gave 2.4 g. (0.0085 mole, 25% yield) of triphenylphosphine oxide, m.p. 157–158°. Thus, the insoluble oil was triphenylphosphine dichloride.

The total yield of triphenylphosphine oxide was 94%.

Reaction of Triphenylphosphine Oxide with Thionyl Chloride.—Thionyl chloride (0.07 mole) was added dropwise to a stirred solution of triphenylphosphine oxide (0.036 mole). The mixture was heated at reflux for 1 hr. As the mixture reached its boiling point, a rapid evolution of gas ensued, lasting about 0.5 hr. The reaction mixture, which had separated into two layers, was vacuum stripped at 120° (0.1 mm.). The residual oil was washed with four 50-ml. portions of benzene, two 50-ml. portions of ether, hydrolyzed with hot water, and titrated with standard base (0.067 mole to phenolphthalein end point). On the basis of this result, it was concluded that the oil contained 0.0335 mole (93% yield) of triphenylphosphine dichloride.

The Cycloaddition of Potassium Diazomethanedisulfonate to Activated Olefins

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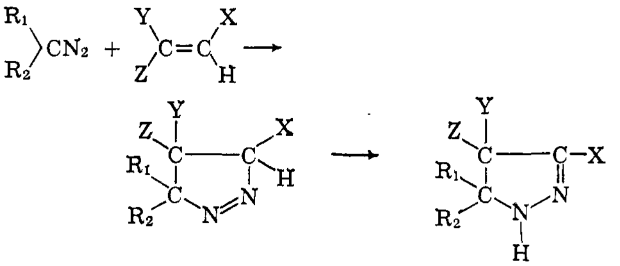
Received May 23, 1963

Potassium diazomethanedisulfonate in aqueous solution reacts with a variety of activated olefins to form 1:1 addition products for which the structure of disulfonated pyrazoline derivatives is proposed. Treatment with acid or base converts these products into monosulfonated pyrazole derivatives, which are readily N-alkylated.

Potassium diazomethanedisulfonate, $(KO_3S)_2CN_2$, was first prepared in 1895 by von Pechmann[1] who also studied some decomposition and addition reactions of this unusually stable diazo compound.[1,2] After von Pechmann's early work the compound apparently received little attention, since, aside from occasional mention in review articles,[3] only a few papers[4] appeared describing some of its reactions and physical properties. This is in striking contrast to other diazoalkanes which have been under continued extensive study ever since their discovery.

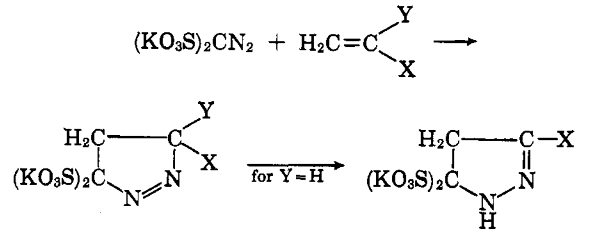
The addition of diazoalkanes to olefins with formation of pyrazolines is well known in the literature.[5] The reaction first yields Δ^1-pyrazolines, which readily rearrange to Δ^2-pyrazolines if a hydrogen substituent is present in the 3-position.



We have found that potassium diazomethanedisulfonate reacts readily with a variety of activated olefins to give disulfonated pyrazoline derivatives in a manner entirely analogous to other diazoalkanes such as diazomethane or diazoacetates. Because of the insolubility of potassium diazomethanedisulfonate in organic solvents, these reactions are most conveniently carried out in aqueous solution and, therefore, the olefinic reaction partner should have at least a moderate solubility in water. This requirement somewhat limits the applicability of this synthetic route. The solubility of the olefins and thereby the ease of reaction can be improved to some extent, however, by the addition of small quantities of methanol or other mutual solvents to the aqueous solution of the diazo compound.

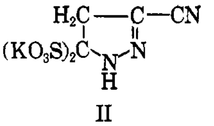
When activated olefins such as acrylonitrile, methacrylonitrile, methyl vinyl ketone, or ethyl acrylate, are added to an aqueous solution of potassium diazomethanedisulfonate, an exothermic reaction occurs and the yellow color of the diazo compound disappears more or less rapidly without evolution of nitrogen.

The reaction products can be precipitated with an excess of methanol and recrystallized from water. The elemental analyses of these products correspond to those of 1:1 adducts of potassium diazomethanedisulfonate and the respective olefins. These products are formulated as disulfonated pyrazolines in analogy with the structures of the adducts of such olefins with other diazoalkanes.



