acceleration in rate on adding amine hydrochlorides is caused by an increase in rate constant of ionization resulting from an increase in ionic strength. The data with lithium perchlorate show that an accelerating effect is indeed present. Within the accuracy of the experiments, the small accelerating effect of the pyridinium perchlorate can be accounted for on the same basis. However, the effect seems too small to account for all the increase in rate observed with the amines, but the previous suggestion of an uncertainty of reaction order in the presence of lithium perchlorate weakens this argument. A more convincing piece of evidence comes from the investigation of the stereochemical result of the decomposition. A decomposition in the presence of 10^{-2} *M* lithium perchlorate gave 2-butyl chloride of predominantly retained configuration with 36% optical purity, and a 10^{-4} *M* solution yielded a chloride with 74% optical purity. This is to be contrasted with the more than 95% optical purity with retention in the absence of salts, and 67% optical purity with *inversion* in the presence of 10^{-3} *M* pyridine hydrochloride.[6] Thus there must be a significant mechanistic difference between the action of lithium perchlorate and pyridine hydrochloride.

The racemization and possible change of kinetic order in the presence of lithium perchlorate are both consistent with the view that the ionic environment may promote ion-pair dissociation, giving therefore a symmetrically solvated carbonium ion.

The departure of the curve in Fig. 1 from linearity can also be attributed to a salt effect on both the second-order and first-order reactions. However, since the salt effects in such non-polar solvents are very complex, we have made no attempts to correct even k_0 for the salt concentration by using the lithium perchlorate data.

Acknowledgment.—We wish to thank the Research Corporation for a Frederick Gardner Cottrell grant which was of much assistance in this work.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

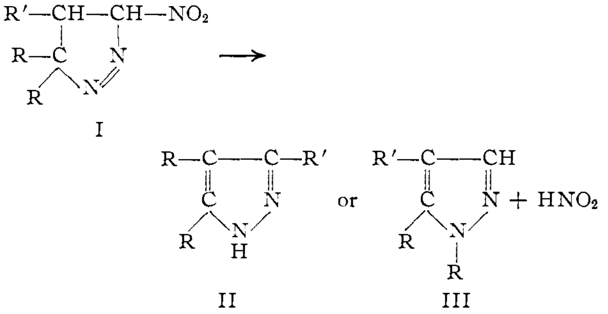
Reactions of Diazo Compounds with Nitroölefins. III. Group Migrations in the Decomposition of Nitropyrazolines

BY WILLIAM E. PARHAM AND WILLIAM R. HASEK[1]

RECEIVED AUGUST 21, 1953

A study of the reactions of certain nitroölefins with disubstituted diazo compounds, and subsequent decomposition of the resulting nitropyrazolines has been made. Loss of nitrous acid from the nitropyrazolines is accompanied by group migrations to carbon, resulting in the formation of 3,4,5-trisubstituted pyrazoles. The pyrazoles are postulated to arise from either a concerted twofold rearrangement of the Wagner–Meerwein type, or from a single migration from an abnormally orientated addition product.

In the preceding articles of this series the reaction of diazomethane and diazoacetic ester with nitroolefins was described,[2,3] and mechanisms[3] for the decomposition of 3-nitropyrazolines by action of acids or bases into pyrazoles, by loss of the elements of nitrous acid, were discussed. As a result of this study, and in view of data available concerning rearrangements of the Wagner–Meerwein type, it was anticipated that the loss of nitrous acid from pyrazolines of type I would give, by migration of R groups, pyrazoles of type II or type III.



I

II

III

A study of the reaction of diphenyldiazomethane with ω-nitrostyrene and 1-nitropropene, and the subsequent decomposition of the resulting nitropyrazolines into pyrazoles constitutes the subject of this report.

When diphenyldiazomethane was allowed to react with ω-nitrostyrene, in the absence of solvent, a crystalline addition product was obtained in 41% yield. Although the structure of this product was not established with certainty, it was formulated as 3-nitro-4,5,5-triphenylpyrazoline (IV),[4] instead of the isomeric pyrazoline V.

