33. *The Action of Titanous Chloride on Nitrophenylhydrazones :* p-*Nitro- and* 2 : 4-*Dinitro-phenylhydrazones.*

By A. KILLEN MACBETH and J. R. PRICE.

THE results of previous workers show that phenylhydrazones may be converted by the action of suitable reducing agents into a mixture of primary bases, the first stage in the reaction evidently being the formation of a symmetrically substituted hydrazine, which subsequently undergoes scission to give the final reaction products. Thus, sodium amalgam converts benzaldehydephenylhydrazone in boiling alcoholic solution into *s*-phenylbenzylhydrazine, whereas in the presence of acetic acid the hydrazone or the hydrazine is converted into benzylamine and aniline (Schlenk, *J. pr. Chem.*, 1908, **78**, 49). A similar result has been recorded for other phenylhydrazones by treatment with activated aluminium (Matzierevich, *J. Russ. Phys. Chem. Soc.*, 1925, **57**, 221) or by electrolytic reduction (Tafel and Pfeffermann, *Ber.*, 1902, **35**, 1510). Catalytic reduction by hydrogen in the presence of colloidal platinum carries the reaction on phenylhydrazones to the *s*-substituted hydrazine stage only (Goodwin and Bailey, *J. Amer. Chem. Soc.*, 1925, **47**, 167).

Since titanous salts are employed as reducing agents mainly in moderately concentrated acid media, hydrolysis of the phenylhydrazones into the constituent phenylhydrazines and carbonyl compounds is to be expected rather than reduction at the double bond of the carbon–nitrogen linkage : and this course is in fact found to be followed. As it was desired to test the suitability of titanous chloride as a quantitative reagent in the analysis of nitrophenylhydrazones, representative compounds of this type were examined. We have confirmed the fact that *p*-nitrophenylhydrazine itself is reduced by this reagent to *p*-phenylenediamine and ammonia (Robinson, *J. Manch. Sch. Tech.*, 1915, **7**, 105). In the case of 2 : 4-dinitrophenylhydrazine no such scission occurs, the reaction evidently yielding 2 : 4-diaminophenylhydrazine on a quantitative basis. The estimation of *p*-nitrophenylhydrazones must therefore be based on a consumption of eight equivalents of hydrogen (or titanous salt), and 2 : 4-dinitrophenylhydrazones on the basis of twelve such equivalents, in accordance with the following equations :

$$NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2 + 8TiCl_3 + 9HCl = C_6H_4(NH_2)_2 + NH_4Cl + 8TiCl_4 + 2H_2O$$
$$(NO_2)_2C_6H_3{\cdot}NH{\cdot}NH_2 + 12TiCl_3 + 12HCl = (NH_2)_2C_6H_3{\cdot}NH{\cdot}NH_2 + 12TiCl_4 + 4H_2O$$

This behaviour of 2 : 4-dinitrophenylhydrazine is in agreement with the observation of Rathsburg (*Ber.*, 1921, **54**, 3183) that the nitro-groups of trinitrophenylmethylnitroamine are quantitatively reduced by titanous chloride without apparent scission of the molecule.* Phenylhydrazine and *p*-bromophenylhydrazine are unattacked by titanous salts, and so no reduction is to be expected in the case of their phenylhydrazones.

EXPERIMENTAL.

Preparation of Materials.—(a) Acetaldehydephenylhydrazone was prepared by the method of Laws and Sidgwick (J., 1911, **99**, 2085) and isolated as the β-form (m. p. 57—58°) on crystal-

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* There is evidently a misprint in this paper, since reference is made to trinitrophenylnitroamine, and not to trinitrophenylmethylnitroamine. The results recorded, however, agree with the latter and not with the former, and the reference given for these substances (van Duin, *Chem. Weekblad*, 1919, **16**, 1111) deals with trinitrophenylmethylnitroamine.

lisation from an acid medium. The same method was applied in the case of acetonephenylhydrazone, which was converted into the hydrochloride (m. p. 143—144°, decomp.). Neither these substances nor phenylhydrazine hydrochloride was reduced by titanous chloride solution under the standard conditions of analysis (Knecht and Hibbert, *Ber.*, 1903, **36**, 1549).

(b) Terpene *p*-nitrophenylhydrazones were prepared by filtering a hot solution of *p*-nitrophenylhydrazine (1·2 g.) in *N*-hydrochloric acid (50 ml.) into an alcoholic solution (10 ml.) of the carbonyl compound (1 g.). The mixture was then poured into 30% acetic acid (100 ml.) and after some hours the product was collected and recrystallised from methyl or ethyl alcohol. The mixing with acetic acid is unnecessary in the case of the simpler aliphatic aldehydes and ketones.

(c) 2 : 4-Dinitrophenylhydrazones were prepared by Brady's method (J., 1931, 756). The m. p.'s were in agreement with those generally recorded in the literature, and the higher m. p.'s for the 2 : 4-dinitrophenylhydrazones of formaldehyde and acetaldehyde given by Bryant (*J. Amer. Chem. Soc.*, 1932, **54**, 3760) were confirmed.

