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# CARBON SUBOXIDE AND SOME OF ITS REACTIONS

## XXIV. Reaction of Carbon Suboxide with 2-Aminobenzimidazoles*

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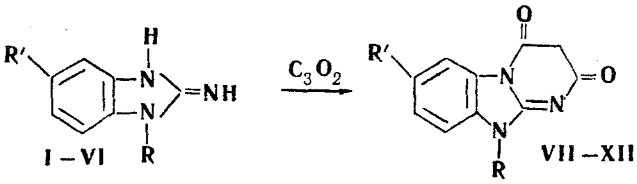
Reaction of carbon suboxide with some 2-aminobenzimidazoles is investigated, and some corresponding 2, 3-(dioxotetrahydropyrimido) benzimidazoles obtained, which arylate to enol form derivatives.

Previous research showed that carbon suboxide reacts with a number of compounds which exhibit amine-imine tautomerism to give a number of condensed heterocyclic systems containing the dioxotetrahydropyrimidine ring [1, 2, 3]. It was assumed that 2-aminobenzimidazoles would also react similarly. It is also known that 2-aminobenzimidazoles (2-aminonaphthimidazoles) react with a number of 1, 3-dicarbonyl compounds to give condensed systems comprising imidazole and pyrimidine rings [4]. As was assumed, carbon suboxide reacts with aminobenzimidazoles according to the following equation



I, VII R=R′=H; II, VIII R=H, R′=$CH_3$; III, IX R=$CH_3$, R′=H;
IV, X R=$C_2H_5$, R′=H; V, XI R=$C_3H_7$, R′=H; VI, XII R=$C_4H_9$, R′=H.

Reaction of carbon suboxide with 2-aminobenzimidazole (I), 2-amino-5-methylbenzimidazole (II), 1-methyl-2-aminobenzimidazole (III), 1-ethyl-2-aminobenzimidazole (VI), 1-n-propyl-2-aminobenzimidazole (V), and 1-n-butyl-2-aminobenzimidazole (VI) gives the corresponding compounds VII-XII.

Compounds Prepared

| Compound number | Decomp temp °C | Formula | N, % | | Yield, % | p-Nitrobenzoate | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Found | Calc. | | Decomp temp °C | Formula | N, % | |
| | | | | | | | | Found | Calc. |
| VII | Over 310 | $C_{10}H_7N_3O_2$ | 20.65<br>20.62 | 20.89 | 92 | — | — | — | — |
| VIII | 283—285 | $C_{11}H_9N_3O_2$ | 19.22<br>19.31 | 19,53 | 85 | — | — | — | — |
| IX | 262—264 | $C_{11}H_9N_3O_2$ | 19.54<br>19.61 | 19,53 | 88 | 258—260 | $C_{18}H_{12}N_4O_5$ | 15,39<br>15.41 | 15.61 |
| X | 281—283 | $C_{12}H_{11}N_3O_2$ | 18.44<br>18.52 | 18.34 | 90 | 195—196 | $C_{19}H_{14}N_4O_5$ | 14.89<br>14.72 | 14,81 |
| XI | 253—255 | $C_{13}H_{13}N_3O_2$ | 17.00<br>17.05 | 17.28 | 85 | 177—178 | $C_{20}H_{16}N_4O_5$ | 14,31<br>14.34 | 14.28 |
| XII | 245—246 | $C_{14}H_{15}N_3O_2$ | 16.17<br>16.28 | 16.34 | 86 | 168—169 | $C_{21}H_{18}N_4O_5$ | 13.57<br>13.62 | 13.79 |

The structures of the compounds synthesized are based on analytical data, the general chemical similarity of the reaction with carbon suboxide, and IR spectra. The presence in the IR spectra of absorption bands in the 1670-1680 $cm^{-1}$ region (tertiary amide) checks the structures of compounds VII-XII.

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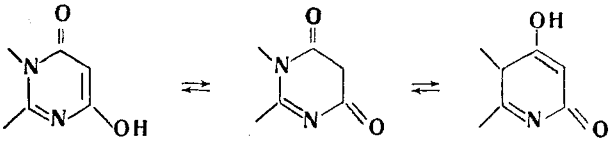
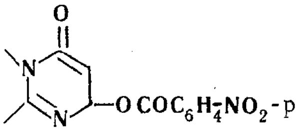
°For Part XXIII see [3].

