CIII.—*The Use of 2 : 4-Dinitrophenylhydrazine as a Reagent for Carbonyl Compounds.*

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SOME years ago Elsmie and the author (*Analyst*, 1926, **51**, 77) directed attention to the advantages of 2 : 4-dinitrophenylhydrazine as a reagent for aldehydes and ketones. Two methods were recommended: (1) boiling the aldehyde or ketone with dinitrophenylhydrazine in alcohol; (2) addition of the carbonyl compound to a solution of dinitrophenylhydrazine hydrochloride in 2*N*-hydrochloric acid. There are, however, objections to both methods. In (1), the sparing solubility of dinitrophenylhydrazine in alcohol, often less than that of the product of the reaction, causes difficulty in purification of the hydrazone unless a considerable excess of carbonyl compound is employed. Further, when the dinitrophenylhydrazone is very sparingly soluble in alcohol, as is the case with certain aromatic derivatives, it forms a protective coating over the dinitrophenylhydrazine and even prolonged boiling does not complete the reaction. The objections to the second method are: (a) the sparing solubility of the hydrochloride (1—2 g. per litre); (b) carbonyl compounds sparingly soluble in water do not react satisfactorily.

Allen (*J. Amer. Chem. Soc.*, 1930, **52**, 2955) has prepared the dinitrophenylhydrazones of a considerable number of aliphatic and aromatic aldehydes and ketones by boiling these compounds in alcohol with dinitrophenylhydrazine in the absence or presence of hydrochloric acid and has fully endorsed our opinion of the value of the reagent. For the last 5 years a solution of dinitrophenylhydrazine hydrochloride in 2*N*-hydrochloric acid has been used by undergraduates in this laboratory as a qualitative test for aldehydes and ketones. Since very little is required, the cost is negligible, and the test has proved quite trustworthy. As pointed out by Allen, it is not very satisfactory for α-hydroxy-aldehydes and ketones and it gives no precipitates with sugars. Ethyl acetoacetate readily gives a dinitrophenylhydrazone (Curtius and Dedichen, *J. pr. Chem.*, 1894, **50**, 267; Purgotti, *Gazzetta*, 1894, **24**, i, 569) but not a pyrazolone, and β-diketones readily yield pyrazoles.

A new method of using this reagent is now described which gives satisfactory results and enables dinitrophenylhydrazones to be prepared in a few minutes. Further, such compounds as piperonal and camphor give at once pure dinitrophenylhydrazones, whereas by the older method it was found impossible to free the product from unchanged dinitrophenylhydrazine. Also, solid dinitrophenylhydrazones have been obtained in certain cases where Allen was unsuccessful, namely, from fenchone, pulegone and commercial ionone.

Experimental.

Preparation and Use of the Reagent.—Dinitrophenylhydrazine may be prepared by the method of Allen (*loc. cit.*) or by dissolving 2 : 4-dinitrochlorobenzene (100 g.) in hot alcohol (250 c.c.) and adding slowly a mixture of 50% hydrazine hydrate (50 c.c.), concentrated aqueous ammonia (25 c.c.), and alcohol (100 c.c.). The dinitrophenylhydrazine crystallises almost at once and after being washed with alcohol and with water is pure. The yield is almost quantitative and the compound may be kept indefinitely.

The dinitrophenylhydrazine (1 g.) is dissolved in concentrated sulphuric acid (2 c.c.), and alcohol (15 c.c.) added. The carbonyl compound (1/200 g.-mol.) is added in alcoholic solution to the freshly prepared reagent. In some cases (aromatic aldehydes and ketones) the dinitrophenylhydrazone crystallises at once and may be collected and washed with cold alcohol; in others (higher aliphatic aldehydes and aliphatic ketones) it may be necessary to dilute the reaction mixture somewhat with 2*N*-sulphuric acid. With fenchone, camphor, acetylacetone, and benzoylacetone it is advantageous to keep the mixture over-night.

