The Syntheses and the Reactions of 9-Anthryldiazomethane and α-Naphthyldiazomethane

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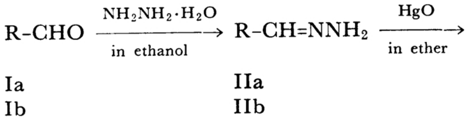
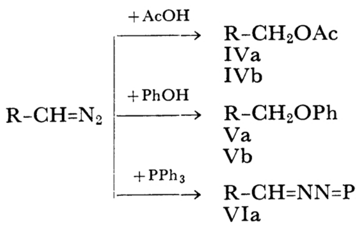
The present paper will describe the syntheses and the reactions of 9-anthryldiazomethane and α-naphthyldiazomethane. The reaction sequence is as follows:



$$\underset{\text{Ia, Ib}}{\text{R-CHO}} \xrightarrow[\text{in ethanol}]{\text{NH}_2\text{NH}_2\cdot\text{H}_2\text{O}} \underset{\text{IIa, IIb}}{\text{R-CH=NNH}_2} \xrightarrow[\text{in ether}]{\text{HgO}}$$

a: R=9-Anthryl
b: R=α-Naphthyl



$$\text{R-CH=N}_2 \left\{ \begin{array}{l} \xrightarrow{+\text{AcOH}} \text{R-CH}_2\text{OAc} \quad \text{IVa, IVb} \\ \xrightarrow{+\text{PhOH}} \text{R-CH}_2\text{OPh} \quad \text{Va, Vb} \\ \xrightarrow{+\text{PPh}_3} \text{R-CH=NN=PPh}_3 \quad \text{VIa} \end{array} \right.$$

Compounds IIIa and IIIb were synthesized by the oxidation of IIa and IIb respectively, according to the method of Miller.[1] These diazomethanes were obtained as red crystals and decomposed, with a loss of nitrogen, at 40—41°C and 63—64°C respectively. Moreover, they were found to be able to initiate the radical polymerization of methyl methacrylate.[2]

The method of the synthesis of IIIa and IIIb and their infrared spectra, showing the diazobands at 2080 cm,$^{-1}$ establish the structures of IIIa and IIIb respectively. The reactions of the diazomethanes with acetic acid or phenol afforded the insertion products of 9-anthrylcarbene and α-naphthylcarbene to the oxygen-hydrogen bond of acetic acid or phenol. The reaction of IIIa with triphenylphosphine gave triphenylphosphine-9-anthraldehyde azine (VIa).

Experimental

9-Anthraldehyde (Ia) was prepared according to the method described in the literature[3]; mp 102—103°C, 80% yield.

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[1] J. B. Miller, *J. Org. Chem.*, **24**, 560 (1959).

[2] M. Imoto, T. Nakaya, T. Tomomoto and K. Ohasi, *Polymer Letters*, in press.

[3] E. Campaigne and W. L. Archer, *J. Am. Chem. Soc.*, **75**, 989 (1953).

9-Anthraldehyde Hydrazone (IIa). A solution of 8.8 g of 9-anthraldehyde in 150 m*l* of absolute ethanol was stirred with 8.5 g of 80% hydrazine hydrate at room temperature for 3 hr. After 10 min, the color of the reaction mixture changed from yellow to dark yellow. The solid product was then filtered off and dried under a vacuum. Recrystallization from ethanol gave red yellow crystals of IIa; mp 124—126°C. The yield was 90%.

Found: C, 81.59; H, 5.41; N, 12.63%. Calcd for $C_{15}H_{12}N_2$: C, 81.82; H, 5.45; N, 12.78%.

9-Anthryldiazomethane (IIIa). A mixture of 4 g of IIa, 5 g of anhydrous sodium sulfate, 50 m*l* of ether, 1 m*l* of ethanol saturated with potassium hydroxide, and 10 g of yellow mercuric oxide was shaken for 5 hr in a pressure bottle. The reaction mixture was then filtered through a glass filter. When the filtrate was concentrated under reduced pressure, red crystals were obtained in a 65% yield. The crystals decomposed, with a loss of nitrogen, at 63—64°C. The infrared spectrum showed a diazo band at 2080 cm^{-1}.