When the pyrazoline IV was treated with hydrochloric acid, oxides of nitrogen were liberated, and a product, melting at 265° and having the composition of a triphenylpyrazole, was obtained in quantitative yield. The structure of this pyrazole was established to be 3,4,5-triphenylpyrazole (VI) by its independent synthesis from benzaldesoxybenzoin

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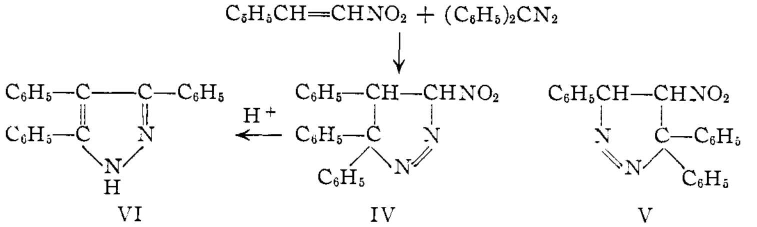
[1] Abstracted from the Ph.D. Thesis of William R. Hasek, University of Minnesota, 1953.

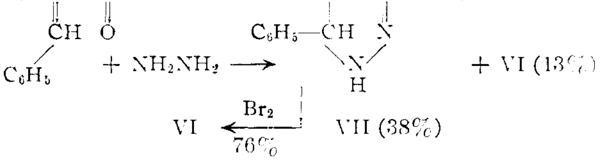
[2] W. E. Parham and J. L. Bleasdale, THIS JOURNAL, **72**, 3843 (1950).

[3] W. E. Parham and J. L. Bleasdale, *ibid.*, **73**, 4664 (1951).

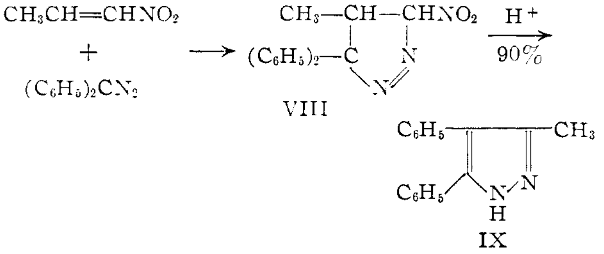
[4] Evidence was presented in the first paper of this series which established the structures of the nitropyrazolines derived from the reaction of nitroölefins with diazomethane and diazoacetic ester. These products were analogous to pyrazolines of type IV. Furthermore, in the great number of cases where a diazo compound has been added to an activated olefin, the direction of addition is again that in which a nitrogen atom of the diazo group becomes attached to the α-carbon of the olefin. The only exception, reported by K. Von Auwers and O. Ungemach, *Ber.*, **66B**, 1205 (1933), is the formation of the two possible adducts from the reaction of ethyl phenylpropiolate with ethyl diazoacetate.



as outlined in the following equations.[5] Isolation of the pyrazole VI (13%) directly from the reaction product obtained from benzaldesoxybenzoin and hydrazine was unexpected. However, analogy is found in the earlier observation that 3,4,5-triphenylisoxazole results directly from the reaction of benzaldesoxybenzoin and hydroxylamine.[6]



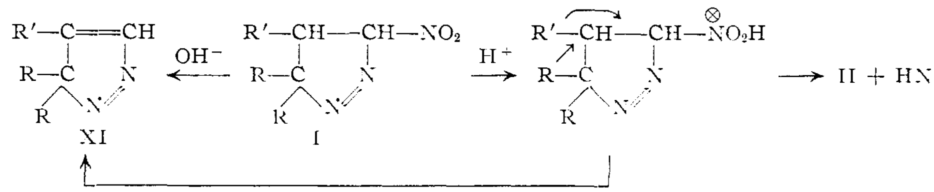
When 1-nitropropene was allowed to react with diphenyldiazomethane at 0°, a crystalline addition product, formulated[4] as 3-nitro-4-methyl-5,5-diphenylpyrazoline (VIII), was obtained in 27% yield.