Compounds prepared. Besides some of those described by Allen, the following compounds have been prepared by the above method.

cyclo*Heptanonedinitrophenylhydrazone*, shining orange-yellow plates from alcohol; m. p. 148° (Found: C, 53·2; H, 5·8. $C_{13}H_{16}O_4N_4$ requires C, 53·4; H, 5·5%); cyclo*octanonedinitrophenylhydrazone*, orange-yellow needles from alcohol; m. p. 163° (Found: N, 18·3. $C_{14}H_{18}O_4N_4$ requires N, 18·3%); cyclo*pentadecanonedinitrophenylhydrazone*, yellow plates from alcohol; m. p. 105° (Found: N, 14·0. $C_{21}H_{32}O_4N_4$ requires N, 13·8%). *Crotonaldehydedinitrophenylhydrazone*, rosettes of crimson needles from benzene–light petroleum; m. p. 190° (Found: C, 48·3; H, 4·1. $C_{10}H_{10}O_4N_4$ requires C, 48·0; H, 4·0%); *glyoxylic acid dinitrophenylhydrazone*, yellow needles from dilute alcohol; m. p. 190° (decomp.) (Found: C, 37·8; H, 2·4. $C_8H_6O_6N_4$ requires C, 37·8; H, 2·4%). *Anisaldehydedinitrophenylhydrazone*, bright red, shining leaflets from xylene; m. p. 250° (Found: N, 17·3. $C_{14}H_{12}O_5N_4$ requires N, 17·7%); m-*hydroxybenzaldehydedinitrophenylhydrazone*, scarlet microscopic prisms from xylene, in which it is sparingly soluble; m. p. 259° (Found: N, 18·4. $C_{13}H_{10}O_5N_4$ requires N, 18·5%); *cuminaldehydedinitrophenylhydrazone*, microscopic red needles from benzene; m. p. 241° (Found: C, 58·6; H, 4·9. $C_{16}H_{16}O_4N_4$ requires C, 58·5; H, 4·9%); *piperonaldinitrophenylhydrazone*, small red octahedra from xylene; m. p. 265° (decomp.) (Found: N, 16·6. $C_{14}H_{10}O_6N_4$ requires N, 17·0%); p-*nitrobenzaldehydedinitrophenylhydrazone*, microscopic orange needles from xylene or quinoline; m. p. 320° (Found: N, 20·8. $C_{13}H_9O_6N_5$ requires N, 21·2%); *phenylacetaldehydedinitrophenylhydrazone*, golden leaflets from alcohol; m. p. 110° (Found: N, 18·4. $C_{14}H_{12}O_4N_4$ requires N, 18·7%). Cinnamaldehydedinitrophenylhydrazone melts at 248°; no value is given by Purgotti (*loc. cit.*, p. 564) (Found: N, 17·5. Calc.: N, 17·9%). *Camphordinitrophenylhydrazone*, orange needles from alcohol; m. p. 175° (Found: C, 57·7; H, 6·0. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·0%). *Fenchonedinitrophenylhydrazone*, orange-yellow needles from alcohol which sinter at 125° and melt at 140°; repeated crystallisation did not alter these temperatures (Found: N, 16·8. $C_{16}H_{20}O_4N_4$ requires N, 16·9%). *Pulegonedinitrophenylhydrazone* separated as a red oil, but a solution of this in light petroleum deposited large crimson plates, m. p. 142° (Found: C, 57·8; H, 6·0. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·0%). *Iononedinitrophenylhydrazone* prepared from the commercial product separated as an oil which solidified after 2 days and crystallised from light petroleum in scarlet needles, m. p. 125—128° (Found: C, 61·4; H, 6·4. $C_{19}H_{24}O_4N_4$ requires C, 61·3; H, 6·5%). 1-(2′ : 4′-*Dinitrophenyl*)-

3 : 5-*dimethylpyrazole*, from acetylacetone and dinitrophenylhydrazine, separated from alcohol in pale lemon leaflets, m. p. 122° (Found : C, 50·5; H, 3·7. $C_{11}H_{10}O_4N_4$ requires C, 50·4; H, 3·8%); 1-(2′ : 4′-*dinitrophenyl*)-3(or 5)-*phenyl*-5(or 3)-*methylpyrazole*, from benzoylacetone, gave very pale yellow leaflets from alcohol; m. p. 151° (Found : C, 59·0; H, 3·7. $C_{16}H_{12}O_4N_4$ requires C, 59·3; H, 3·7%).

Other dinitrophenylhydrazones are described by Allen, Brady and Elsmie, Purgotti, and Curtius and Dedichen (*locc. cit.*).

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