rose to 35°. Soon a thick red solid mass separated. The precipitate was collected, washed with ethanol, and dried at 60°. The yield was 111 g. (66%), m.p. 142–144. Recrystallization from isopropyl alcohol raised the m.p. to 143–143.5°.

Anal. Calcd. for $C_6H_7N_3O_3$: C, 42.60; H, 4.17; N, 24.85. Found: C, 42.55; H, 4.04; N, 24.6.

Preparation of III from the Crude Distillate Resulting from the Thermal Decomposition of 1-Hydrazino-2-propanol.—Substitution of the crude distillate[2] (b.p. 125–145°) for methylhydrazine resulted in a 34% yield of III based on the hydrazino alcohol.

Acknowledgment.—We wish to thank Dr. Pauline Chang[5] for sending us a copy of the infrared spectrum of 3-pyrazolidinone hydrochloride, and Benjamin Stevenson and Michael Heigle of these laboratories for technical assistance.

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[8] All m.p.'s except where noted were taken on a Fisher–Johns block and are corrected. The elemental analyses and molecular weight determination were carried out under the direction of Mr. Gordon Ginther and Dr. Victor Ells of these laboratories, and Schwarzkopf Analytical Laboratory, Woodside, N. Y.

[9] This compound was first prepared by R. Raffauf of this laboratory.

Preparation of Aryldiazoalkanes by the Bamford–Stevens Reaction

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In their first paper on the decomposition of toluene-*p*-sulphonylhydrazones by alkali,[2] Bamford and Stevens noted that this reaction constituted a moderately successful method for the preparation of aryldiazo compounds. For example, benzaldehyde toluene-*p*-sulfonylhydrazone afforded a 60% yield of phenyldiazomethane upon treatment with ethanolic sodium ethoxide at 50° for five to eight hours. The reaction was somewhat less useful for the preparation of 1-phenyldiazoethane,

$$C_6H_5CHNNHTs \xrightarrow[CH_3CH_2OH]{NaOCH_2CH_3} C_6H_5CHN_2\ (60\%)$$

yielding 27% of the diazo compound in seven hours at 65–70°. Possibly because of this lack of general applicability and the long reaction times necessary, the method has not taken a significant place among the methods available for the preparation of aryldiazoalkanes.[3]

In view of the ready availability of toluene-*p*-sulfonylhydrazones, it seemed desirable to us to examine the effect of some experimental variables on the synthetic utility of the Bamford–Stevens reaction. It was considered that there might be a convenient set of conditions which would give aryldiazomethanes in reasonable yields. In particular, the effect of some different bases and solvents on the decomposition of

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[1] Sloan Foundation Fellow, 1962.

[2] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952).

[3] J. Meinwald, P. G. Gassman, and E. G. Miller, *J. Am. Chem. Soc.*, **81**, 4751 (1959); P. Yates and B. L. Shapiro, *J. Org. Chem.*, **23**, 759 (1958); C. D. Gutsche and E. F. Jason, *J. Am. Chem. Soc.*, **78**, 1184 (1956).