STUDIES ON THE SCHIFF BASES - ENAMINES EQUILIBRIUM (1)

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The possibility of Schiff bases to react in the enamine form, previously observed in some acylations (2, 3, 4) and other reactions (5, 6), has now been investigated by means of two typical reagents of the enamine function: p-nitrophenyl-azide and tosyl-azide.

The following Schiff bases were examined: N-(ethylide-ne)-propylamine; N-1-(propylidene)-propylamine; N-2-(propylidene)-propylamine; N-2-(bu-tylidene)-propylamine; N-1-(butylidene)-propylamine; N-2-(butylidene)-propylamine; N-2-(pentylidene)-propylamine and N-3-(pentylidene)-propylamine. I.R. and N.M.R. studies on these substances are in favour for their Schiff bases structures; the existence of enamine forms must however be taken into account since from the reaction with p-nitrophenyl-azide and tosyl-azide aminotriazolines and amidines respectively were obtained in high yields. (Both aminotriazolines and ami-

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dines represent the normal reaction products of the above reagents with enamines (9, 10)). The reactions are carried with a molar ratio 1:1 in CHCl₃ at the boiling point of the mixture. Reaction times of 4-8 hours are required with 4-nitrophenylazide. With tosylazide heating was continued until no more N₂ was evolved (2-3 hours). The reactions are thus exemplified in the case of N-1-(propylidene)-propylamine:

A peculiar behaviour was observed in the case of N-2-(propylidene)-propylamine which with 4-nitrophenyl-azide yielded 1-propyl-5-methyl-v-triazole and 4-nitro-aniline:

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REFERENCES

- (1) 16th paper by this laboratory on enamine chemistry.
- (2) V. E. Haury, E. Cerrito and S. A. Ballard, <u>U. S. Patent 2,418,173</u>.
- (3) N. V. de Bataafsche Petroleum Maatschappij, <u>Brit. Patent 638,091</u>.
- (4) J. Moszew, A. Inasinski, K. Kubiczek and J. Zawrzykraj, Roczniki Chem., 34, 1169 (1960); Bull. Acad. Polon. Sci., 8, 405 (1960); J. Moszew, A. Inasinski, and J. Boksa, Ibid., 8, 409 (1960); J. Moszew and A. Inasinski, Ibid., 8, 413 (1960); J. Moszew, J. Bojarski and A. Inasinski, Ibid., 8, 417 (1960); J. Moszew, Z. Wilkos and U. Zieba, Ibid., 12, 511 (1964).
- (5) K. Alder and G. Stein, Ann., 501, 1 (1933).
- (6) R. W. Layer, "The Chemistry of Imines" in <u>Chem. Rev.</u>, 63, 489-510 (1963).
- (7) R. Tiollais, Bull. soc. chim. Fr., 1947, 708.
- (8) D. G. Norton, V. E. Haury, F. C. Davis, L. J. Mitchell and S. A. Ballard, <u>J. Org. Chem.</u>, <u>19</u>, 1054 (1954).
- (9) R. Fusco, G. Bianchetti, D. Pocar and R. Ugo, <u>Gazz</u>. <u>chim. ital.</u>, <u>92</u>, 1040 (1962); <u>Chem. Ber.</u>, <u>96</u>, 802 (1963).
- (10) R. Fusco, G. Bianchetti and D. Pocar, <u>Gazz. chim. ital.</u>, <u>91</u>, 849, 933 (1961).