

## Selective *N*-Prop-2-ynylation of Heterocycles induced by Solid-Liquid Phase Transfer Catalysis without Solvent and Use of Solid Inorganic Supports

Hervé Galons,<sup>\*a</sup> Isabelle Bergerat,<sup>a</sup> Claude Combet-Farnoux,<sup>a</sup> Marcel Miocque,<sup>a</sup> Guy Decodts,<sup>b</sup> and Georges Bram<sup>b</sup>

<sup>a</sup> Laboratoire de Chimie Organique, U.A. CNRS 496, Avenue J. B. Clément, 92290 Châtenay-Malabry, France

<sup>b</sup> Laboratoire des Réactions sélectives sur support, U.A. CNRS 478, Université Paris-Sud, Batiment 410, 91405 Orsay, France

Complementary processes promote the *N*-prop-2-ynylation of heterocycles: solid-liquid phase transfer catalysis without added solvent in the presence or absence of alumina or titanium dioxide and alkylation on 'basic' alumina in 'dry media'.

*N*-prop-2-ynyl derivatives of heterocycles (**1**) are of interest but their usual synthesis by alkylation in basic media gives rise to low yields of (**2**), together with allenes (**3**) and alkynamines (**4**), compounds (**3**) and (**4**) being resonance stabilized.<sup>1</sup> Very recently, alkylation in dipolar aprotic solvents has been used more successfully.<sup>2</sup> Liquid-liquid phase transfer catalysis (P.T.C.) is efficient for *N*-prop-2-ynylation of imidazole derivatives<sup>3</sup> but when it is applied to imidazole itself, only allenylimidazole is obtained. With 9-acridone, the same procedure led to a mixture of allenyl (**3**) and prop-1-ynyl (**4**) compounds.<sup>4</sup>

We report that *N*-prop-2-ynyl derivatives (**2**) are selectively obtained when heterocycles are alkylated using solid-liquid P.T.C. without solvent,<sup>5</sup> or on 'basic' alumina in 'dry media' (*i.e.* in the absence of any organic solvent<sup>6,7</sup>). In some cases,

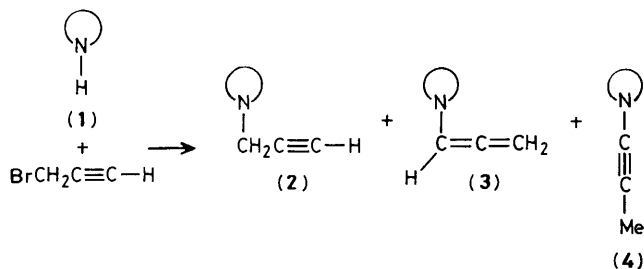
solid-liquid P.T.C. without solvent, in the presence of mineral oxides, works efficiently. The results of our experiments are summarized in Table 1.

In the alkylation of 9-acridone and benzimidazole, solid-liquid P.T.C. without any solvent exclusively leads to prop-2-ynyl derivatives (**2**), but variable amounts of allenyl isomers (**3**) are formed in the case of pyrrole, imidazole, and 2-methylbenzimidazole (expts. 1, 4, 12). The formation of alkynamines (**4**) is never observed. On the other hand, alkylation of heterocycles on 'basic' alumina in 'dry media' (expts. 9, 15) is always selective but appears to be less efficient (expt. 15). Furthermore, addition of small amounts of mineral oxides to the reaction medium during solid-liquid P.T.C. without solvent is noteworthy: silica reduces the yields (expt. 11) as previously reported in the case of indole alkylation;<sup>6</sup>

**Table 1.** Alkylation of heterocycles (1) by prop-2-ynyl bromide.

Experiment	(1)	Method <sup>a</sup>	Temp./°C	Yields/%	
				(2)	(3)
1	Pyrrole	A	20	20	46
2	Pyrrole	B	20	55	0
3	Indole	A	20	83	2
4	Imidazole	A	20	35	45
5	Imidazole	A	55	0	81
6	Imidazole	B	20	85	12
7	Imidazole	C	20	74	1
8	Imidazole	D	20	0	0
9	Imidazole	F	20	76	0
10	Benzimidazole	A	20	81	0
11	Benzimidazole	E	20	55	0
12	2-Methylbenzimidazole	A	20	45	34
13	2-Methylbenzimidazole	B	20	72	0
14	9-Acridone	A	20	95	0
15	9-Acridone	F	20	42	0

<sup>a</sup> Method A—E: reactions were carried out with equimolar amounts (10 mmol) of heterocycle, prop-2-ynyl bromide, and finely ground potassium hydroxide. Aliquat 336 (0.5 mmol) is the catalyst. A: solid-liquid P.T.C.; B: solid-liquid P.T.C. + alumina (1 g); C: solid-liquid P.T.C. + titanium dioxide (1 g); D: solid-liquid P.T.C. + zinc oxide (1 g); E: solid-liquid P.T.C. + silica (1 g). Method F: equimolar amounts of reagents (10 mmol) were impregnated<sup>7</sup> onto alumina (4 g).



alumina or titanium dioxide enhance the selectivity of the reaction, the yield being only slightly reduced (expt. 2, 6, 13). Zinc oxide completely inhibits the reaction, prop-2-ynyl bromide being converted to allenyl bromide. This property of zinc oxide to catalyse allene formation is well documented.<sup>8</sup>

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