3. *Complexes of Polynitro-compounds. Part II. Compounds of Polynitro-substances with Derivatives of* 1-*Keto*-1 : 2 : 3 : 4-*tetrahydrocarbazole.*

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The capacity of 1-ketotetrahydrocarbazole (K) to provide crystalline termolecular (1 : 2) compounds containing one molecule of certain polynitro-substances (*e.g.*, *m*- or *p*-dinitro- and *s*-trinitro-benzene, picric acid; Part I, J., 1935, 976) is found to be retained in some degree by six of the seven monomethyl homologues (2 to 8). This is apparently the first direct demonstration of a relationship between the constitution of a substance containing only one aromatic system (simple or condensed) and the composition of such ternary molecular compounds with polynitro-materials.

EXPERIMENTAL.

Suspensions of the appropriate hydroxymethylene *cyclo*ketones (from *cyclo*ketone, ethyl formate and "atomised" sodium) afforded the following phenylhydrazones on treatment with a neutral solution of diazotised amine. When 3-methyl*cyclo*hexanone was used, the yield was poor. The crude products were recrystallised from alcohol: cyclo*hexane*-1 : 2-*dione*-1-m-*tolylhydrazone*, light brown plates, m. p. 156—158° (Found: N, 13·1. $C_{13}H_{16}ON_2$ requires N, 13·0%); cyclo*hexane*-1 : 2-*dione*-1-(6'-*cyano*-m-*tolylhydrazone*), light brown, minute, prismatic needles, m. p. 123° (Found: N, 17·6. $C_{14}H_{15}ON_3$ requires N, 17·4%) (the customary indolising media—hydrochloric acid, acetic acid, dilute sulphuric acid—do not afford a homogeneous product from this compound); cyclo*hexane*-1 : 2-*dione*-2-(4'-*nitrophenylhydrazone*)-1-(6'-*cyano*-m-*tolylhydrazone*), from acetic acid, was obtained on recrystallisation from alcohol as a brown powdery solid (microscopic needle clusters), m. p. 214—215° (Found: N, 22·4. $C_{20}H_{20}O_2N_6$ requires N, 22·3%); cyclo*hexane*-1 : 2-*dione*-1-o-*carboxyphenylhydrazone*, light brown prisms, m. p. 185—186° (Found: N, 11·5. $C_{13}H_{14}O_3N_2$ requires N, 11·4%).

The product obtained as above from 3-methyl*cyclo*hexanone and aniline (heterogeneous crystals, m. p. 190—205°. Found: N, 13·1. $C_{13}H_{16}ON_2$ requires N, 13·0%) was not further investigated prior to indolisation; the reagents there used apparently hydrolysed any 3-methyl-*cyclo*hexane-1 : 2-dione-2-phenylhydrazone which had been added.

4-*Methyl*cyclo*hexane*-1 : 2-*dione*-2-*phenylhydrazone* was obtained in light yellow, rectangular plates, m. p. 139—141° (Found: N, 13·1. $C_{13}H_{16}ON_2$ requires N, 13·0%). It was also obtained by the Japp–Klingemann reaction (cf. Lions, *Proc. Roy. Soc. N.S.W.*, 1932, **66**, 516) from 4-methyl*cyclo*hexanone-2-carboxylic acid—obtained in poor yield by the method of Gardner, Perkin, and Watson (J., 1910, **97**, 1769)—in salmon-pink plates, m. p. 139—140° (Found : N, 13·1%). Both specimens afforded the same product on indolisation. No evidence of stereoisomerism was obtained.

The 1-keto-tetrahydrocarbazoles desired were, with the exception noted, readily obtained from the appropriate phenylhydrazone in good yield (70—80%) by suitable modification of the procedure given in Part I, but no addition of boiling water was necessary to precipitate the benzo- or carboxy-ketotetrahydrocarbazoles. Of the characteristic *p*-nitrophenylhydrazones prepared in acetic acid from several of these indoles, none retained the capacity of K's *p*-nitrophenylhydrazone (Part I) to combine with alcohol in producing a complex of contrasted colour.

1-*Keto*-2-*methyltetrahydrocarbazole*-p-*nitrophenylhydrazone* gave brick-red prisms from alcohol, m. p. 226—228° (Found : N, 16·9. $C_{19}H_{18}O_2N_4$ requires N, 16·8%).

1-*Keto*-3-*methyltetrahydrocarbazole* was obtained in yellowish flat needles, m. p. 194—195°, from acetone (Found : N, 7·1. $C_{13}H_{13}ON$ requires N, 7·0%), in 70% yield. The nature of its picrate (see table) is incompatible with the properties of the salt-like picrates from indolenines (cf. Plancher, *Atti R. Accad. Lincei*, 1900, **9**, I, 221). The p-*nitrophenylhydrazone* gave purple prismatic needles, m. p. 265—267° (darkening), from alcohol (Found : N, 17·0%).

