

Short Communications

Pakistan J. Sci. Ind. Res., Vol. 18, Nos. 1-2, Feb-April 1975

REACTIONS OF DIAZENES

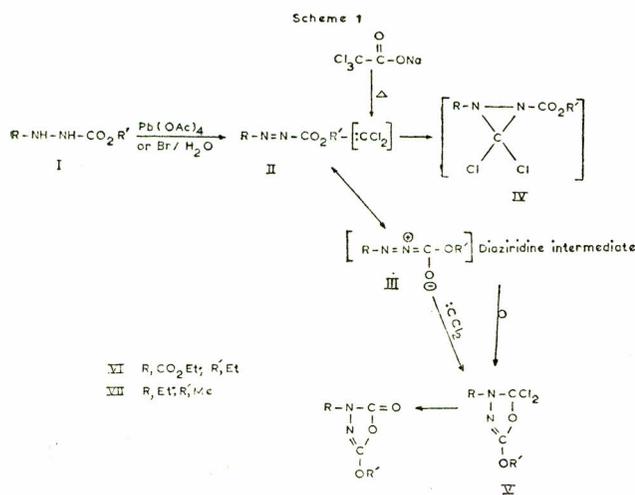
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(Received September 20, 1974; revised November 19, 1974)

The products of the reaction of carbenes with diazo compounds have previously been assigned a diaziridine structure. Later their structure was modified in view of the new evidence becoming available.

As a simple variant of this, the reaction of dichlorocarbene with suitable diazenes led to the characterization of 1,3,4-oxadiazolin-5-ones one of the major products. The later heterocyclic ring system is known to exhibit important pharmacological and therapeutic properties.^{4,7} So far its synthesis has been limited to the reaction of alkyl isocyanates with alkoxy carbonyl nitrenes,^{5,7} or the reaction of alkyl carbazates with carbonyl chloride,^{1,2} or cyclization of *N*-alkyl-*N*-carbalkoxy substituted ureas in the presence of strong mineral acids.³ Nevertheless, difficulties do come across when one desires to obtain a specific derivative of the aforesaid ring system with special substituents which cannot stand the drastic reaction conditions involved in the strong mineral acid catalysis³ or the effect of UV light in the photolytic process etc.⁷ Dichlorocarbene was generated by thermolysis of sodium trichloroacetate⁸ in peroxide free dioxane. The reaction sequence is shown in scheme 1.



The reaction may proceed via a 1,1-cycloaddition of the carbene to the diazene. The 1,1-dipolar character of carbenes⁹ and the nitrenes^{5,6} has been clearly manifested in their various addition reactions.

The driving force for the isomerization to the thermodynamically more stable 5-membered heterocycle may be provided by release of ring strain. One may also envisage a direct formation of V, by the addition of the carbene to the resonance from III. We at this stage cannot decide in favour of either of the above stated, or other possibilities. More work needs to be done to learn about the mechanism of its formation. This, however, does not in any way minimize the utility and scope of this reaction.

Characterization of VI is based on its hydrolysis with quantitative amount of 0.5N NaOH to diethylhydrazodiformate, which was identified by its identical IR, R_f value on TLC, and the mixed melting point with authentic material, and its ethanolic hydrolysis with sodium ethoxide to tricarbethoxyhydrazine.⁶ Compound VII was simply identified by its hydrolysis to methyl-3-ethylcarbazate, and its identical R_f value with the known material. The overall yields of 1,3,4-oxadiazolin-5-ones varied from 14% (for compound VII) to 18% (for compound VI).

Experimental

All mps. were taken in sulphuric acid bath, and are uncorrected. The IR spectra were recorded on a Perkin-Elmer model 137 infracord spectrophotometer (thin film/KBr pellet).

Preparation of Diethylazodicarboxylate (DAD). It was obtained by $\text{Br}_2/\text{H}_2\text{O}$ oxidation¹⁰ of the corresponding hydrazoester as given in the literature.

Preparation of Lead Tetraacetate. Red lead oxide (Pb_3O_4) is converted to $\text{Pb}(\text{OAc})_4$ by the method essentially described in the literature,^{11a} reduced to 1/15th of the original scale to suit our requirements.

