

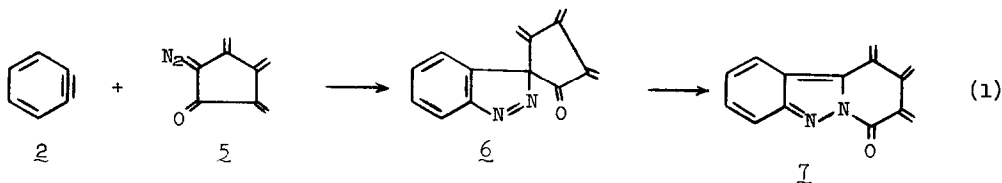
REARRANGEMENT, EXTRUSION, AND POLYMERIZATION REACTIONS UPON ADDITION OF ACETYLENES  
TO 3-DIAZOOXINDOLE AND SIX-MEMBERED RING  $\alpha$ -DIAZO KETONES

Tsuneyoshi Yamazaki and Harold Shechter

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

(Received in USA 6 November 1973; received in UK for publication 13 March 1973)

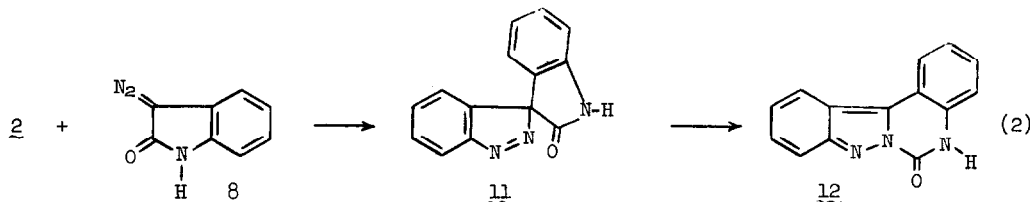
Azibenzil ( $C_6H_5-CN_2-CO-C_6H_5$ , 1) reacts with benzyne <sup>1a</sup>(2) at  $41^\circ$  to give 1-benzoyl-3-phenylindazole (4); the 1,3-dipolar adduct apparently formed, 3-benzoyl-3-phenylindazole (3), undergoes 1,3-migration or/and successive 1,2-rearrangements of its benzoyl group to yield 4 rather than loss of nitrogen and subsequent carbenic processes. <sup>1b</sup> 5-Membered ring  $\alpha$ -dialzo ketones (5) and 2 however give thermally stable 2-acylindazoles (7, Eq 1); in these systems, the 1,3-dipolar adducts (6) undergo spontaneous 1,2-rearrangement of their acyl moieties. <sup>1c,d</sup> A study is now reported of reactions of acetylene derivatives with 3-



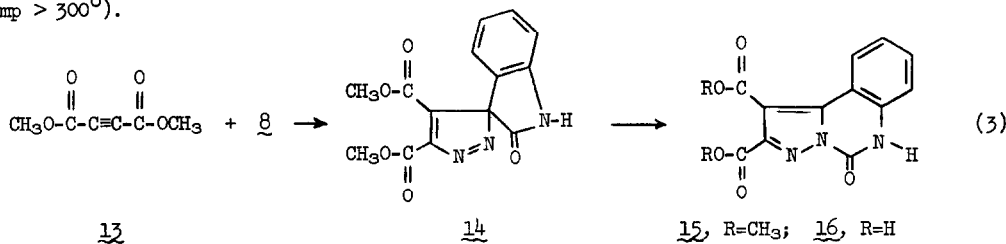
diazooxindole (8), phenanthrene-9,10-diazooxide (9), and 2-diazocyclohexanone (10). The research objectives were to (1) investigate the products and the mechanisms of the rearrangement, intermolecular, and/or decomposition reactions of the spiroindazoles and spiropyrazoles generated, and (2) obtain information which might lead to better understanding of the mechanisms of conversion of 3- and possibly 2-substituted indazoles to their 1-substituted isomers. <sup>1c</sup>

3-Diazooxindole (8) and benzyne <sup>1a</sup>(2, Eq 2) at  $41^\circ$  in dichloromethane yield 2-carbamoylindazole <sup>1e</sup>12 (yellow, 91%, mp  $> 300^\circ$ ,  $\nu_{C=O}$  at  $1740\text{ cm}^{-1}$ ). Adduct 11 could not be detected nor could 12 be isomerized. Migration of the carboxamido moiety in 11 to give 12 is the first example of sigmatropic[1,5] rearrangement of such a group. The structure of

12 was established by synthesis from 3-(o-nitrophenyl)indazole (yellow, mp 170-171°; prepared from o-nitrophenyldiazomethane and 2) by reduction with zinc and acetic acid to 3-(o-aminophenyl)indazole (white, 83%, mp 190-191°), and reaction with phosgene.<sup>1f</sup>