1-*Keto*-4-*methyltetrahydrocarbazole* was obtained in colourless plates, m. p. 131°, from acetone (Found : N, 7·1%). The p-*nitrophenylhydrazone* gave dark red prisms, m. p. 227—229° (darkening), from alcohol (Found : N, 16·9%).

1-*Ketotetrahydrocarbazole*-8-*carboxylic acid* was obtained in colourless needles, m. p. 279—281° (sintering at 262°, darkening), from alcohol (Found : N, 6·2. $C_{13}H_{11}O_3N$ requires N, 6·1%). Indolisation of the starting material with 20% sulphuric acid afforded an identical product. The acid was sparingly soluble in hot or cold water. The p-*nitrobenzyl* ester gave small colourless needles, m. p. 189°, from alcohol (Found : N, 7·8. $C_{20}H_{16}O_5N_2$ requires N, 7·7%), and regenerated the original acid on brief (30 mins.) boiling with alcoholic caustic potash (10%).

This acid partly sublimed unchanged above 295°, but some decomposition occurred, accompanied by evolution of carbon dioxide; it was, however, largely unaffected by treatment with quinoline and copper-bronze (sealed tube, 5 hrs. at 310°). When the acid or its sodium salt (colourless needles from moderately concentrated alkali solution; m. p. above 300°) was heated with soda-lime, deep-seated decomposition ensued with the formation of evil-smelling yellow sublimates. Preliminary experiments had shown that 1-ketotetrahydrocarbazole sublimes unchanged at 240—280°. These results, in conjunction with those obtained from the above cyanophenylhydrazone, led to the abandonment of efforts to synthesise directly 1-keto-5-methyltetrahydrocarbazole.

1-*Keto*-5 (or 7)-*methyltetrahydrocarbazole* was obtained (*vide infra*) in colourless plates, m. p. 160—161°, from alcohol (Found : N, 7·2% *).

1-*Keto*-6-*methyltetrahydrocarbazole*-p-*nitrophenylhydrazone* gave dark red, iridescent plates, m. p. 260° (decomp.), from alcohol (Found : N, 16·8% *).

1-*Keto*-7 (or 5)-*methyltetrahydrocarbazole* was obtained in brownish plates, m. p. 196° (Found : N, 7·2%). This configuration is assigned to the product obtained in small quantity (*ca.* 1 g.) when the hot indolising mixture (7 g. of phenylhydrazone, 42 c.c. of acetic acid, and 7 c.c. of concentrated hydrochloric acid) was treated with successive small quantities of boiling water. The residual solids (m. p. 125—140°. Found : N, 7·1%) could not be further separated by fractional crystallisation from alcohol, acetone, or acetic acid. Alternatively, by complete precipitation of the indolised materials (m. p. 150—190°. Found : N, 7·2%), followed by recrystallisation from alcohol and treatment of their solution in alcohol (60 pts.) with picric acid (0·5 mol.), the picrate of the 7 (or 5)-isomer (see table) was obtained in 10% yield, and a similar further quantity resulted from cautious concentration of the filtrate. The residual mixed picrates could not be resolved by fractionation; but during one attempt with aqueous alcohol hydrolysis took place in such a manner as to precipitate the 5 (or 7)-isomer (0·1 g.), m. p. 157—160° [mixed m. p. with the 7 (or 5)-isomer, 130—143°].

The following *molecular compounds*, all of which appear to be new, were best prepared from an appropriate concentration of the components in the solvent indicated; they were, where practicable, recrystallised from that solvent before analysis. Those formed from *s*-trinitrobenzene (X), picric acid (Y), or *m*-dinitrobenzene (Z) compare directly with the analogous complexes XK_2, YK_2, ZK_2 described in Part I. Alternative figures for nitrogen analyses are derived from separate preparations.

Poly-nitro-component.	Amino-component.	Complex.	N, %.		Description.	M. p.	Solvent.
			Found.	Calc.			
X	A. 2-Methyl-K	XA	13·7 13·8	13·6	Canary-yellow needles	180°	C_2H_5·OH (1 : 1 soln.)
„	„	XA_2	11·6 11·5	11·45	Golden-yellow prismatic needles	186—187	C_6H_6 (1 : 1 or 1 : 2 soln.)
Y	„	YA_2	11·3 11·2*	11·2	Orange-yellow felted needles	154—155	C_2H_5·OH
X	B. 3-Methyl-K	XB_2	11·5	11·45	Golden-yellow needles	187—188	„
Y	„	YB_2	11·5	11·2	Orange-red needles	169	C_6H_6
X	C. 4-Methyl-K	XC_2	11·6	11·45	Deep golden-yellow needles	177	C_2H_5·OH
Y	„	YC_2	11·2	11·2	Red flat needles	157—159	„
X	D. 5 (or 7)-Methyl-K	XD_2	11·5*	11·45	Orange-yellow felted needles	190—192	„
Y	„	YD_2	11·2*	11·2	Orange-red prismatic needles	158—159	„
X	E. 6-Methyl-K	XE	13·5*	13·6	Yellow fluffy needles	174—176	„
Y	„	YE	13·1*	13·1	Buff minute needles	156—158	„
Z	„	ZE	11·4*	11·45	Yellow stiff needles	Incongruent	„
X	F. 7 (or 5)-Methyl-K	XF_2	11·7*	11·45	Orange-yellow fine needles	201—203	„
Y	„	YF_2	11·1* 11·2	11·2	Orange-red plates	183	„
X	G. 8-Methyl-K	XG	13·7 13·7	13·6	Golden-yellow felted needles	179—180	„
Y	„	YG	13·2	13·1	Orange-red needles	161—162	„
Z	„	ZG_2	9·9* 9·8*	9·9	Yellow plates	Incongruent	C_2H_5·OH + m-$C_6H_4(NO_2)_2$
X	P. 5 : 6-Benzo-K	XP	12·7	12·5	Yellow fibrous needles	229—231	CH_3·CO_2H
Y	„	YP	12·2	12·1	Light-red fibrous needles	212—214 (decomp.)	„
X	Q. 7 : 8-Benzo-K	XQ	12·3	12·5	Bright yellow needles	240—241	„
Y	„	YQ	12·1	12·1	Red needles	220—222 (decomp.)	„