Found: C, 82.43; H, 4.75%. Calcd for $C_{15}H_{10}N_2$: C, 82.57; H, 4.59%.

9-Anthrylacetoxymethane (IVa). Into a solution of 3 g of IIIa in 150 m*l* of *n*-hexane, 1.5 m*l* of acetic acid was added. The color of the reaction mixture changed from red to yellow after a little time. The solvent was removed by distillation to give yellow crystals. Recrystallization from ethanol gave IVa as yellow needles in an almost quantitative yield; mp 111—112°C. The infrared spectrum exhibited an acetate band at 1720 cm^{-1}.

Found: C, 81.36; H, 5.83%. Calcd for $C_{17}H_{14}O_2$: C, 81.50; H, 5.60.

9-Phenoxymethylanthracene (Va). Two grams of phenol were added to a solution of IIIa in 100 m*l* of *n*-hexane. After the reaction mixture had then been heated at 80°C for 12 hr, the solvent was removed under reduced pressure, thus separating yellow crystals. Recrystallization from ethanol gave Va as yellow needles in a 53% yield; mp 144—145°C. The infrared spectrum showed an absorption at 1230 cm^{-1} due to the ether bond.

Found: C, 88.84; H, 5.84%. Calcd for $C_{21}H_{16}O$: C, 88.73; H, 5.63.

Triphenylphosphine - 9 - anthraldehyde Azine (IVa). This azine was obtained by the method described by Wittig *et al.*[4] A mixture of 3 g of IIIa and 3.5 g of triphenylphosphine in 50 m*l* of ether was allowed to stand for two days at room temperature. The resulting crystals were collected and dried in a vacuum. Recrystallization from benzene gave VIa as red crystals in a 82% yield; mp 155—157°C.

Found: C, 82.56; H, 5.34%. Calcd for $C_{33}H_{25}N_2P$: C, 82.50; H, 5.21.

α-Naphthaldehyde (Ib) was prepared according to the method of King *et al.*,[5] bp 160—162°C/18 mmHg; yield, 75%.

α-Naphthaldehyde Hydrazone (IIb). This compound was obtained in the same manner as has been described for IIa. Two recrystallizations of the crude product from ethanol gave white crystals in a 80% yield; mp 91—92°C.

Found: C, 77.62; H, 6.25; N, 16.47%. Calcd for $C_{11}H_{10}N_2$: C, 77.65; H, 5.88; N, 16.47.

α-Naphthyldiazomethane (IIIb). The procedure used in making IIIb was the same as has been described, for IIIa. The red crystalline product decomposed, with a loss of nitrogen, at 40—41°C. This product could not be satisfactorily analyzed because it decomposed even at room temperature.

α - Naphthylacetoxymethane (IVb). This compound was prepared by the same method as has been described for IVa. The product was distillled twice, bp 140—142°C/4 mmHg, reported, 142—143/4 mmHg.[6] The yield was quantitative. The infrared spectrum exhibited an acetate band at 1720 cm^{-1}.

Found: C, 78.00; H, 6.12%. Calcd for $C_{13}H_{12}O_2$: C, 78.00; H, 6.00.

α-Phenoxymethylnaphthalene (Vb). Two grams of phenol were added to a solution of 2 g of IIIb in 200 m*l* of *n*-hexane. After the reaction mixture had then been heated at 60°C for 12 hr, the solvent was removed under reduced pressure. The residue was then distilled, bp 144—148°C/12 mmHg. The product obtained by the distillation began to crystallize after a while. The crystalline solid was recrystallized from ethanol to give Vb as white platelets, with a melting point of 66—67°C, in a 77% yield.

Found: C, 86.81; H, 6.51%. Calcd for $C_{17}H_{14}O$: C, 87.18; H, 5.98.

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4) G. Wittig and M. Schlosser, *Tetrahedron,* **18,** 1025 (1962).

5) F. E. King, P. L'Ecuyer and H. T. Openshaw, *J. Chem. Soc.,* **1936**, 352.

6) W. E. Conrad and S. M. Dec, *J. Org. Chem.,* **23,** 1700 (1958).