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A NOVEL THERMAL REARRANGEMENT OF N-CYANO-N-(α-CYANOBENZHYDRYL)-ANILINE

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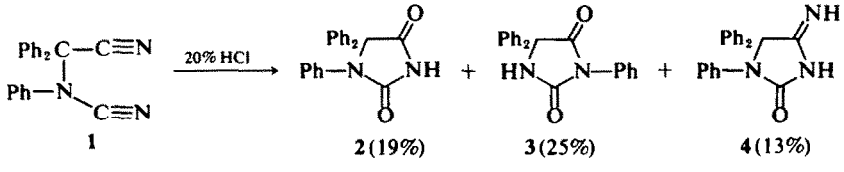
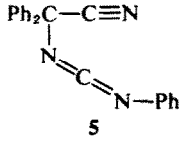
Abstract—The title compound **1** is rearranged, when refluxed with toluene, to the carbodiimide **5** and the cyanoaniline **7**. While rearrangements analogous to the transformation **1**→**5** have recently been observed, the transformation **1**→**7** is novel.

Acid hydrolisis of the title compound (**1**) furnishes two isomeric hydantoins (**2**, **3**) and an imido derivative (**4**) of the former.[1] The formation of **3** clearly involves a rearrangement. Since N-cyano-N-tritylanilines are known to furnish the isomeric carbodiimides on thermal treatment (the rearrangement being catalysed by acid),[2] the formation of **3** from **1** was rationalised by assuming initial isomerisation of **1** to the carbodiimide **5** and subsequent hydrolysis and ring closure of the latter to **3**.[1]

In order to test the above hypothesis, a toluene solution of **1** was refluxed for 1 hr. A carbodiimide band (at 2150 cm^{-1}) was found to be present in the IR spectrum of a sample taken from the mixture at this point. In contrast to the case of the N-cyano-N-tritylanilines,[2] however, complete disappearance of the cyanamide band at 2218 cm^{-1} could not be achieved: prolonged refluxing of the mixture caused the carbodiimide band to disappear gradually, but the cyanamide band was still present.



1 2 (19%) 3 (25%) 4 (13%)



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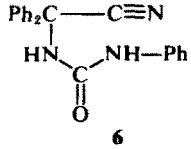

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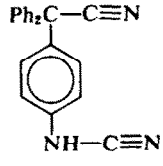

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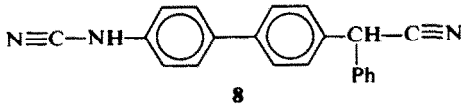

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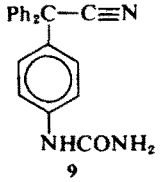

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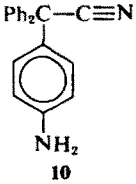

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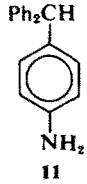

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When the reaction was followed by TLC, the starting substance was used up completely within 1 hr. At this point light petroleum was added to the mixture, when a crystalline isomer (A) of the starting compound was precipitated in 24% yield. The dry residue of the mother liquor of this product was worked up by TLC to yield 41% of the oily carbodiimide **5**, whose structure was established by acetic acid catalysed hydration to the known urea **6**.[1] The dry residue was, alternatively, subjected to hydration without preliminary purification by TLC and thereby furnished 51% of **6**. Prolonged refluxing of the carbodiimide in toluene caused polymerisation of **5**. No carbodiimide band was present in the IR spectrum of the polymeric product. Since dimeric and trimeric carbodiimides are rather well known,[3] the structure of our product was not investigated in detail.

The most important bands, diagnostic for its structure, in the IR spectrum of compound **A** were the following: 3240 (NH), 2245 (C≡N), 825, 760 and 700 cm^{-1} (*p*-di- and mono-substituted benzene ring, respectively). The presence of these bands allowed us to assign either **7** or **8** as the structures of **A**. The NMR spectrum exhibited only aromatic proton signals and, depending on the conditions, a broad NH signal but *no* signal due to the presence of a diaryl-methyl proton, this fact being sufficient for elimination of structure **8**. Support for structure **7** came from the mass spectrum which displays a group of fairly abundant peaks at *m/e* 192, and 190. The first of these corresponds to elimination of C_6H_4NHCN from the molecular ion while the second peak is due to ions formed by hydrogen loss from the *m/e* 192 ion. Elimination of the C_6H_4NHCN fragment from the molecular ion of **8** appears rather unlikely whereas, in the case of **7**, the corresponding cleavage should proceed easily.

