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NEW REARRANGEMENT REACTIONS AS REVEALED IN DECOMPOSITION OF 3-BENZYL-3-CYANOINDAZOLE

Robert E. Bernard and Harold Shechter

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

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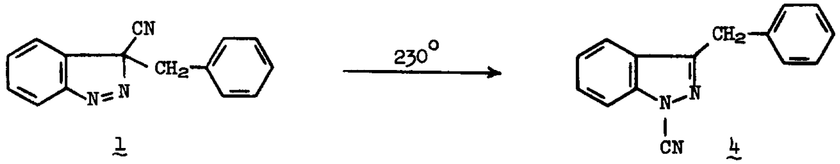
3,3-Disubstituted indazoles decompose via diazo and subsequent carbenic processes to benzocyclopropenes and/or their isomers.[1] We now report the decomposition of 3-benzyl-3-cyanoindazole (1) in efforts to develop a synthesis of benzylidenebenzocyclopropene (3) from 1-benzyl-1-cyanobenzocyclopropene (2). Thermolysis of 1 however results primarily in



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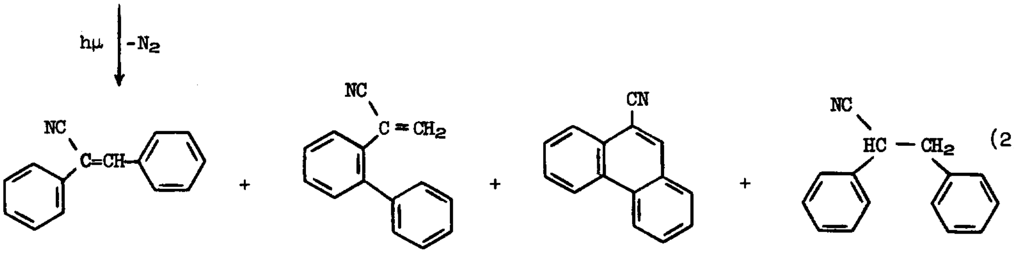
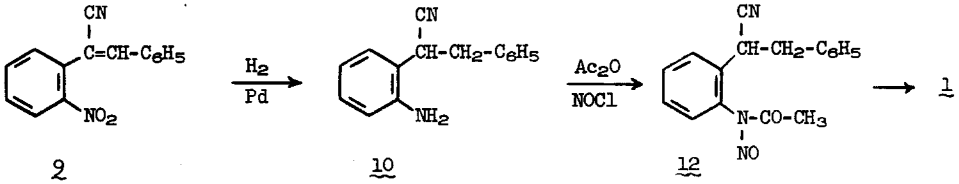


(2)

5a, cis
5b, trans
6 7 8

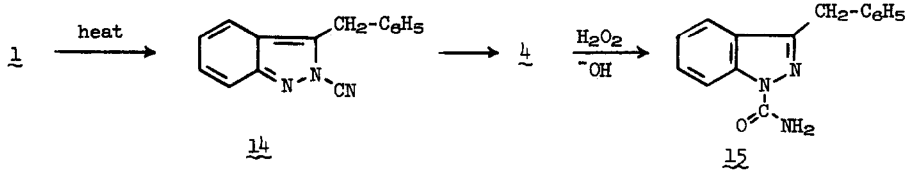
1,3-rearrangement of its cyano group to yield 3-benzyl-1-cyanoindazole (4, Eq 1), whereas photolysis of 1 leads to loss of nitrogen and formation of cis and trans-2,3-diphenylacrylonitriles (5a and 5b), o-phenylatroponitrile (6), 9-cyanophenanthrene (7), and 2,3-diphenylpropionitrile (8).[1e] Thermal conversion of 1 to 4 is the first example of rearrangement of an isolable 3,3-disubstituted indazole.[1e] Photolysis of 1 to 5a, 5b, and 6 however involves carbenic processes in which there are hydrogen migration and novel phenyl migration of the 1,4-type. Formation of **7** from **1** is also of note in that carbenic ring closure at the *ortho* position of the benzyl group and dehydrogenation are involved.