The known occurrence of keto-enol tautomerism in the pyrimidothiazole system was a reason for assuming that this kind of tautomerism also exists in a pyrimidobenzimidazole system. Possible enol structures are A and B



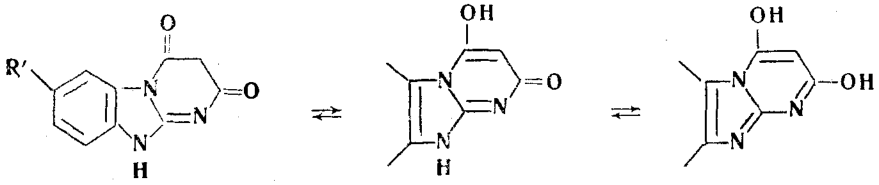
A B

It is found that compounds IX-XII react with p-nitrobenzoyl chloride to give the p-nitrobenzoates of the appropriate enol form.



The structure put forward for these compounds follows from the elementary analyses and IR spectra, the latter exhibiting absorption in the 1720-1730 $cm^{-1}$ region (ester group), as well as from the chemical properties. Hydrolysis of the p-nitrobenzoates gives IX-XII and p-nitrobenzoic acid.

The existence of dienol forms of VII and VIII is not excluded



However, acetylation of compounds VII-VIII gave products whose structures could not be determined.

## Experimental

Carbon suboxide was prepared as previously described [5], and led directly from the pyrolysis furnace into solutions of the 2-aminobenzimidazoles I-VI, prepared by known methods and whose physical properties corresponded to those reported in the literature [6-10].

Compounds VII-XII (table) were prepared by a general method. 0.5 g amine (I and II) was dissolved in acetone-benzene (1:3) and compounds III-VI in benzene. A steady stream of carbon suboxide was passed in at 60-70° C which gave rise to a corresponding formation of a pink precipitate, which was washed on the filter paper with ether. The product yields are given in the table. EtOH was used for recrystallizing. Crystallization alone was sufficient for purification of compounds VII-VII. For analysis, the latter were precipitated with AcOH from alkaline solution, then recrystallized from EtOH. Compounds VII-XII were readily soluble in alkalies, but insoluble in most organic solvents.

To prepare the p-nitrobenzoates, 0.1 g Na was dissolved in dry EtOH, an equivalent amount of the compound IX-XII added, and the mixture warmed gently until solution was complete. All the EtOH was vacuum-distilled off, dry benzene was added, followed by a slight excess of p-nitrobenzoyl chloride. The suspension was heated for 2 hr on a water-bath. The solution was filtered, and the benzene completely evaporated to leave a dry residue which was semi-liquid; this solidified on adding MeOH. The yellow products were recrystallized from MeOH, yield 60-70%. The p-nitrobenzoates were also prepared without adding NaOEt, but the yields were somewhat less.

## REFERENCES

1. L. B. Dashkevich, ZhOKh, 31, 3757, 1961.
2. L. B. Dashkevich and E. S. Korbelainen, ZhOKh, 34, 3427, 1964.
3. L. B. Dashkevich and E. S. Korbelainen, KhGS [Chemistry of Heterocyclic Compounds], p. 595, 1965.
4. W. Reid and W. Muller, J. pr. Chem., 8, 132, 1959.

5. L. B. Dashkevich, V. A. Buevich, and B. E. Kuvaev, ZhOKh, 30, 1946, 1960.
6. C. Giunio and P. Giulio, Gazz. chim. ital., 65, 38, 1935.
7. P. Pierron, Ann. Chim. et Phys., 15, 189, 1908.
8. A. M. Simonov and N. D. Vitkevich, ZhOKh, 30, 590, 1960.
9. A. M. Simonov and A. D. Garnovskii, ZhOKh, 31, 114, 1961.
10. A. M. Simonov and A. F. Pozharskii, ZhOKh, 31, 3970, 1961.

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