Preparation of Sodium Trichloroacetate. The method given in literature^{11b} was used for its preparation.

Preparation of *N*-Ethyl-*N'*-carbomethoxydiazene (II). It is prepared by the lead tetraacetate oxidation of methyl-3-ethylcarbazate.

Preparation of Methylcarbazate. To an ice-cold solution of 23.1 g (250 mmole) of diethyl carbonate in 15 ml methanol was added dropwise a methanol solution of 56.2 ml (270 mmoles) of hydrazine hydrate (24%) in a R.B. flask fitted with a condenser and a drying tube. The reaction mixture was stirred by a magnetic stirrer for 1/2 hr with cooling in ice/water, then it was allowed to stand for 1/2 hr during which time a white solid crystallized out. Recrystallization from MeOH gave 19 g (84.5%) needles, m. p. 68°C (lit¹² m. p. 73°C).

Preparation of Methyl-3-ethylcarbazate (I). A solution of 32.8 g (210 mmoles) ethyl iodide in 55 ml MeOH was added dropwise with cooling at a very slow rate to a concd. solution of 19 g (210 mmoles) of methylcarbazate in 15 ml MeOH. At the end of addition the solvent was removed which gave a syrupy white liquid. TLC with $\text{CHCl}_3 : \text{MeOH} :: 98 : 2$ eluent showed two products. To the syrupy liquid about 20-25 ml dry petroleum ether (b.p. 65-86°C) was added and it was allowed to remain in the freezing chamber of refrigerator overnight.

White crystals were obtained which were filtered and washed with petroleum ether. The melting point (117°C) of the white crystalline solid and IR spectrum agreed with that of the known material.⁷

Lead Tetraacetate Oxidation.¹⁴ A solution of 5.9 g (50 mmole) methyl-3-ethyl-carbazate in 10 ml CHCl₃ was stirred with 24.4 g (55 mmoles, 10% excess) Pb(OAc)₄ in 125 ml chloroform. The reaction mixture was heated on a water-bath for 20 min. After filtration it was washed twice with 15 ml portions of 0.5N HCl, and twice with 15-ml portions of water, followed by washing with 15-ml portions of 2.5% NaHCO₃ solution and later twice with 15-ml portions of water. After drying the organic layer, the solvent was removed on rotary evaporator. An orange coloured liquid b.p. 52–54°C/20 mm Hg, was obtained. Usually undistilled material was used for routine work.

Reaction of N-ethyl-N'-carbomethoxydiazene with Sodium Trichloroacetate. To a solution of 2.6 g (22.4 mmoles) of the said diazene (II) in 40 ml peroxide free dioxane was added 5.06 g (22.4 mmoles) sodium trichloroacetate. The reaction mixture was refluxed in a R.B. flask, fitted with a condenser and a drying tube for 24–36 hr. At the end of this period it was transferred to a beaker of water. After filtration, water layer was extracted three times with 15-ml portions of CHCl₃. After drying the CHCl₃ layer with Na₂SO₄(an) chloroform and dioxane was distilled off under reduced pressure. A very highly viscous material was left in the distilling flask. Efforts to initiate crystallization in this syrupy liquid failed. TLC with CHCl₃:MeOH::97:3 eluent showed four spots. From this methyl-3-ethylcarbazate was characterized on the basis of same R_f (0.9) as that of the control run. This probably is obtained by the reaction of diazene with water. TLC in acetone nitromethane benzene::1:3:10 eluent, showed five spots in all. Two of which were assigned to methyl-3-ethylcarbazate (R_f 0.8), and 4-ethyl-2-methoxy-1,3,4-oxadiazolin-5-one (VII) (R_f 0.28) by the identical R_f value with those of control runs of known materials.⁷

The later compound was collected by thick layer chromatography, and subjected to hydrolysis with quantitative amount (25 ml 0.5N NaOH solution), refluxed for 7½ hr. It was extracted with CHCl₃ after cooling and neutralization to pH 7.0 with 10% HCl. Work up of organic layer gave white solid, m. p. 117°C. IR is also identical to independently synthesized material (I).