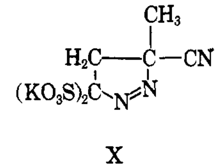
The infrared spectra of these adducts show that the functional groups X are preserved during the addition reaction.

Support for the proposed cyclic structure of these compounds is obtained from a comparison of the infrared and ultraviolet spectra of the addition products from acrylonitrile and methacrylonitrile. The proposed structures for these two products are as follows.



II

and



X

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(1) H. v. Pechmann and P. Mank, *Ber.*, **28**, 2374 (1895).

(2) H. v. Pechmann, *ibid.*, **29**, 2161 (1896).

(3) *E.g.*, R. Huisgen, *Angew. Chem.*, **65**, 439 (1955).

(4) H. J. Backer, *Rec. trav. chim.*, **48**, 619 (1929); A. Hantsch and J. Lifschitz, *Ber.*, **45**, 3023 (1912); F. Nesh, *J. Phys. Chem.*, **62**, 566 (1958); A. O. Rogers and M. A. Stevens (to Du Pont), U. S. Patent 2,825,747 (March 4, 1958).

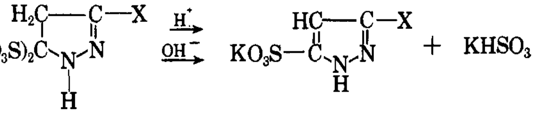
(5) Summary in R. C. Elderfield, "Heterocyclic Chemistry," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957; H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

Compound X cannot rearrange to a Δ^2-pyrazoline since it has a blocking CH_3 group in the 3-position. It shows a rather weak CN peak at 2248 cm.$^{-1}$ (isolated nitrile group). Compound II absorbs at 2229 with markedly higher intensity which indicates the presence of a conjugated nitrile group, while the presence of a N–H group is evident from a band at 3330 cm.$^{-1}$ which is absent in the infrared spectrum of compound X. In the ultraviolet compound X in aqueous solution absorbs at 3250 Å., ϵ_{max} 50 in contrast to compound II with absorption at 2850 Å., ϵ_{max} 10,000. This high absorptivity clearly indicates the presence of conjugated multiple bonds in compound II in agreement with the proposed structure. A similarly high absorptivity was reported recently[6] for 3-carbethoxy-Δ^2-pyrazoline, while the nonconjugated 5-carbethoxy-Δ^2-pyrazoline absorbed with markedly lower intensity.

The addition of potassium diazomethanedisulfonate is distinctly slower with methacrylonitrile than with acrylonitrile, which is in accord with the retarding effect of an α-CH_3 group recently reported[7] for the addition of diphenyldiazomethane to acrylic and methacrylic esters.

With suitably activated dienes double addition of potassium diazomethanedisulfonate can occur; see Table (I). This has been demonstrated in the case of divinyl sulfone which yields a tetrasulfonated bis-(pyrazoline) sulfone.

The disulfonated Δ^2-pyrazolines readily lose the elements of $KHSO_3$ upon treatment with either acid or base with the formation of pyrazole monosulfonates



Depending on the reaction conditions the substituent X may also be altered during the conversion of these pyrazolines to pyrazoles. Thus, nitrile and carbethoxy substituents are hydrolyzed to carboxyl groups under acid treatment, while a nitrile substituent is preserved under basic conditions, and an acetyl substituent remains unchanged in both acid and base treatment.

The pyrazole monosulfonates are generally less soluble in water than the corresponding pyrazoline disulfonates. They are very soluble, however, in potassium hydroxide solutions with a distinct lowering of the pH of the originally strongly basic solution, which suggests that the N–H group in these pyrazoles is acidic enough to form alkali salts under these conditions.

The pyrazole monosulfonates are readily N-alkylated, *e.g.*, with dimethyl sulfate in alkaline solution. N-Alkylation is demonstrated by the disappearance of the N–H band in the infrared spectrum.

Experimental

Potassium diazomethanedisulfonate (I) was prepared according to von Pechmann's procedure[1] from potassium nitrite and monopotassium aminomethanedisulfonate, which in turn was prepared by the method of Bannard and Ross.[8]

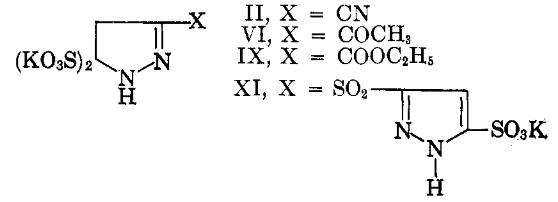
Addition of Potassium Diazomethanedisulfonate to Activated Olefins. 3-Cyano-Δ^2-pyrazoline-5,5-disulfonic Acid, Dipotassium Salt (II).—To a stirred solution of 10 g. (0.034 mole) of I in 30 ml. of distilled water at 25° was added 5 ml. (0.076 mole) of acrylonitrile. An exothermic reaction set in immediately and after 5 min. the yellow color of the diazo compound had disappeared with the formation of white crystals. After 30 min., 200 ml. of methanol was added and the precipitate filtered and dried (10.8 g., 96%). Recrystallization from 30 ml. of water gave 8.68 g. (77%) of white needles; m.p. >300°, crystals turned brown >220°.