The action of hydrochloric acid on the nitropyrazoline VIII resulted in the elimination of the elements of nitrous acid, and the formation, in 90% yield, of a pyrazole which subsequently was proved to be 3-methyl-4,5-diphenylpyrazole (IX). The structure of IX was established by its oxidation (54% yield) to the known 4,5-diphenylpyrazole-3-carboxylic acid (X) and conversion of the latter by decarboxylation, into 3,4-diphenylpyrazole (100% yield). The acid X was identical to a sample prepared according to the method previously reported by Borsche and Hahn.[7]

The results of these experiments clearly establish that the elimination of nitrous acid from nitropyrazolines of type I is accompanied by the migration of groups, resulting in the formation of pyrazoles of type II. This acid-catalyzed reaction can be regarded as a concerted twofold rearrangement[8,9] of the Wagner–Meerwein type.

One might expect pyrazolenines XI to result by action of acid or alkali upon I. It appears, however, that if such pyrazolenines are formed they rearrange spontaneously, for VI was obtained in 80% yield by action of alkali upon IV. It is of interest to note that the reaction[10] of ethyl 3,3,4-triphenylpyrazolenine-5-carboxylate with acid or alkali leads to the formation of 3,4,5-triphenylpyrazole.



That aryl groups are not required for these reactions was shown by the conversion of 1-nitropropene and dimethyldiazomethane into 3,4,5-trimethylpyrazole (10.5% over-all yield, I → II, R = R′ = CH_3).

Experimental

Reaction of ω-Nitrostyrene with Diphenyldiazomethane.—A mixture of diphenyldiazomethane (3.50 g., 0.18 mole) and ω-nitrostyrene was allowed to stand at room temperature for 48 hours without solvent. The reaction mixture changed in appearance from a deep red oil to an orange-yellow solid. The solid was recrystallized from ethanol to give 2.56 g. (41% yield) of 3-nitro-4,5,5-triphenylpyrazoline (IV, white needles melting at 138–139° dec.).

Anal. Calcd. for $C_{21}H_{17}O_2N_3$: C, 73.45; H, 4.99; N, 12.24. Found: C, 73.65; H, 4.94; N, 12.19.

Conversion of 3-Nitro-4,5,5-triphenylpyrazoline (IV) into 3,4,5-Triphenylpyrazole (VI). **a.**—Concentrated hydrochloric acid (1.0 ml.) was added to a solution of IV (0.95 g., 0.0028 mole) in 50 ml. of warm ethanol. Oxides of nitrogen were liberated at once (starch–iodide test of vapors). The mixture was heated on a steam-bath for 20 minutes (until a negative starch–iodide test was obtained), neutralized with concentrated sodium hydroxide, and filtered while hot to remove precipitated sodium chloride. The filtrate was cooled and 0.71 g. of feathery white needles (m.p. 265°) were collected. The mother liquor was poured into 150 ml. of water and an additional 0.11 g. of product (m.p. 255–260°) was obtained. The combined solids were recrystallized from ethanol to give 0.82 g. (100% yield) of VI melting at 265°.

Anal. Calcd. for $C_{12}H_{16}N_2$: C, 85.10; H, 5.44; N, 9.46. Found: C, 85.10; H, 5.37; N, 9.67.

b.—A solution of IV (0.13 g., 0.00038 mole), potassium hydroxide (0.05 g., 0.00089 mole) in warm ethanol (10 ml.) was heated on a steam-bath for 15 minutes. The precipitate that was obtained when the reaction mixture was cooled, weighed 0.09 g. (80% yield) and melted at 264°. A mixed m.p. with the product obtained in (a) was 264°.

Proof of Structure of VI. a. 3,4,5-Triphenylpyrazoline (VII).—Anhydrous hydrazine (2.5 ml., 0.078 mole) was added to a solution of benzaldesoxybenzoin[11] (1.75 g., 0.00617 mole, m.p. 100–101°) in warm absolute ethanol (35 ml.). The solution was heated under reflux for six hours. The

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[5] 3,4,5-Triphenylpyrazole had previously been reported by (a) E. Fctors, *Chem. Zentr.*, **I**, 914 (1924), and (b) J. van Alphen, *Rec. trav. chim.*, **62**, 491 (1943); however, their methods of synthesis were not unambiguous and there was a wide discrepancy in the reported melting points (229–230°, and 265°, respectively).

[6] *Cf.* E. P. Kohler and G. K. Barrett, This Journal, **46**, 2110 (1924).

[7] W. Borsche and H. Hahn, *Ann.*, **537**, 236 (1939).

