

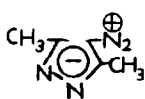
SOME ASPECTS IN REACTIVITY OF 4-DIAZO-3,5-DIMETHYLPYRAZOLE

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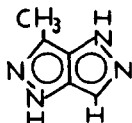
Reactivity of 4-diazo-3,5-dimethylpyrazole(I)² appealed to our interest, because the compound has the mesoionic structure. On the occasion of thermal treatment of I, the change of solvent brings the change of consequence. This feature is shown in Table 1. Structures of II,

Table 1

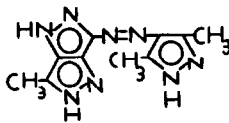
refluxed in	forming mainly	via	yield(%)
t-BuOH-AcOH	II ³ , m.p.236-237°(sublimation)	intramolecular coupling	70
t-BuOH	III, over m.p.300°(H ₂ O)	intra- and intermolecular coupling	45
EtOH	CH ₃ CHO	oxidation	85
C ₆ H ₆	IV, m.p.132-133°(dil.EtOH)	Gomberg-Bachmann reaction ⁴	38



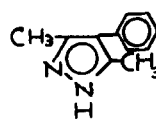
I



II



III

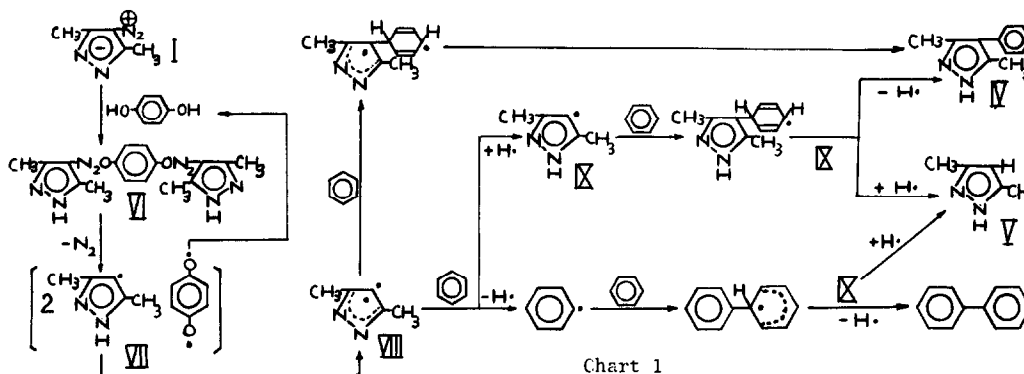


IV

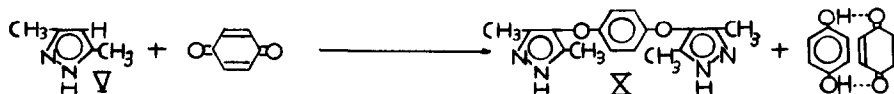
III and IV were supported by satisfactory microanalytical and the following spectral data. II: NMR(CD₃COCD₃) 2.32(3H,s,CH₃), 6.30(2H,b,NH) and 7.10 ppm(1H,s,CH); IR(KBr) 3166 cm⁻¹(NH); UVmax(EtOH) 223 and 265 nm(3.75). III: NMR(CD₃COCD₃) absent(CH), 2.44(3H,s,CH₃), 2.55(6H,s,CH₃) and 15.30 ppm(3H,b,NH); UVmax(EtOH) 221(4.03) and 360 nm(4.27). IV: NMR(CDCl₃) 2.35(6H,s,CH₃), 7.30(5H,m,C₆H₅) and 10.95 ppm(1H,bs,NH). Moreover, an additional proof was supplied for the structure of III by the observation that coupling of II with I in t-BuOH yielded III accompanying disappearance of the band due to CH in NMR.

To make a further progress in this study, our interest was concentrated on the Gomberg-Bachmann reaction⁴ of I which is explained fully as follows. By refluxing I in benzene for 14 hrs, the reaction afforded II, 3,5-dimethylpyrazole(V) and biphenyl in 15, 12 and 7 % yields respectively besides IV in 36 % yield⁵. Replacing benzene by nitrobenzene, the reaction gave 4-nitrophenyl-3,5-dimethylpyrazole in ratio of *o*-, *m*- and *p*-isomers 10:3:3⁶. This result as well as the formation of biphenyl suggests that the reaction proceeds probably through radical mechanism. The consideration of this nature of reaction was attributable to a later finding that addition of hydroquinone in 5 wt. % to quantity of I resulted in yield-up of IV by 32 % and reduction of reaction time by 13 hrs. In this case, hydroquinone was recovered almost quantitatively as a precipitate by concentration of the reaction mixture indicating catalytic nature of it and the products were separated from the mother liquor by column chromatography on silica gel. From these observations, a following deduction is speculatively drawn for the reaction

pathway⁷: Hydroquinone adds to the diazo compound(I) to form the diazonium salt(VI) which decomposes into 3,5-dimethylpyrazolediyl radical(VIII) with loss of nitrogen reproducing hydroquinone through disproportionation of a pair of radicals(VII). The biradical(VIII) thus generated captures benzene in different fashion. (a) When benzene adds to VIII, IV is formed. (b) When VIII attracts a hydrogen from benzene, 3,5-dimethylpyrazolyl radical(IX) and phenyl radical are produced, which pass into biphenyl,V and IV through attack to another molecule of benzene and then transference of H[•] to IX (see Chart 1). Actually, when both acetone solutions of I and an equimole of hydroquinone were combined and chilled, the diazonium salt(VI) was isolated as a precipitate: m.p.55-65°(decomp.);IR(nujol) 2180 cm⁻¹(-N≡N);Anal.Found:C,54.38; H,4.68;N,31.82. VI behaved in refluxing benzene analogously to the scheme shown in Chart 1. These findings offer a support for the deduction described above.



Benzoquinone also functions catalytically like hydroquinone. This may be attributable to the formation of quinhydrone by reaction of benzoquinone and V which is involved in the diazo compound(I) in a slight quantity, because *o,o'*-di-4(3,5-dimethylpyrazolyl)hydroquinone (X) and quinhydrone were formed from a mixture of benzoquinone and V by refluxing in benzene. X:Anal.Found:C,64.27;H,6.16;N,18.47. Colorless needles(AcOEt) of m.p.over300°(subl.).



References and Footnotes

- 1) To whom inquiries should be addressed.
- 2) H.P.Patel and J.M.Tedder, *J.Chem.Soc.*, 1963, 4589.
- 3) An analogous work: D.G.Farnum and P.Yates, *J.Am.Chem.Soc.*, 84, 1399(1962).
- 4) W.E.Eachmann and R.A.Hoffman, "Organic Reactions" Vol.2 ed. by R.Adams, John & Wiley and Sons, Inc., New York (1944) p.224.
- 5) After removal of precipitating II, other products existing in the mother liquor were isolated by chromatography on silica gel.
- 6) Isomer characterization was done by means of IR spectral data. *o*-Isomer; yellowish needles of m.p.189-190°(C₆H₆), IR(KBr) 785 cm⁻¹. *p*-Isomer; yellowish needles of m.p. 194-196°(CHCl₃-Et₂O), IR(KBr) 852 cm⁻¹. Isomer ratio was measured by gas chromatography.
- 7) Of course, discussion on more reliable standpoint must be needed in future, because there are no positive evidences for generation of such radicals as proposed and for exclusion of other possible reaction mechanisms.