Sulphonamidomercuration; a New Method for Amination of Olefins

By JOSÉ BARLUENGA,* CARMEN JIMÉNEZ, CARMEN NÁJERA, and MIGUEL YUS
(*Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Oviedo, Spain*)

Summary The addition of toluene-*p*-sulphonamide to olefins in the presence of anhydrous mercury(II) nitrate and subsequent sodium borohydride reduction leads to the corresponding *N*-alkyl-sulphonamides; the use of 1,4-

and 1,5-dienes yields saturated nitrogen-containing heterocycles, the synthesis of tosylated pyrrolidine being a stereoselective reaction.

The mercuration–demercuration of olefins in the presence of different nucleophiles has proved to be an excellent method for the Markovnikov functionalization of alkenes.[1] We have recently reported the first example of the addition of carboxamides to olefins using mercury(II) nitrate.[2] In our studies on mercuration reactions we have now discovered that toluene-*p*-sulphonamide ($TsNH_2$) is sufficiently nucleophilic for use in the mercuration of olefins and dienes using mercury(II) nitrate.†

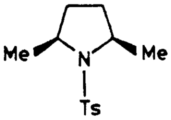
Thus, when toluene-*p*-sulphonamide was allowed to react with different olefins in the presence of anhydrous mercury(II) nitrate‡ in methylene dichloride followed by *in situ* demercuration with sodium borohydride in aqueous sodium hydroxide–n-butylamine, the corresponding *N*-substituted sulphonamides (**1**) were obtained. When hexa-1,4-diene and hexa-1,5-diene were used as starting materials in the same reaction a pyrrolidine derivative was obtained exclusively, the addition being stereoselective; n.m.r. data for this compound are in good agreement with the *cis*-structure (**2**) from comparison with data for the *N*-aryl-analogue.[3] The sulphonamidomercuration–demercuration of cyclo-octa-1,5-diene yielded a mixture of tosylated 9-azabicyclo[3.3.1]- and [4.2.1]-nonanes (**3**) and (**4**) (Scheme and Table).

$$R^1CH{=}CHR^2 + TsNH_2 \xrightarrow{\text{i,ii}} \underset{(\mathbf{1})}{TsNHCHR^1CH_2R^2}$$

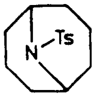
a: $R^1 = \text{n-}C_4H_9$, $R^2 = H$
b: $R^1 = \text{n-}C_5H_{11}$, $R^2 = H$
c: $R^1 = \text{n-}C_6H_{13}$, $R^2 = H$
d: $R^1 = Ph$, $R^2 = H$
e: $R^1\text{–}R^2 = -[CH_2]_3-$
f: $R^1\text{–}R^2 = -[CH_2]_4-$

SCHEME. i, $Hg(NO_3)_2$; ii, $NaBH_4$.

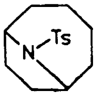
This synthesis, in our opinion, is of additional interest owing to the possibility of transforming the sulphonamides (**1**) into other nitrogen-containing systems;[4] for example, treatment of these compounds with sodium in liquid ammonia yields *N*-alkyl amines,[4] the method being an indirect way to add ammonia to alkenes.



(**2**)



(**3**)



(**4**)

TABLE. Synthesis of *N*-substituted toluene-*p*-sulphonamides (**1**)—(**4**).

Starting alkene	Product[a,b] (% yield)	% Yield[a] of Hg^0	M.p.,T/°C
Hex-1-ene	(**1a**) (52)	98	120—122[c]
Hept-1-ene	(**1b**) (46)	61	123—125[d]
Oct-1-ene	(**1c**) (74)	79	121—123[c,e]
Styrene	(**1d**) (31)	68	80—82[f]
Cyclopentene	(**1e**) (52)	99	81—83[g]
Cyclohexene	(**1f**) (66)	92	83—85[h]
Hexa-1,4-diene[i]	(**2**) (80)	99	98—100[d]
Hexa-1,5-diene	(**2**) (63)	97	"
Cyclo-octa-1,5-diene	(**3**) + (**4**)[j] (73)	90	146—147[k]

[a] Based on mercury(II) nitrate. Yields of isolated product before recrystallization have not been optimized. [b] All compounds reported gave i.r., ^1H n.m.r., and ^{13}C n.m.r. spectra in accord with the proposed structures. G.l.c. and n.m.r. data of the reaction products before recrystallization allowed us to exclude the existance of isomers different from (**1a**)—(**1d**) and (**2**). [c] From CCl_4. [d] From C_6H_{14}–$CHCl_3$. [e] Lit. (A. Nickon and A. S. Hill, *J. Am. Chem. Soc.*, 1964, **86**, 1152): b.p. 200 °C at 10 mmHg. [f] From EtOH–H_2O; lit. (M. B. Watson and G. W. Youngson, *J. Chem. Soc.*, 1954, 2145): m.p. 81—82 °C. [g] From $CHCl_3$; lit. (F. W. Bollinger, F. N. Hayes, and S. Siegel, *J. Am. Chem. Soc.*, 1953, **75**, 1729): m.p. 84 °C. [h] From MeOH; lit. (J. F. Carson, *J. Am. Chem. Soc.*, 1953, **75**, 4337): m.p. 85·7—86·4 °C. [i] *cis–trans*-Isomer mixture (Aldrich). [j] 44% (**3**), 56% (**4**) (^1H n.m.r.) (M. Barrelle and M. Apparu, *Tetrahedron*, 1977, **33**, 1309). [k] From MeOH.

In a typical reaction, anhydrous mercury(II) nitrate (Fluka; 10 mmol)§ was added to a stirred solution of the olefin (10 mmol) and toluene-*p*-sulphonamide (60 mmol) in methylene dichloride (30 ml) and the mixture was heated under reflux for 24 h. The mixture was cooled to 0 °C and then n-butylamine (10 ml), 10% aqueous sodium hydroxide (30 ml), and a solution of sodium borohydride (10 mmol)§ in 10% aqueous sodium hydroxide (10 ml) were added. The precipitated mercury(0) was filtered off, and the organic layer was separated from the filtrate and dried (Na_2SO_4). Finally, the solvents were removed and the residue recrystallized to yield the products (**1**)—(**4**).

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† The addition of $TsNH_2$ to olefins in the presence of mercury(II) acetate failed.

‡ The use of $Hg(NO_3)_2.H_2O$ leads to lower yields.

§ In the case of dienes 20 mmol were used.

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[2] J. Barluenga, C. Jiménez, C. Nájera, and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1981, 670.
[3] J. Barluenga, C. Nájera, and M. Yus, *J. Heterocycl. Chem.*, in the press.
[4] J. E. Bäckwall, K. Oshima, R. E. Palermo, and K. B. Sharpless, *J. Org. Chem.*, 1979, **44**, 1953.