Final proof of structure **7** was obtained by a three step degradation of **A** through **9** and **10** to **11** which was identified, in form of its hydrochloride, by comparison with an authentic sample prepared essentially according to literature.[4] The transformation **10**→**11** deserves some comment: it has been achieved by reduction with sodium and ethanol, in analogy to the method used by Biltz for the transformation of cyanotriphenylmethane into triphenylmethane.[5]

The formation of the two isomerization products **5** and **7** may be rationalized by assuming hetero- or homolysis of the central CN single bond of **1** (in Scheme 1 only the heterolysis of this bond has been depicted) and subsequent recombinations of the resulting mesomeric ion or radical pairs.

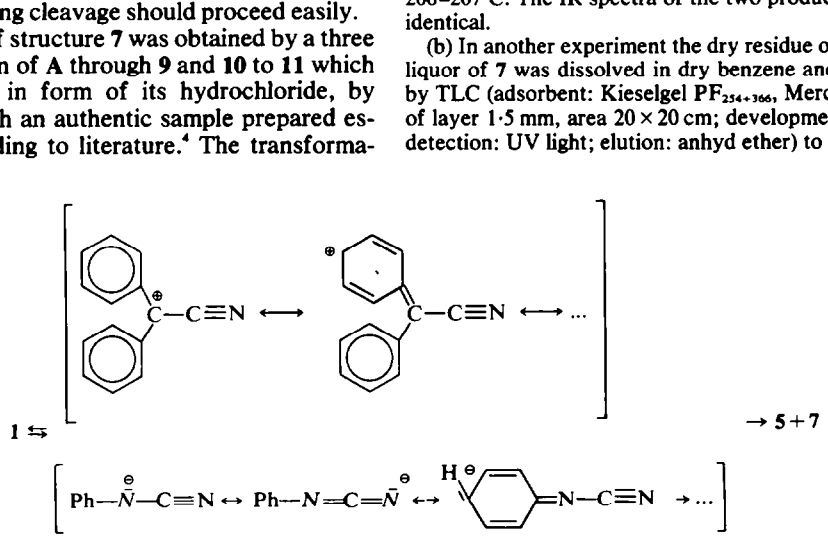
EXPERIMENTAL

Thermolysis of N-*cyano*-N-(*α*-*cyanobenzhydryl*)-*aniline* (**1**)

