223. *Complexes of Polynitro-compounds. Part I. Compounds of Polynitro-hydrocarbons with* 1-*Keto*-1 : 2 : 3 : 4-*tetrahydrocarbazole.*

By Andrew Kent.

1-Ketotetrahydrocarbazole rivals naphthalene (Hepp, *Annalen*, 1882, **215**, 375) in its ability to form crystalline complexes with polynitro-hydrocarbons. It is further distinctive in the nature of its products, as these frequently belong to that rare ternary (1 : 2) type containing but one molecule of the polynitro-compound which, on Pfeiffer's calculation, occurs in only 1—2% of recorded instances (" Organische Molekulverbindungen," Stuttgart, 1927, p. 336).

The examples tabulated below permit consideration of the effect on molecular composition and on stability towards thermal and solvent dissociation, of structural variation in the components of the molecular compounds described.

1-*Ketotetrahydrocarbazole.*—The following preparation avoids the considerable resinification which accompanies Coffey's original procedure (*Rec. trav. chim.*, 1923, **42**, 531), or prolonged (3 hrs.) boiling with acetic acid alone. *cyclo*Hexane-1 : 2-dione monophenylhydrazone (10 g.) is dissolved in boiling glacial acetic acid (60 c.c.). The burner is removed while concentrated hydrochloric acid (10 c.c.) is added in small quantities through the condenser. When the resultant ebullition has moderated, the whole is boiled for 2 minutes and then diluted with boiling water (40 c.c.). The product (yield, 75—80% of the theoretical) is obtained, on cooling, in fine long needles, m. p. 164—167°, and 169° after one recrystallisation from dilute acetone or acetic acid. The persistent slight coloration of the solid can be removed by addition of a crystal of potassium permanganate to an acetone solution.

Estimates of approximate solubility at room temperature indicated that this keto-amine is somewhat more soluble in benzene (100 parts dissolve *ca.* 3·6 parts at 20°) than in alcohol (100 parts dissolve *ca.* 2·4 parts at 20°).

The p-*nitrophenylhydrazone*, prepared in acetic acid, is obtained on recrystallisation from this solvent as deep red needles, m. p. 252—253° (Found : N, 17·8. $C_{18}H_{16}O_2N_4$ requires N, 17·5%). Efforts to indolise this substance with the usual reagents gave negative results : methods involving the addition of hydrogen chloride or concentrated hydrochloric acid precipitate a lemon-yellow hydrochloride (decomp. 210—212°), which is stable in the absence of excess of water.

The deep red *p*-nitrophenylhydrazone, from acetic acid or acetone, is readily discoloured by absolute alcohol and recrystallises from this solvent as fine bottle-green needles, to which the original colour is restored by mild heating (which is accompanied by loss of weight), or by brisk rubbing on porous pot. The green modification is apparently a binary *complex* with the solvent (Found : Loss of weight, 13·0. $C_{18}H_{16}O_2N_4,C_2H_6O$ requires C_2H_6O, 12·6%).

1-Ketotetrahydrocarbazole picrate was obtained from 1 : 1 to 1 : 3 concentrations of the reactants in alcohol or benzene as light red, long needles, m. p. 165—166° (Found : N, 11·8; $C_{12}H_{11}ON$, by trituration with dilute aqueous ammonia, 60·6. Calc. for $C_6H_3O_7N_3,2C_{12}H_{11}ON$: N, 11·7; $C_{12}H_{11}ON$, 61·7%). This substance was unaffected in colour or m. p. by recrystallisation from 50% aqueous alcohol, acetone, or acetic acid. Plancher, Cecchetti, and Ghigi (*Gazzetta*, 1929, **59**, 346) record m. p. 162°.

Further *complexes* of 1-ketotetrahydrocarbazole were obtained with the following polynitro-hydrocarbons from an alcoholic solution of the constituents, and were recrystallised from that solvent for analysis : (a) and (e) are also precipitated when cold saturated alcoholic solutions of the necessary components are mixed, (c) may be successfully recrystallised only from concentrated solution, as dilution produces visible dissociation (cf. acenaphthene styphnate; Gibson, J., 1908, **93**, 2099). Melting ranges and composition were checked by simultaneous comparison with a melt of the substances concerned, in the proportion indicated by analysis : and the stability of the complexes was further investigated by attempted recrystallisation from benzene.