Reaction of DAD with Sodium Trichloroacetate. 4.0 g (23 mmoles) of DAD was treated with 8.44 g (45 mmoles) of Na₂OCCl₃. The reactions conditions employed and the work up procedure was exactly the same as described above. TLC of the crude product in the eluent (CHCl₃:MeOH::97:3) led to the characterization of diethylhydrazoformate (R_f 0.82) compared with control run. A compound (VI), with R_f 0.36 was collected by thick layer chromatography. Ethanolysis of this product with NaOEt/EtOH gave a liquid, tricarbethoxyhydrazine, identified by the comparison of its boiling point with the known⁶ material b.p. 203°C/20 mm Hg, lit b.p. 184–86°C/9mm Hg.

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DETERMINATION OF THE PARTICLE SIZE AND SPECIFIC SURFACE OF CRYSTALLINE LEAD MONOXIDE

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(Received September 28, 1973; revised November 6, 1974)

The most outstanding property of finely divided substances is the large surface to mass ratio which they possess. Particle size, therefore, has a direct bearing on the properties of a material.

To standardize the results obtained with a certain substance it is very essential that the sample should be a representative one. A representative sample

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could be achieved by having a specific particle size range with a known specific surface. Recently it has been of interest to investigate the effect of particle size on the kinetics of reduction. For this work lead monoxide was chosen as a representative material.

Experimental

Lead monoxide was melted in a recrystallized alumina crucible placed in a muffle furnace, maintained at 925–950°C. The molten mass was poured into a stainless-steel tray sprinkled with amorphous powder of lead monoxide in order to avoid the contamination with the metal surface. The amorphous powder sticking to the crystalline lumps of lead monoxide was removed by washing and the crystalline mass dried in an oven at 110°C. Wet grinding was carried out in a rod-mill on the crystalline lead monoxide. The ground material was sieved wet to get the sample of $-75 + 45 \mu$ size. Particle size measurements were carried out by using the Vicker's projection microscope with a magnification of 400. The specific surface of the powder was determined by using the gas permeability method. The apparatus as described by Lea and Nurse¹ was used for the determination of the specific surface.

Result and Discussion

The particle size distribution as determined microscopically has been shown in Fig. 1. The determination of each particle size-range was carried out in triplicate. The sample prepared by sieve analysis for the size range of $-75 + 45 \mu$ shows close agreement with the microscopic results as 73% of the particles fall in the range of $-90 + 40 \mu$. The specific surface calculated by air permeability was found to be 1477 cm²/g.

Initial steps for getting the material to the specific size range are very important and would vary from material to material. Thus in the case of PbO dry grinding and dry sieving could not work. The method proved unsatisfactory due to the tendency of the mill to overgrind and the sieves to blind, resulting in poor recovery of material of the desired

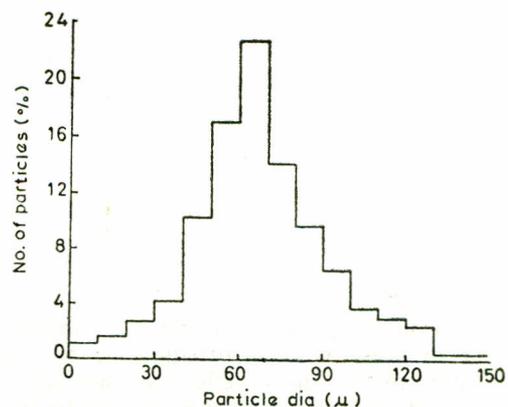


Fig. 1. Particle size distribution of the bulk sample of the lead monoxide.

size. Consequently the material was prepared by wet milling and sieving.

Since the determination of dimensions involves the counting of a large number of particles, diameters are commonly measured by optical methods or sieving. Several definitions of the diameter are based on the assumption that one can estimate the length, breadth and thickness of the particle². Martin's diameter³ were used as a measure of the particle size in the present studies and the average is a representative size-range.

Acknowledgement. The author is grateful to Mr. F.A. Garner, Lecturer, Department of Minerals Engineering, University of Birmingham, for his fruitful discussions and suggestions.

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