Indazole **1** (mp 99-101°)[2a,b] was prepared (Eq 3) from 2-(*o*-nitrophenyl)-3-phenylacrylonitrile (**9**)[2c] by (1) hydrogenation over palladium in ethanol at 25° to give 2-(*o*-aminophenyl)-3-phenylpropionitrile (**10**, 29%)[2d] which was acetylated to 2-(*o*-acetamidophenyl)-3-phenylpropionitrile (**11**, mp 142-144°),[2a,b] (2) nitrosation of **11** by nitrosyl chloride at 5° in acetic anhydride-acetic acid-sodium acetate, and (3) isomerization of 2-(N-nitroso-*o*-acetamidophenyl)-3-phenylpropionitrile (**12**) *in situ* in wet chloroform at 25° and cyclization (21%). The structure of **1**[2f] was established by its spectra and its conversion by alkaline hydrogen peroxide to 3-benzylindazole (**13**, 82%).[2g]



(3)

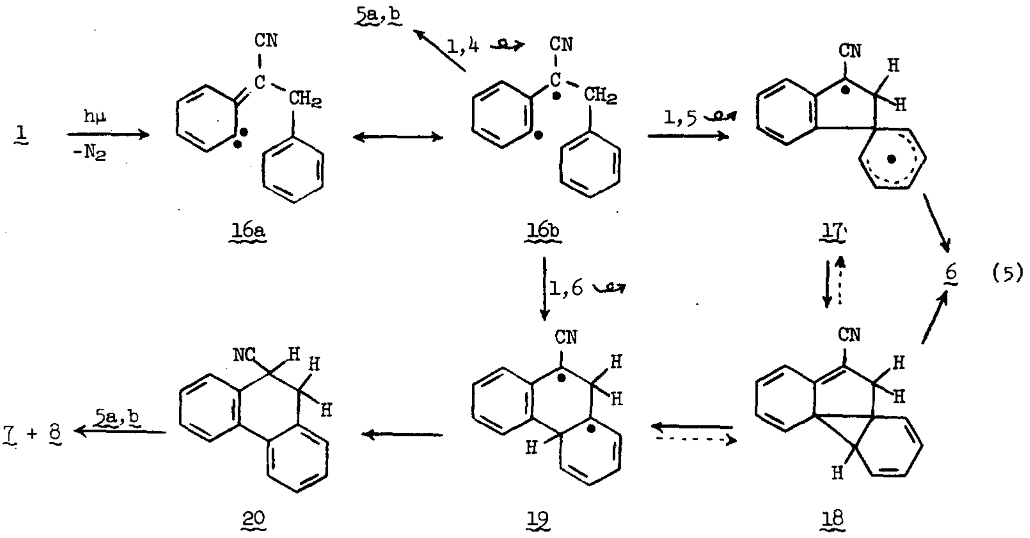
Thermolysis of **1** in diphenyl ether[3a] occurs above 230° to give its N-cyano isomer **4** (89%, Eq 1); **5b** (3%) and **8** (8%) are also formed as will be discussed. Indazole **4** is assigned the structure indicated rather than 3-benzyl-2-cyanoindazole (**14**, Eq 4) from its conversion by alkaline hydrogen peroxide to 3-benzyl-1-indazolecarboxamide (**15**, Eq 4; mp 199°), by the similarity of the ultraviolet absorption of **4** to **15** and other 3-substituted indazoles,[3b] and by the fact that **4** and **15** are not isomerized by heat. Rearrangement of **1** to **4** is thus analogous to the prior observation that azibenzil reacts with benzyne to give 1-benzoyl-3-phenylindazole instead of 3-benzoyl-3-phenylindazole.[1d] Although there is as yet no direct information with respect to the mechanism of isomerization of **1**, as will be seen in subsequent communications, it is likely that the reaction involves successive



(4)

1,2-rearrangements via 14 to 5 rather than 1,3-rearrangement.[3c] The thermodynamic factor leading to isomerization is the greater stability of 4 than of 14 than of 1.