In preliminary investigations 1 : 1 solutions of the components were generally used. Following filtration of the solid complex and concentration of the mother-liquor, evidence suggestive of the composition later confirmed by analysis was readily obtained.

A 1 : 2 solution of X and A in absolute alcohol precipitated XA_2 with a few crystals of the XA type : this heterogeneous solid rapidly became homogeneous XA_2 (Found : N, 11·6%) in contact with the liquor. In no other instance was evidence obtained that variation in solvent or in relative concentration of components could produce alternative molecular compounds.

YB_2 or ZE, and especially the latter, gave visible evidence of partial dissociation into their colourless components on attempted recrystallisation from dilute alcoholic solution. ZG_2, even from concentrated alcoholic solution, precipitated only its components, unless some additional Z, recoverable from the mother-liquor after filtration, had been introduced before crystallisation began.

Although coloured crystals were visible, the precipitate from a 1 : 1 or 1 : 2 alcoholic solution of Z and A was clearly contaminated by uncombined material. Neither E nor G provided coloured precipitates when dissolved with *p*-dinitrobenzene in absolute alcohol.

Analysis of coloured complexes was invariably preceded by examination of the specimen's homogeneity under a low-power microscope. Micro-analyses (N*) were conducted by Mr. J. M. L. Cameron.

XG and YG resemble XK_2 and YK_2 in recrystallising unchanged from benzene, and Dr. G. Thomson very kindly undertook the following molecular-weight determinations (cryoscopic method) of the amino-component :

Compound.	*c* (g./100 g. C_6H_6).	*M* (found).	Formula wt.
K	0·909, 1·22	211·5, 219	185
G	0·883, 1·24	282·4, 282·1	199

DISCUSSION.

The molecular compounds of this series show no standard concomitant (*e.g.*, colour, stability) of variation in composition. With two exceptions (XB_2, and notably XE) the derivatives of *s*-trinitrobenzene melt at a higher temperature than either constituent: and the more deeply coloured picrates melt consistently at a somewhat (24° ± 7°) lower temperature than the analogous derivatives of X (cf. Pfeiffer, "Organische Molekülverbindungen," Stuttgart, 1927, p. 357).

Some evidence has already been offered (Part I) against the possibility that ternary complex-formation in this series results from prior association of the component amine; and the molecular-weight determinations now provided indicate a negative correlation between degree of association and facility in production of crystalline ternary derivatives.

Crystalline convenience has been suggested (Bennett and Wain, J., 1936, 1115) as a primary factor in ternary complex-formation of an apparently erratic type like 1 β-naphthol : 2 tetramethylphthalan; but this appears inapplicable to a series of such high consistency as the above (cf. Lowry, *Chem. and Ind.*, 1924, **43**, 220).

It seems reasonable, therefore, to assume that such ternary complex-formation by K and its homologues is achieved by duplication of whatever mechanism is involved in the formation of the normal binary type. The isolation of XA and XA_2 suggests that in solutions of suitable materials both types are present in characteristic ratios which may, on occasion, permit isolation of either by variation of solvent and/or concentration (cf. alternative 2 : 1 and 1 : 1 types; Sudborough, J., 1916, **109**, 1342).

It is clear on the other hand (cf. XK_2, XE, XP) that crystalline ternary complex-formation cannot be predicted with confidence on constitutional grounds (cf. the ternary complex of *s*-trinitrobenzene with benzene; Hammick, Hills, and Howard, J., 1932, 1530, and its binary complexes with toluene, etc.; Pfeiffer, *Annalen*, 1917, **412**, 297).

The effect, on crystalline complex-composition, of an additional nitro-group in ZG_2 and XG resembles that exhibited in the corresponding compounds of 4 : 4′-bisdimethylaminodiphenylmethane (Romburgh, *Rec. trav. chim.*, 1888, **7**, 228) and in other complexes of K [Part I, cf. compound (c) or (d) with (b)].

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