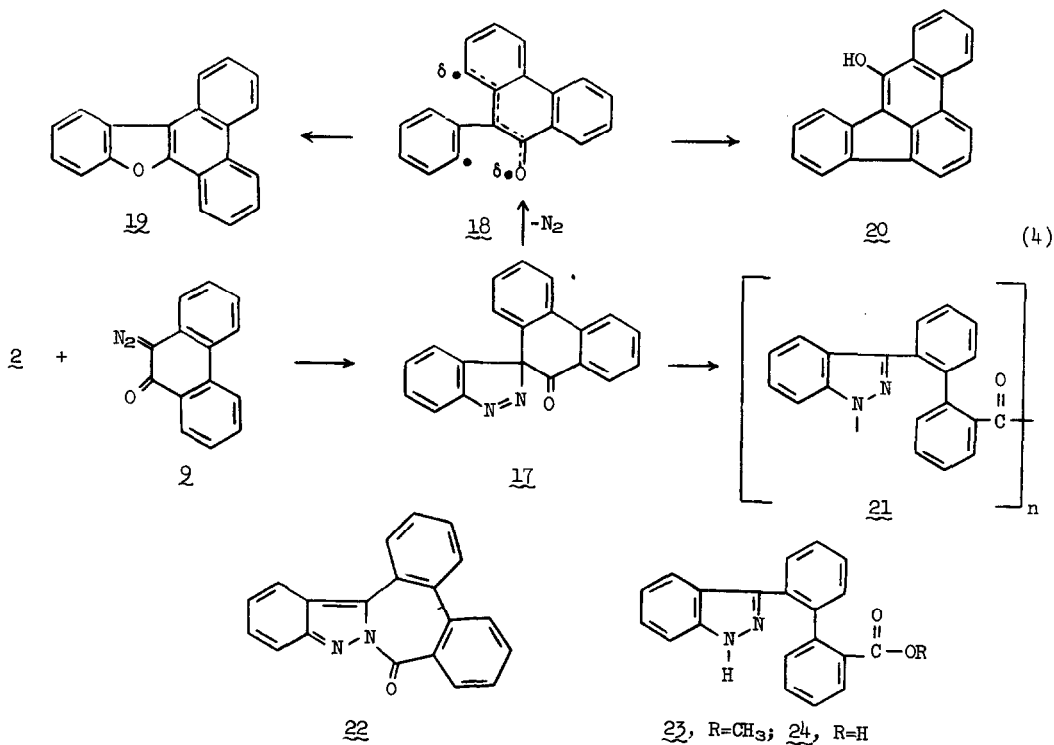


Reaction of 8 and dimethyl acetylenedicarboxylate (13) at 41° gives N-carbamoylpyrazole 15 (Eq 3, white, 83%, mp 249-250°). The result of interest is that in 14, a spiroindazole in which the nucleophilicity of the heterocyclic moiety is severely depressed, sigmatropic-[1.5] rearrangement of the carboxamido group occurs. Pyrazole 15 is thermally stable, and its structure is indicated by its carbamoyl carbonyl absorption at 1730-1740 cm<sup>-1</sup> and its acidic carbamoyl moiety (N-H), conversion by sodium methoxide to a salt which upon acidification regenerates 15, reaction with diazomethane to give isomeric N-methyl (white, mp 200°) and o-methyl derivatives,<sup>1g</sup> and base-catalyzed hydrolysis to dicarboxylic acid 16 (white, mp > 300°).