Anal. Calcd. for $C_4H_3N_3O_6S_2K_2$: C, 14.50; H, 0.91; N, 12.68; S, 19.35. Found: C, 14.6; H, 1.2; N, 12.4; S, 19.0.

The infrared and ultraviolet spectra of this material have been discussed earlier.

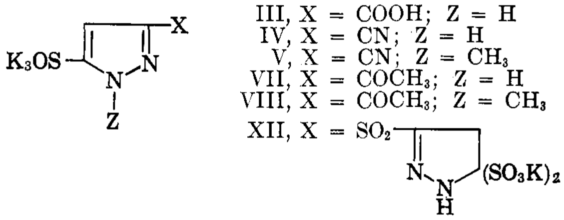
TABLE I

Δ^2-PYRAZOLINE DISULFONATES



II, X = CN
VI, X = $COCH_3$
IX, X = $COOC_2H_5$
XI, X = SO_2—

PYRAZOLE SULFONATES



III, X = COOH; Z = H
IV, X = CN; Z = H
V, X = CN; Z = CH_3
VII, X = $COCH_3$; Z = H
VIII, X = $COCH_3$; Z = CH_3
XII, X = SO_2—

3-Carboxypyrazole-5-sulfonic Acid, Potassium Salt (III).—A solution of 8.68 g. (0.026 mole) of II in 40 ml. of concentrated HCl was heated to 100° for 2.75 hr.; sulfur dioxide was evolved. White crystals separated on cooling; they were collected, dried (7.25 g.), and recrystallized from 20 ml. of water to give 5.6 g. (86%) of white needles, m.p. > 300°. The infrared spectrum indicated hydrolysis of –CN to –COOH (C=O at 1725, –OH at 3200–2300 cm.$^{-1}$, H_2O at 3500 cm.$^{-1}$).

Anal. Calcd. for $C_4H_3N_2O_5SK \cdot H_2O$: C, 19.35; H, 2.03; N, 11.28; S, 12.91. Found: C, 19.5; H, 1.9; N, 11.1; S, 12.7.

Recrystallization of the monohydrate from concentrated HCl gave the anhydrous compound as white crystals, m.p. >300° (C=O at 1725, –OH at 3200–2300 cm.$^{-1}$).

Anal. Calcd. for $C_4H_3N_2O_5SK$: C, 20.87; H, 1.31; N, 12.17; S, 13.92. Found: C, 20.8; H, 1.9; N, 11.8; S, 13.7.

3-Cyanopyrazole-5-sulfonic Acid, Potassium Salt (IV).—To a solution of 3.9 g. (0.07 mole) of KOH in 20 ml. of water was added 10 g. (0.03 mole) of II and the mixture warmed gently until a clear solution was obtained. After 30 min. the solution was neutralized with a slight excess of acetic acid and cooled in ice. The product separated as white crystals, which were collected, dried (6 g.), and recrystallized from 12 ml. of water to give 5.07 g. (79%) of fine white needles, m.p. >300°. The infrared spectrum showed a N–H band (3200), a strong nitrile band (2250), and also traces of a carbonyl impurity (probably amide, 1720, 1645 cm.$^{-1}$) which could not be removed by repeated recrystallization from water.

Anal. Calcd. for $C_4H_2N_3O_3SK$: C, 22.75; H, 0.95; N, 19.90. Found: C, 22.8; H, 1.1; N, 19.6.

3-Cyano-1-methylpyrazole-5-sulfonic Acid, Potassium Salt (V).—To a solution of 0.7 g. (0.0125 mole) of KOH and 2.1 g. (0.01 mole) of IV in 6 ml. of water was added 1 ml. (0.011 mole) of dimethyl sulfate. After the addition of 3 ml. of water the mixture was stirred at room temperature for 1.5 hr., then cooled in ice and the crystals filtered and dried (1.8 g., 80%). Recrystallization from 2 ml. of water gave 1.4 g. (62%) of white crystals, m.p. >300°. The infrared spectrum showed a strong nitrile band (2230 cm.$^{-1}$) and no N–H band, but again traces of a carbonyl impurity not removable by repeated recrystallization.