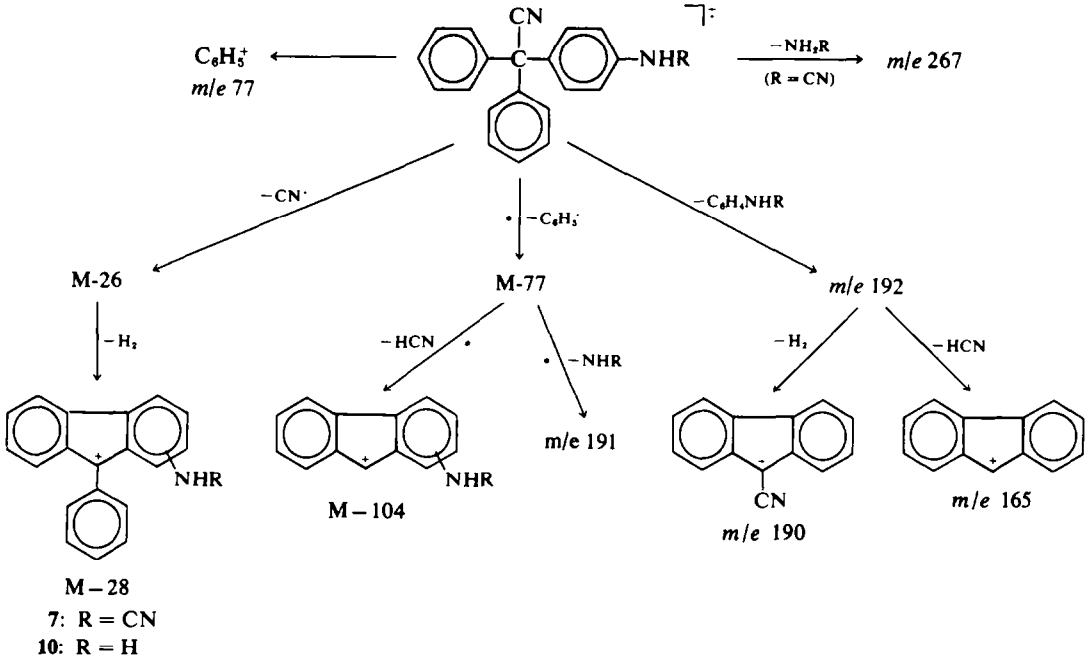
(a) A mixture of **1**[1] (1·0 g; 3·2 mmoles) and anhyd toluene (50 ml) was refluxed for 1 hr. The resulting soln was allowed to cool and light petroleum (350 ml) was added. The mixture was kept overnight in a refrigerator to yield **7** (0·24 g; 24%), m.p. 185–186° from aqueous MeOH. (Found: C, 81·32; H, 5·14; N, 13·24. Calc for $C_{21}H_{15}N_3$ (309·37): C, 81·53; H, 4·89; N, 13·58%); IR spectrum (KBr): see theoretical part; NMR (DMSO-d_6): ArH δ 7·75–6·83, m; NH δ 4·95 ppm, b; MS (direct insertion at 120°C): *m/e* 309 (100%, M); 283 (2·5%, M-26); 282 (3·8%); 281 (2·9%); 267 (10·0%, M-42); 240 (4·8%); 232 (88·5%, M-Ph); 205 (12%, M-104); 192 (10·6%, M-117); 191 (19·6%); 190 ($C_{14}H_8N$, 28·8%); 165 (29·1%, $C_{13}H_9$); 77 (6·1%); 51 (7·6%). Metastable peaks corresponding to the following processes were observed: $267 \xrightarrow{-27} 240$; $232 \xrightarrow{-27} 205$; $309 \xrightarrow{-77} 232$; $232 \xrightarrow{-41} 191$. The most important fragmentation modes are shown in Scheme 2.

The mother liquor of the crude **7** was evaporated to dryness *in vacuo* (bath temp: 60°) to yield an oily product. This was dissolved in benzene (9 ml); 96% AcOH (3 ml) was added and the mixture was stirred at r.t. for one day to yield crystalline **6** (0·54 g; 51%), m.p. and mixed m.p. with an authentic sample:[1] 205–206° (EtOH), lit. m.p.:[1] 206–207°C. The IR spectra of the two products were also identical.

(b) In another experiment the dry residue of the mother liquor of **7** was dissolved in dry benzene and worked up by TLC (adsorbent: Kieselgel $PF_{254+366}$, Merck, thickness of layer 1·5 mm, area 20 × 20 cm; development: benzene; detection: UV light; elution: anhyd ether) to yield 43% of



SCHEME 1



SCHEME 2

oily **5** which resisted all attempts of crystallization, IR (film): 2150 vs; 1600 w; 1500 w; 1460 w; 760 m, 700 m.

(c) Prolonged refluxing of the above carbodiimide in toluene and addition of light petroleum furnished a crude product which was recrystallized from DMF-MeOH to yield polymeric material, m.p. 242–244° (DMF-MeOH). IR (KBr): 3020 w; 1630 b, vs; 1600; 1500 s; 1450 s; 1390 m; 1240 s; 860 m; 755 s; 690 s.

MS (direct insertion): evaporation did not take place up to 180°C. In the spectrum obtained at about 190°C the mass number of the highest peak (*m/e* 309) corresponded to the molecular weight of the monomer. At about 200°C low intensity peaks were observed above *m/e* 600. Apparently thermal degradation of the polymer takes place at these elevated temperatures.