[8] *Cf.* ref. 3 for a discussion of mechanisms for the acid- and base-catalyzed conversions of nitropyrazolines, by loss of the elements of nitrous acid, into pyrazoles.

[9] The possibility of a single rearrangement from an abnormally oriented pyrazoline has not, as yet, been excluded.

[10] J. van Alphen, *Rec. trav. chim.*, **62**, 485 (1943).

[11] E. Knoevenagel and A. Weissgerber, *Ber.*, **26**, 442 (1893).

precipitate (1.04 g.), obtained when the reaction mixture was cooled, was treated with 5 ml. of warm ethanol to dissolve the more soluble component. The filtrate was cooled and 0.70 g. (38%) of 3,4,5-triphenylpyrazoline (VII) was collected. The pyrazoline, m.p. 101–104° from ethanol, was unstable and turned brown when exposed to air.

Anal. Calcd. for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.06; H, 6.01; N, 8.62.

The solid which did not dissolve when the original reaction product was treated with ethanol melted at 160–167°, solidified, and remelted at 250–260°. This material melted at 264–265° after one crystallization from ethanol and proved to be 3,4,5-triphenylpyrazole (m.p. and mixed m.p. 264–265°).

b. **Conversion of VII to VI.**—Bromine was added dropwise to 3,4,5-triphenylpyrazoline (0.101 g., 0.000339 mole) in carbon tetrachloride (3 ml.) until the color of bromine persisted. The mixture was heated on a steam-bath for several minutes and then the bromine and solvent were allowed to evaporate. The residue was recrystallized from ethanol to give 3,4,5-triphenylpyrazole (0.076 g., 76% yield, m.p. 265°). A mixed melting point of this product with a sample of VI obtained from IV was 265°.

Reaction of 1-Nitropropene with Diphenyldiazomethane.—A solution containing 1-nitropropene[12] (8.25 g., 0.0948 mole, b.p. 45–47° (15 mm.), $n^{25.5}\text{D}$ 1.4503), diphenyldiazomethane (18.4 g., 0.0948 mole) and petroleum ether (105 ml., b.p. 30–60°) was allowed to stand in a refrigerator. The precipitate that formed (7.2 g. after five days, 7.9 g. or 27% after five weeks) melted at 133–137° dec. 3-Nitro-4-methyl-5,5-diphenylpyrazoline (VIII) melted at 140–141° dec. (recrystallization from ethanol).

Anal. Calcd. for $C_{16}H_{15}O_2N_3$: C, 68.31; H, 5.38; N, 14.94. Found: C, 68.30; H, 5.31; N, 15.03.

Conversion of 3-Nitro-4-methyl-5,5-diphenylpyrazoline (VIII) into 3-Methyl-4,5-diphenylpyrazole (IX).—The procedure used was essentially that described for the conversion of IV to VI. A two-hour heating period was necessary for the elimination of oxides of nitrogen. From 3.22 g. (0.0114 mole) of VIII, 26 ml. of ethanol and 2 ml. of concentrated hydrochloric acid there was obtained 2.41 g. (90% yield) of product melting at 176–180°. The melting point of the product was raised to 183–184° by crystallization from ethanol; 185–186° by sublimation.

Anal. Calcd. for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.75; H, 6.13; N, 12.02.

Oxidation of IX to 4,5-Diphenylpyrazole-3-carboxylic Acid.—A mixture of IX (0.37 g., 0.016 mole), potassium permanganate (0.50 g., 0.032 mole), water (5 ml.) and *t*-butyl alcohol[13] (6 ml.) was heated on a steam-bath until the permanganate was consumed (about three hours). The manganese dioxide was removed by filtration and most of the alcohol was removed by distillation. The mixture was cooled and unchanged starting material (0.14 g.) was removed by filtration. The filtrate was acidified and the crude acid (0.14 g., m.p. 267–268°, 54% based on pyrazole consumed) was collected. The acid melted at 271° after recrystallization from methanol–water. This acid caused no depression in melting point when admixed with a sample of 4,5-diphenylpyrazole-3-carboxylic acid (m.p. 269°) prepared by the method previously reported by Borsche and Hahn.[7]

4,5-Diphenylpyrazole.—Samples of 4,5-diphenylpyrazole-3-carboxylic acid (100 mg.), prepared either from IX or from desylglyoxylic ester[7] were heated at 280° for several minutes in an atmosphere of nitrogen. The product (100% yield) was then sublimed at 150° (1 mm.) to give 80 mg. (96% yield) of 4,5-diphenylpyrazole melting at 155° (reported[14] m.p. 155°).