Phellandral forms a p-*nitrophenylhydrazone*, yellow-orange rosettes from methyl alcohol, m. p. 169—170° (Found : C, 66·8; H, 7·4. $C_{16}H_{21}O_2N_3$ requires C, 66·9; H, 7·3%), and a 2 : 4-*dinitrophenylhydrazone*, small orange to red-orange needles from chloroform–ethyl alcohol, m. p. 202—203° (Found : C, 57·6; H, 5·7. $C_{16}H_{20}O_4N_4$ requires C, 57·8; H, 6·0%).

The following 2 : 4-*dinitrophenylhydrazones* were prepared : of diethyl ketone, orange needles from alcohol, m. p. 156° (Found : C, 49·45; H, 5·4. $C_{11}H_{14}O_4N_4$ requires C, 49·6; H, 5·3%); of *o*-chlorobenzaldehyde, orange needles from glacial acetic acid, m. p. 209° (Found : Cl, 11·1. $C_{13}H_9O_4N_4Cl$ requires Cl, 11·1%); of 4-*iso*propyl*cyclo*hexan-1-one, orange-yellow plates from alcohol, m. p. 119—120° (Found : C, 56·4; H, 6·15. $C_{15}H_{20}O_4N_4$ requires C, 56·25; H, 6·25%); of thujone, orange-yellow plates from alcohol, m. p. 116—117° (Found : N, 17·0. $C_{16}H_{20}O_4N_4$ requires N, 16·9%); of protocatechualdehyde, dark red micro-crystals from methyl alcohol, m. p. 275° (decomp.) (Found : N, 17·6. $C_{13}H_{10}O_6N_4$ requires N, 17·6%); of vanillin, orange-red micro-crystalline prisms from glacial acetic acid, m. p. 267—268° (Found : C, 50·6; H, 3·6. $C_{14}H_{12}O_6N_4$ requires C, 50·6; H, 3·6%); and of veratraldehyde, microscopic orange prisms from ethyl acetate, m. p. 264—265° (Found : C, 51·8; H, 4·1. $C_{15}H_{14}O_6N_4$ requires C, 52·0; H, 4·05%).

Analytical Results.—In the table the percentages shown in the last column were determined experimentally on the basis of the number of equivalents of titanous chloride (or titanous sulphate) shown. The standard volumetric method for the estimation of nitro-groups was employed, some 75% excess of titanous chloride being used, and the unoxidised residue being measured either by direct titration with standardised methylene-blue, or by back-titration with titanous chloride after the addition of excess of the methylene-blue. Some of the dinitrophenylhydrazones examined were too sparingly soluble for use in the estimations, and as a rule the nitrophenylhydrazones of aromatic aldehydes and ketones are of this type.

Substance.	$TiCl_3$, equivs.	% found.
p-Nitrophenylhydrazine	8	100·3
Acetaldehyde-*p*-nitrophenylhydrazone	8	98·3
n-Butaldehyde-*p*-nitrophenylhydrazone	8	100·0
Phellandral-*p*-nitrophenylhydrazone	8	100·3
l-4-*iso*Propyl-Δ^2-*cyclo*hexen-1-one-*p*-nitrophenylhydrazone	8	99·0
2 : 4-Dinitrophenylhydrazine	12	100·3
Formaldehyde-2 : 4-dinitrophenylhydrazone	12	99·8
Acetaldehyde-2 : 4-dinitrophenylhydrazone	12	100·9
n-Butaldehyde-2 : 4-dinitrophenylhydrazone	12	100·0
n-Heptaldehyde-2 : 4-dinitrophenylhydrazone	12	100·0
Acetone-2 : 4-dinitrophenylhydrazone	12	100·0
Diethyl ketone-2 : 4-dinitrophenylhydrazone	12	100·2
Thujone-2 : 4-dinitrophenylhydrazone	12	99·2
4-*iso*Propyl*cyclo*hexan-1-one-2 : 4-dinitrophenylhydrazone	12	100·0
l-4-*iso*Propyl-Δ^2-*cyclo*hexen-1-one-2 : 4-dinitrophenylhydrazone	12	100·2

Hydrolysis of Hydrazones.—It was thought desirable to apply a test to detect the hydrolysis of the phenylhydrazones during the titanium estimations. The carbon dioxide issuing from the reaction flask carries with it vapours of the carbonyl compounds, and if these are passed into a solution of 2 : 4-dinitrophenylhydrazine in 10% sulphuric acid, precipitates of the re-formed hydrazones are obtained, but in amounts too small to admit of identification. In a larger-scale experiment *n*-butaldehyde-2 : 4-dinitrophenylhydrazone was refluxed with 3*N*-hydrochloric acid as in the titanium estimation method, and the carbon dioxide was passed into a sulphuric acid solution of 2 : 4-dinitrophenylhydrazine : after filtration and recrystallisation, the precipitate had m. p. 121—122°, alone or mixed with authentic *n*-butaldehyde-2 : 4-dinitrophenylhydrazone.

JOHNSON CHEMICAL LABORATORIES,
UNIVERSITY OF ADELAIDE.

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