N-[p-(α-*Cyanobenzyldryl*)*phenyl*] *urea* (**9**). A mixture of **7** (0.36 g; 1·2 mmoles) and AcOH (10 ml) was refluxed for 15 min. Water was added to precipitate crystalline **9** (0·32; 84%), m.p. 226–227° from aqueous MeOH. (Found C, 76·99; H, 5·29; N, 12·74. Calc for $C_{21}H_{17}N_3O$ (327·39): C, 77·04; H, 5·23; N, 12·84%). IR (KBr): 3500–3000 b, with local maxima at 3400, 3260, 3150 (ν NH); 2260 vw (ν C≡N); 1670 vs (Amide I); 820 m; 760 s and 700 s (aromatic γ C—H and γ C—C).

p-(α-*Cyanobenzhydryl*)-*aniline* (**10**). A mixture of **9** (0·16 g; 0·5 mmoles), 33% NaOH aq (3 g) and 1,2-ethanediol (7 ml) was refluxed for 3 hr. The resulting soln was diluted with water to yield, after cooling, crystalline **10** (0·13 g; 93%), m.p. 181–182° from aqueous MeOH or gasoline.

The elemental composition ($C_{20}H_{16}N_2$) was established by high resolution mass spectrometry.

MS (direct insertion at 150°): *m/e* 284 (80%, M); 258 (3%, M-26); 256 (2%, M-28); 207 (100%, M-77); 192 (2%, M-92); 190 (8%); 180 (13%); 164 (7%); 77(3%). Metastable peaks have been observed for the following processes: 207 $\xrightarrow{-27}$ 180; 284 $\xrightarrow{-77}$ 207. The most important fragmentation modes are shown in Scheme 2.

IR 3430 + 3330 (ν NH_2); 2250 vw (ν C≡N); 820 m, 755 s and 695 s (aromatic γ C—H and γ C—).

p-*Aminotriphenylmethane hydrochloride* (**11**·HCl)

(a) Metallic Na (0·3 g; 12·5 mmoles) was added in three portions to a continuously stirred soln of **10** (80 mg; 0·3 mmoles) in EtOH (5 ml), the second and third portions of the metal being added after the previous portions had completely dissolved. About 5 hr were required in order that the total amount of the metal dissolved. The resulting thick paste was evaporated to dryness. Water (20 ml) and benzene (10 ml) were added, and the aqueous layer was extracted with two additional portions (10 ml, each) of benzene. The combined benzene solns were dried over $MgSO_4$, and a stream of dry HCl was introduced. The mixture was evaporated to dryness and recrystallized from a 1:4 mixture (v/v) of EtOH and conc HCl to yield 30 mg (36%) of **11**·HCl, m.p. 157–158°, identical according to m.p., mixed m.p. and IR spectra with an authentic product obtained as described under (b).

(b) *p*-Nitrotriphenylmethane[4] (1·5 g; 5·2 mmoles) was reduced in the presence of a Pd/C catalyst (about 1 g) in a mixture of EtOH (50 ml), benzene (10 ml) and conc HCl (10 ml) at 760 Torr and r.t. The catalyst was removed, and the resulting soln was evaporated to dryness. The residue was recrystallised as described above to yield **11**·HCl (0·8 g; 52%), m.p. 157–158° from benzene-ether. (Found: Cl, 11·91; N, 4·81. Calc for $C_{19}H_{18}ClN$ (295·81): Cl, 11·98; N, 4·75.) IR (KBr): 2850 b, vs; 2550, s; 2000 b, m; 1520 + 1500 d, m; 820 m; 760 m; 740 s; 730 m; 710 s.

The reduction of the nitro derivative has been described in literature but the m.p. of the hydrochloride of the resulting **11** ("turns brown at 100°")[4] is erroneous.

Mass spectra were obtained at an electron energy of 70 eV with the aid of an AEI MS-902 mass spectrometer equipped with a direct sample insertion system. The exact mass measurements were carried out with an accuracy of 2 ppm. The NMR spectra were obtained at 60 MHz with the aid of a Varian A60D spectrometer using TMS as internal reference.

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