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SYNTHESIS OF 3-METHYL-7-PHENYLIMIDAZO-[1,2-*b*]-1,2,4-TRIAZINE

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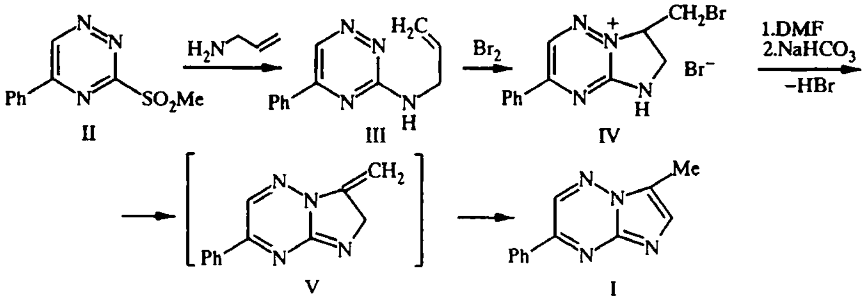
*The bromocyclization of 3-allylamino-5-phenyl-1,2,4-triazine gives 3-bromomethyl-7-phenyl-2,3-dibromo-1H-imidazo[1,2-*b*]-1,2,4-triazinium bromide, which is transformed into 3-methyl-7-phenylimidazo-[1,2-*b*]-1,2,4-triazine.*

Some imidazo[1,2-*b*]-1,2,4-triazines have shown intense luminescence and the capacity to generate laser emission [1-3]. Two major approaches have been developed for the synthesis of such compounds based on the reaction of α-diketones with 1,2-diaminoimidazoles and the condensation of 3-amino-1,2,4-triazines with α-haloketones [4].

In the present communication, we report a new approach for the synthesis of imidazo[1,2-*b*]-1,2,4-triazine derivatives using the preparation of 3-methyl-7-phenylimidazo[1,2-*b*]-1,2,4-triazine (I) as an example. Thus, the replacement of the methylsulfonyl group in 3-methylsulfonyl-5-phenyl-1,2,4-triazine (II) by the action of allylamine in THF gives 3-allylamino-5-phenyl-1,2,4-triazine (III), whose bromocyclization leads to 3-bromomethyl-7-phenyl-2,3-dihydro-1H-imidazo[1,2-*b*]-1,2,4-triazinium bromide (IV). Heating IV in DMF at reflux with subsequent treatment with saturated aqueous sodium bicarbonate leads to imidazo[1,2-*b*]-1,2,4-triazine I. The process likely occurs through the intermediate formation of methylene derivative (V).



The structure of imidazotriazine I was indicated by PMR spectroscopy and elemental analysis.

EXPERIMENTAL

The PMR spectra were taken on a Bruker WP-80 spectrometer at 80 MHz with TMS as the internal standard.

A sample of 3-methylsulfonyl-5-phenyl-1,2,4-triazine was obtained according to Rykowski [5].

3-Allylamino-5-phenyl-1,2,4-triazine (III). A sample of 0.32 ml (4.5 mmoles) allylamine was poured into a solution of 1 g (4.25 mmoles) 3-methylsulfonyl-5-phenyl-1,2,4-triazine in 10 ml abs. THF and the mixture was stirred for 12 h. The reaction mixture was then poured into 50 ml water. The yellow precipitate formed was filtered off and recrystallized from hexane to give 0.76 g (85%) III, mp 112-114°C. PMR spectrum in $CDCl_3$: 3.90-4.10 (2H, m, NCH_2), 5.10-5.55 (2H, m, CCH_2), 5.80-6.30 (1H, m, CH), 7.30-7.75, 7.90-8.20 (5H, m, Ph), 9.05 ppm (1H, s, 6-H).

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3-Bromomethyl-7-phenyl-2,3-dihydro-1H-imidazo[1,2-*b*]-1,2,4-triazinium Bromide (IV). A solution of 0.32 ml (6.2 mmoles) bromine in 15 ml ether was added dropwise with stirring to a solution of 1.05 g (6.2 mmoles) triazine III in 15 ml ether over 1 min. After 10 min, the precipitate was filtered off and washed with 10 ml acetone to give 1.54 g (79%) III, mp 210-212°C (dec.). PMR spectrum in CD_3CN: 3.90-4.08 (1H, m, H_{CH_2Br}), 4.12 (2H, d, J = 3.0 Hz, NCH_2), 4.30-4.49 (1H, m, H_{CH_2Br}), 5.65-5.76 (1H, m, 3-H), 7.55-7.90 and 8.30-8.60 (5H, m, Ph), 10.10 ppm (1H, s, 6-H).

3-Methyl-7-phenylimidazo[1,2-*b*]-1,2,4-triazine (I). A solution of 1 g (3 mmoles) bromide IV in 10 ml DMF was heated at reflux for 15 min. After cooling, the reaction mixture was poured into 40 ml saturated aqueous $NaHCO_3$. The crystalline precipitate was filtered off and recrystallized from ethanol to give 0.36 g (52%) I, mp 102-104°C. PMR spectrum in $CDCl_3$: 2.61 (3H, d, J = 1.1 Hz, CH_3), 7.40-7.60 and 8.10-8.30 (5H, m, m, Ph), 7.80 (1H, q, 2-H), 8.89 (1H, s, 6-H).

REFERENCES

1. M. V. Povstyanoi, V. P. Kruglenko, and V. F. Gachkovskii, Izv. Vyshh. Uchebn. Zaved. Khim. Khim. Tekhnol., **22**, 23 (1979).
2. V. P. Kruglenko, O. A. Logunov, A. V. Startsev, M. V. Povstyanoi, A. V. Startsev, and Yu. Yu. Stoilov, Kvant. Élektron., **7**, 2136 (1980).
3. V. S. Zuev, V. P. Kruglenko, O. A. Logunov, A. V. Startsev, M. V. Povstyanoi, A. V. Startsev, and Yu. Yu. Stoilov, Kvant. Élektron., **8**, 1567 (1981).
4. E. S. H. Ashry, N. Rashed, M. Taha, and E. Ramadam, Adv. Heterocycl. Chem., **59**, 39 (1994).
5. A. Rykowski, Pol. J. Chem., **57**, 631 (1983).