			N, %.			M. p. solid.		
Compound.	Polynitro-component.	Composition.	Found.	Calc.	Description.	From C_2H_6O.	From melt.	On attempted recrystn. from C_6H_6.
a	1 : 3 : 5-$C_6H_3(NO_2)_3$	1 : 2	12·0	12·0	Deep yellow, short needles	180—182°	178—182°	Unchanged (N, 12·3)
b	1 : 2 : 4- ,,	1 : 1	14·1	14·0	Bright red needles	129—131	125—130	Unchanged (N, 13·9)
c	*m*-$C_6H_4(NO_2)_2$	1 : 2	10·7	10·4	Orange-yellow prisms	120—139	119—141	Dissociated
d	*p*- ,,	1 : 2	10·4	10·4	Orange-yellow, fine needles	140—142	139—143	Unchanged from conc. soln. (N, 10·2); dissociated from dil. soln.
e	2 : 4 : 6-$C_6H_2Me(NO_2)_3$	1 : 1	13·9	13·6	Greenish-yellow needles	129—131	126—131	Unchanged (N, 13·7)
f	2 : 4 : 5- ,,	1 : 2	11·8 *	11·7	Orange leaflets	127—140	125—138	Unchanged (N, 11·9) *
g	2 : 4-$C_6H_3Me(NO_2)_2$	1 : 1	11·7	11·45	Greenish-yellow needles	98—126	98—126	Dissociated
h	2 : 5- ,,	1 : 2	10·4	10·15	Deep yellow prisms	142—143	140—144	Unchanged (N, 10·0) *
i	3 : 5· ,,	1 : 1	11·4	11·45	Greenish-yellow, minute blades	108—118	108—119	Dissociated

When the components of (i) are dissolved together in benzene, the precipitate obtained on cooling, according to the proportions employed, is unassociated amine or the efflorescent compound $C_7H_6(NO_2)_2,C_6H_6$ (Staedel, *Annalen*, 1883, **217**, 193): on the other hand, (c) and (g) may be prepared in this solvent if sufficient excess of the more soluble component be introduced, and a similar procedure was found to precipitate from alcohol the corresponding compounds of naphthalene (cf. Hepp, *loc. cit.*, pp. 379, 380).

o-Dinitrobenzene and 2 : 6-dinitrotoluene (cf. Kremann and Müller, *Monatsh.*, 1921, **42**, 182) and 2 : 4 : 6-trinitro-*m*-xylene (cf. Efremov and Tikhomirova, *Chem. Abstr.*, 1929, **23**, 2349) gave no indication of complex formation with this amine.

1 : 2 : 3 : 4-Tetrahydrocarbazole forms a *compound* with *s*-trinitrobenzene (red needles, from alcohol, m. p. 159—161°) of the usual binary type (Found : N, 14·8. $C_6H_3O_6N_3,C_{12}H_{13}N$ requires N, 14·6%), and the corresponding picrate (Perkin and Plant, J., 1921, **119**, 1831) is of the same composition (Found : $C_{12}H_{13}N$, by trituration with dilute aqueous ammonia, 42·4. Calc. for $C_6H_3O_7N_3,C_{12}H_{13}N$: $C_{12}H_{13}N$, 42·7%).

DISCUSSION.

No evidence was obtained that any of the compounds (a)—(i) could be obtained crystalline with its components in alternative proportion. The variation in molecular composition of compounds obtained under similar conditions [cf. particularly (a) and (e)] renders it most improbable that the ternary form results from prior association of two mols. of keto-amine.

If such variation be conditioned by the chemical structure of the components, it may be relevant that the compounds of *s*-trinitrobenzene with other cinnamoyl substances like coumarin and carbostyril (Sudborough *et al.*, J., 1911, **99**, 216; 1916, **109**, 1347) are of the same type as (a) : on the other hand, considering the polynitro-components in the above table as derivatives of *m*- and *p*-dinitrobenzenes, the addition of further nitro- and/or methyl groups is associated with changes in molecular composition which bear no simple relationship to the nature or position of the entrant groups [*e.g.*, (i) and (a) compared with (h) and (b), (a) and (e) with (b) and (f), etc.]. Comparing the compositions of (e) and the corresponding picrate, it is further evident that the addition of " positive " groups has no consistent result ; and the effect of hydroxyl groups in this case is under investigation.

From recorded data it appears also that the various polynitro-substances do not necessarily combine in a fixed ratio with other components capable of ternary compound formation. Thus, whereas benzene forms compounds analogous in composition with (a) (Hammick, Hills, and Howard, J., 1932, 1530) and with (i) (Staedel, *loc. cit.*), 4 : 4′-bisdimethylaminodiphenylmethane combines as in (c) with *m*-dinitrobenzene, but gives a binary complex with *s*-trinitrobenzene (Romburgh, *Rec. trav. chim.*, 1888, **7**, 228).

The relative stability towards thermal and solvent dissociation of (h) is of interest in view of Kremann's assumption (*Monatsh.*, 1911, **32**, 609) that a methyl group in the *o*-position to a nitro-group exerts a " steric valence-hindrance " effect : in this compound, moreover, both nitro-groups appear to be active. It is further notable that (b) recrystallises unchanged from benzene, although the disparity in solubility (*ca.* 40 : 1) of the components is very great.

(f) and (h) are apparently the first recorded instances of 1 : 2 molecular compound formation by polynitrotoluenes, and (d) the first compound of this category recorded for *p*-dinitrobenzene.

Micro-analyses (*) were conducted by Mr. J. M. L. Cameron. The author is further indebted to Mr. H. D. MacMurray for assistance with the necessary macro-analyses, and to Mr. J. Bruce for specimens of 2 : 5-dinitro- and of 2 : 4 : 5-trinitro-toluene.

THE UNIVERSITY OF GLASGOW. [*Received, April* 18*th*, 1935.]