Photolysis of 1 (Hanovia 450 watt lamp, Pyrex filter) in pentane at 25° and in ether at -70° results in extrusion of nitrogen to yield 5a (14, 11%), 5b (26, 47%), 6 (34, 20%), 7 (5, 3%), and 8 (5, 2%), respectively. The major products 5a and 5b result from 1,4-hydrogen migration[4a] (Eq 5) in the triplet[1b,c] (16b) and/or the prior singlet carbenes;



neither 2 nor 3 were observed. The result of particular novelty is transfer of the phenyl group to the carbenic site to give 6. Phenyl migration in 16a may be formalized as in 17 and/or via 18 (Eq 5) and thus the carbenic process is analogous to Ar_1-5 aryl participation and rearrangement in cationic systems.[4b,c] The conversion of 16a to 6 or to 18 and then 6 is of further note in that, upon dissection of the system, it indicates that there might be important topological interrelationships between 2,5-hexadien-1-ylidenes (21) and 1,3,5-cyclohexatriene (22) and bicyclo[3.1.0]hex-2-ene (23) systems.[4d]

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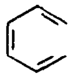

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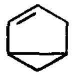

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Photolysis of 1 also results in minor oxidation-reduction to give 7 and 8 in near-equal quantities. Formation of 7 and 8 (Eq 2) might involve carbenic insertion to 19 or/and 18 followed by isomerization to 9-cyano-9,10-dihydrophenanthrene (20)[4e] which is disproportionated by 5a,b. Photolysis of 5a and 5b to 9-cyano-11,12-dihydrophenanthrene[4f] and dehydrogenation by 5a and 5b (even in the presence of oxygen[1e,4f]) did not occur sufficiently rapidly under the conditions for photolysis of 1 to account for 7 and 8. Conversion of 1 to 7 implies that carbenic processes involving Ar_1-6 phenyl participation may be mechanistically and synthetically important in appropriate systems.

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REFERENCES

1. (a) R. Anet and F. A. L. Anet, J. Amer. Chem. Soc., 86, 525 (1964); (b) G. L. Closs, L. R. Kaplan, and V. I. Bendall, ibid., 89, 3376 (1967); (c) G. Baum, R. Bernard, and H. Shechter, ibid., 89, 5307 (1967); (d) G. Baum, Ph.D. Thesis, The Ohio State University, Columbus, Ohio; Diss. Abstr., 27, 97B (1966); Chem. Abstr., 65, 20071g (1966); (e) R. E. Bernard, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1967; Diss. Abstr., 28, 4925B (1968); Chem. Abstr., 69, 86892b (1968).

2. (a) All new compounds reported gave satisfactory analyses; (b) the nmr, ir, uv, and mass spectra of all compounds described are consistent with their assigned structures;[2e] (c) J. D. London and G. Tennant, J. Chem. Soc., 3466 (1960); (d) 3-benzylindole (51%) and 3-cyano-1-hydroxy-2-phenylindole (6%) are also formed; (e) R. H. Cornforth and R. Robinson, ibid., 680 (1942); (f) a possible coupling product of 12 excluded by the structural proof is 4-cyano-3,4-dihydro-3-phenylcinnoline; (g) F. Hunziker, H. Lehner, O. Schindler, and J. Schmutz, Pharm. Acta. Helv., 38, 539 (1963).

3. (a) Similar results are obtained in biphenyl; (b) O. E. Polansky, E. Rieger, and G. Derflinger, Monatsch. Chem., 92, 1131 (1961); (c) T. Yamazaki and H. Shechter, completed work to be published.

4. (a) 1,4-Hydrogen migration occurs in decomposition of 6-carbomethoxy-3,3-dimethylindazole to 4-carbomethoxyisopropenylbenzene;[1a] (b) R. Heck and S. Winstein, J. Amer. Chem. Soc., 79, 3105 (1957); (c) R. J. Ouellette, R. Papa, M. Attea, and C. Levin, ibid., 92, 4893 (1970); (d) J. Meinwald and P. H. Mazzocchi, ibid., 89, 1755 (1967) and references therein; (e) it is possible that 20 decomposes in part to 7 thermally. 9,10-Dicarboximido-9,10-dihydrophenanthrene loses hydrogen on melting to give 9,10-dicarboximidophenanthrene; M. V. Sargent and C. J. Timmons, ibid., 85, 2186 (1963); (f) F. B. Mallory, J. T. Gordon, and C. S. Wood, ibid., 85, 828 (1963).