Reaction of Dimethyldiazomethane with 1-Nitropropene.—Dimethyldiazomethane, contaminated with some xylene and water, was prepared by modifications of the procedures previously described by Staudinger and Gaule[15] and Guha and Sankaran.[16] The red oil containing dimethyldiazomethane was dissolved in 10 ml. of cold ether and 1-nitropropene was added dropwise to the solution. The color of the diazo compound was rapidly discharged, and when the solution changed from pale red to pale yellow, addition of nitroölefin was terminated. In one run a total of 1.22 g. (0.014 mole) of 1-nitropropene was required, indicating that there was 0.98 g. (0.014 mole) of dimethyldiazomethane present. The ether was removed by distillation and the residual oil was treated with 1.00 ml. of concentrated hydrochloric acid. An immediate evolution of oxides of nitrogen was observed. The solution was warmed on a steam-bath for one-half hour and then the cold reaction mixture was extracted with small portions of ether. The aqueous solution was made alkaline with sodium hydroxide and then allowed to stand at 0° for 12 hours. The long white needles that formed (0.16 g., 10.5% based on nitroölefin employed) melted at 133–137°, 137–138° after recrystallization from water. The picrate of this product melted at 237–239°. 3,4,5-Trimethylpyrazole is reported to melt at 137–138°.[17] The picrate of 3,4,5-trimethylpyrazole is reported to melt at 237–239°.[17]

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[12] E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928).

[13] When *t*-butyl alcohol was omitted the acid was not obtained even though all of the permanganate was consumed.

[14] W. Wislicenus and A. Ruthing, *Ann.*, **379**, 256 (1911).

[15] H. Staudinger and A. Gaule, *Ber.*, **49**, 1904 (1916).

[16] P. C. Guha and D. K. Sankaran, *ibid.*, **70**, 1689 (1937).

[17] L. Knorr and B. Oettinger, *Ann.*, **279**, 247 (1894).

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE WHITMORE LABORATORY, THE PENNSYLVANIA STATE COLLEGE]

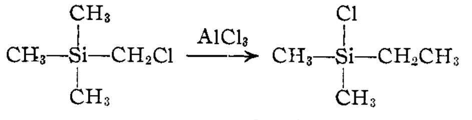
New Intramolecular Rearrangements of α-Chloroalkylsilicon Compounds[1,2]

BY LEO H. SOMMER, DONALD L. BAILEY, JACK R. GOULD AND FRANK C. WHITMORE[3]

RECEIVED APRIL 18, 1953

Three new examples of the intramolecular rearrangement of alkyl from silicon to carbon have been found, thereby demonstrating the generality of this phenomenon for organosilicon compounds.

In continuation of previous work which demonstrated, for the first time, the phenomenon of intramolecular rearrangement of alkyl from silicon to carbon in a change analogous to the Wagner–Meerwein rearrangements so common in organic chemistry[4]



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}-CH_2Cl \xrightarrow{AlCl_3} CH_3-\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{Si}}-CH_2CH_3 \quad (1)$$

the present paper reports further examples of the intramolecular rearrangement of α-chloroalkylsilicon compounds with aluminum chloride.

The products obtained from the reaction of aluminum chloride with α-chloroethyltrimethylsilane (R = Me) and α-chloroethyltriethylsilane (R = Et) are indicated by equation 2.

In 2a rearrangements entirely analogous to 1 have occurred. In 2b the presence of carbon and

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[1] Paper 37 in a series on organosilicon chemistry; for paper 36 see P. D. George, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **75**, 6308 (1953).

[2] Presented in part before the Division of Organic Chemistry at the 113th Meeting of the American Chemical Society in Chicago, April 22, 1948.

[3] Deceased.

[4] F. C. Whitmore, L. H. Sommer and J. Gould, THIS JOURNAL, **69**, 1976 (1947).