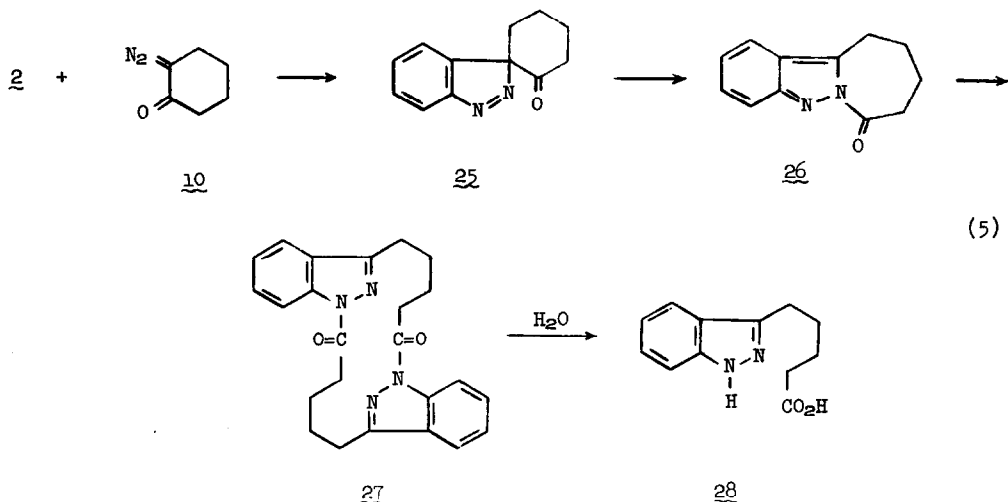
Phenanthrene-9,10-diazooxide (9) adds to 2<sup>1a</sup> (Eq 4) in dichloromethane at 41° to give 17 (white, 91%, mp 142.5-144°, >C=O at 1700 cm<sup>-1</sup>), the first example of an isolable 3-acyl-3-substituted indazole. Adduct 17 photolyzes (Hanovia medium pressure mercury lamp) in dichloromethane with 91% extrusion of nitrogen to yield furan 19 (white, 47%, mp 156°) and fluoranthene 20 (grey, 21%, mp 208.5). Coupling product 19 was identified by comparison with an authentic sample;<sup>1h</sup> 20 was assigned from its OH absorption (3500 cm<sup>-1</sup>), mass spectrum, and the similarity of its ultraviolet spectrum to that of fluoranthenes.<sup>1i</sup> Thermolysis of 17 in refluxing cumene or diglyme differs in part from photolysis in that along with formation of 19 (31-47%) and 20 (11-21%), nitrogen is retained and poly-N-acylindazole 21 (11-34%) is produced. 2-Acylindazole 22, the 1,2-rearrangement product of 17, could not be

prepared. Conversion of 17 to 21, though the resultant of internucleophilic processes, is analogous to conversion of 3 to 4<sup>1b</sup> and suggestive that the latter isomerization may not involve successive 1,2-rearrangements which are totally intramolecular. A further feature of 17 is its sensitivity to acid catalysis. Thus trifluoroacetic acid or boron trifluoride-etherate transforms 17 rapidly to 21 (~95%). Similarly methanolysis of 17 yields methyl ester 23 (white, mp 184°). Polymer 21 is a highly insoluble amorphous white solid (mp > 300°) whose carbonyl (1700 cm<sup>-1</sup>) and uv absorption are similar to that of 4. Base-catalyzed hydrolysis of 21 yields carboxylic acid 24; at ~ 300°, 23 and 24 are converted to 21.



Addition of 2-diazocyclohexanone (10) to 2 (Eq 5) in dichloromethane at 41° was studied in attempts to prepare 25 and/or 26. Capture of 2 by 10 is inefficient; however, the reaction product (27, white, 25%, mp 226.5°) is a dimer of 26. The structure of 27 is assigned from its analysis, molecular weight (calcd 400.46, found 400), carbonyl absorption at 1700 cm<sup>-1</sup>, the similarity of its ultraviolet absorption to that of 1-acetylindazole, and hydrolysis to ω-(3-indazolo)-pentanoic acid (28, white, 100%, mp 126°). Although the mechanism of

conversion of 2 and 10 to 27 is not known, it is likely that 25 and possibly 26 are involved. Conversion of 25 to 27 under such mild conditions is similar in type and possibly in mechanism to formation of 22 from 17 and reinforces the possibility that isomerization of 3 to 4 might not be the resultant of successive sigmatropic processes.



The factors involved in isomerization and intermolecular reactions of 2-acylindazoles are being presently studied.

Acknowledgment: The National Science Foundation and The National Institutes of Health are gratefully acknowledged for support of this investigation.

#### REFERENCES

- (a) As generated from benzenediazonium carboxylate, L. Friedman and F. M. Logullo, *Org. Syn.*, 48, 12 (1968); (b) G. Baum, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1965; *Diss. Abstr.*, 27, 97B (1966); (c) T. Yamazaki and H. Shechter, *Tetrahedron Lett.*, in press; (d) M. Franck-Neumann and C. Buchecker, *ibid.*, 937 (1972) have described related sigmatropic rearrangements of 3-substituted pyrazoles; (e) all new isolable compounds of the present work gave proper analyses and appropriate ir, uv, nmr, and mass spectra; (f) this new heterocycle synthesis appears to be of general applicability; (g) detected in solution by nmr methods; (h) J. N. Chatterjia, V. N. Mehrota, and S. K. Roy, *Chem. Ber.*, 96, 1156 (1963); (i) E. Clar, "Polycyclic Hydrocarbons," Vol. 2, Academic Press, London, 1964, Chapter 41.