Anal. Calcd. for $C_5H_4N_3O_3SK$: C, 26.66; H, 1.79; N, 18.65. Found: C, 26.1; H, 2.1; N, 18.8.

3-Acetyl-Δ^2-pyrazoline-5,5-disulfonic Acid, Dipotassium Salt (VI).—To a stirred solution of 15 g. (0.05 mole) of I in 75 ml. of

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(6) D. S. Matteson, *J. Org. Chem.*, **27**, 4293 (1962).

(7) R. Huisgen, *et al.*, *Angew. Chem.*, **73**, 170 (1961).

(8) R. A. B. Bannard and J. H. Ross, *Can. J. Chem.*, **32**, 49 (1954).

water at 25° was added 5 ml. (0.09 mole) of freshly distilled methyl vinyl ketone. After the exothermic reaction had subsided and the solution had become colorless, the product was precipitated with 300 ml. of methanol, filtered, dried (16.5 g., 89%), and recrystallized from 25 ml. of water to give 9.2 g. (50%) of white needles, m.p. >300° with discoloration above 200°. The infrared spectrum indicated the presence of a carbonyl group (1690) and a NH group (3300 cm.$^{-1}$).

Anal. Calcd. for $C_5H_6N_2O_7S_2K_2$: C, 17.23; H, 1.73; N, 8.04; S, 18.40. Found: C, 17.5; H, 1.7; N, 7.6; S, 17.5.

3-Acetylpyrazole-5-sulfonic Acid, Potassium Salt (VII). A.—A solution of 5 g. (0.0136 mole) of VI in 20 ml. of concentrated HCl was heated to 100° for 3.5 hr. (sulfur dioxide evolved), then evaporated to dryness, and the yellow-white residue recrystallized from 9 ml. of water to give 2.45 g. (78%) of slightly tan crystals which upon repeated crystallization from 5 ml. of water gave 1.95 g. (63%) of white crystals, m.p. >300°. The infrared spectrum showed the presence of a carbonyl group (1700) and a NH group (3200 cm.$^{-1}$).

Anal. Calcd. for $C_5H_5N_2O_4SK$: C, 26.30; H, 2.21; N, 12.27; S, 14.04. Found: C, 26.3; H, 2.3; N, 12.1; S, 13.8.

B.—To 0.85 g. (0.015 mole) of KOH in 5 ml. of water was added 5.25 g. (0.0143 mole) of VI, which caused the pH of the mixture to drop to ~8. After the addition of 5 ml. of water, the mixture was warmed until a clear solution was obtained and then cooled in ice. The crystalline deposit was filtered (2.65 g., 81%) and recrystallized from 6 ml. of water to give 2.1 g. (61%) of a white crystalline product, the infrared spectrum of which was identical with that of A.

3-Acetyl-1-methylpyrazole-5-sulfonic Acid, Potassium Salt (VIII).—To a solution of 0.46 g. (0.008 mole) of KOH in 3.5 ml. of water was added 1.42 g. (0.0062 mole) of VII and 0.6 ml. (0.0064 mole) of dimethyl sulfate. The mixture was shaken and cooled, after 30 min. warmed to complete solution, then cooled in ice. A white solid separated which was filtered, dried, (0.55 g., 36%), and recrystallized from 30 ml. of methanol to give 0.38 g. (25%) of white crystals, m.p. >300°. The infrared spectrum showed the carbonyl band (1670 cm.$^{-1}$) and no N–H band .

Anal. Calcd. for $C_6H_7N_2O_4SK$: C, 29.75; H, 2.91; N, 11.55. Found: C, 30.0; H, 2.6; N, 11.4.

3-Carbethoxy-Δ^2-pyrazoline-5,5-disulfonic Acid, Dipotassium Salt (IX).—To a stirred solution of 5 g. (0.017 mole) of I in 40 ml. of water at 25° was added 15 ml. of methanol (to increase the solubility of the olefin) and 2.5 ml. (0.027 mole) of ethyl acrylate. The mixture was colorless after 1.25 hr. and the product was precipitated with 300 ml. of methanol, filtered, and dried to give 5.9 g. (92%) of white powder. This material could not be recrystallized because of its extremely high solubility in water. Its infrared spectrum had absorption bands for ester carbonyl (1710 cm.$^{-1}$) and sulfonate groups. Further evidence for structure IX was obtained from acid treatment of the crude adduct.

Two grams (0.0053 mole) in 10 ml. of concentrated HCl was heated to 100° for 2 hr., then cooled and the resulting solid (1.18 g.) recrystallized from 3.5 ml. of water to give 0.75 g. (61%) of white needles, which were identical with compound (III) by comparison of the infrared spectra.

3-Cyano-3-methyl-Δ^1-pyrazoline-5,5-disulfonic Acid, Dipotassium Salt (X).—To a solution of 15 g. (0.05 mole) of I in 100 ml. of water was added 35 ml. of methanol (to increase solubility of the olefin) and then 5 ml. (0.087 mole) of methacrylonitrile. After 6 hr. stirring of the mixture at room temperature the yellow color of the diazo compound had disappeared and an almost white precipitate formed. After the addition of 350 ml. of methanol the precipitate was filtered, dried (18.4 g.), and recrystallized from water to give 15.8 g. (86%) of fine white needles m.p. >300°. The infrared and ultraviolet spectra of this product have been discussed earlier.

Anal. Calcd. for $C_5H_5N_3O_6S_2K_2 \cdot H_2O$: C, 16.53; H, 1.99; N, 11.56; S, 17.64. Found: C, 16.5; H, 1.8; N, 11.4; S, 17.4.

Bis(Δ^2-pyrazoline-3)-sulfone-5,5,5′,5′-tetrasulfonic Acid, Tetrapotassium Salt (XI).—To a stirred solution of 2.94 g. (0.01 mole) of I in 25 ml. of water at 25° was added 0.6 g. (0.005 mole) of divinyl sulfone. After 1.75 hr., the yellow color of the diazo compound had disappeared with the formation of white crystals. The product was precipitated with 225 ml. of methanol, filtered, dried (3.43 g., 96%), and recrystallized from water to give 2.9 g. (81%) of white crystals, dec. point 200–205°. The infrared spectrum showed the presence of N–H groups (3300 cm.$^{-1}$).

Anal. Calcd. for $C_6H_6N_4O_{14}S_5K_4 \cdot 2H_2O$: C, 10.13; H, 1.42; N, 7.88. Found: C, 10.3; H, 1.6; N, 7.7.

Bis(pyrazole-3-)sulfone-5,5′-disulfonic Acid, Dipotassium Salt (XII).—A mixture of 1.5 g. (0.0022 mole) of XI and 10 ml. of concentrated HCl was heated to 100° for 3.5 hr.; sulfur dioxide was evolved. White crystals separated upon cooling; they were collected, dried (0.97 g.), and recrystallized from water to give 0.63 g. (64%) of white product, m.p. >300°. The infrared spectrum showed the presence of N–H groups (3150 cm.$^{-1}$).

Anal. Calcd. for $C_6H_4N_4S_3O_8K_2 \cdot 2H_2O$: C, 15.32; H, 1.71; N, 11.92. Found: C, 15.9; H, 1.6; N, 11.7.

Configurational Stabilities in Cyclic Systems. I

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Received February 19, 1963

Base-induced equilibration of a series of methyl esters of some cyclic 1,2-dicarboxylic acids has been carried out. The relative order of stability of the configurational isomers in each system has been determined and a discussion of conformational and configurational factors in three-, four-, five-, and six-membered ring systems is presented.

Although the stereochemical science of cyclohexyl systems has been highly developed, relatively little is known about the smaller carbocyclic ring systems. The present work was undertaken in an effort to examine conformational and configurational factors in the three- to five-membered ring systems and derivatives thereof.

As a relatively simple beginning, we have undertaken a study of the equilibration of *cis* and *trans* isomers of suitably substituted systems in order to ascertain substituent interactions and the effect of the ring structure and geometry on the relative stability of configurational isomers. Similar investigations[1–3] have proved to be of significant value in the determination of stereochemical factors in other systems.

The present work is a study of relative stabilities of cyclic 1,2-dicarboxylic acid esters of the cyclopropane, cyclobutane, cyclopentane, and cyclohexane ring systems.

The pure *cis*- and *trans*-dimethyl esters of the several cyclic dicarboxylic acids were prepared by conventional means and were subjected to equilibration with sodium methoxide. Equilibrium was approached from both the *cis* and the *trans* side in each case. The composition of the equilibrium mixtures were determined by v.p.c.

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[1] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[2] D. Y. Curtin, H. Gruen, Y. G. Hendrickson, and H. E. Knipmeyer; *J. Am. Chem. Soc.*, **83**, 4838 (1961).

[3] N. L. Allinger and R. J. Curby, *J. Org. Chem.*, **26**, 933 (1961).