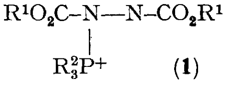
New Synthesis of Monosaccharide Carbonates

By GRZEGORZ GRYNKIEWICZ, JANUSZ JURCZAK, and ALEKSANDER ZAMOJSKI*
(*Institute of Organic Chemistry, Polish Academy of Sciences,* 01-224 *Warszawa, Poland*)

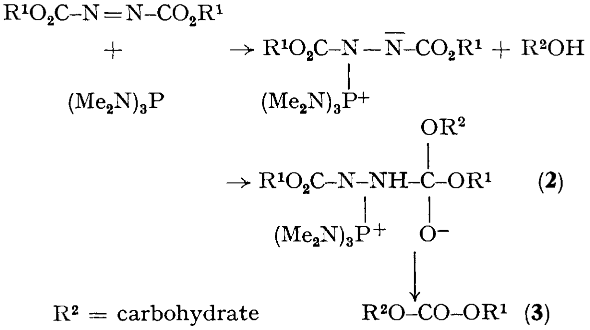
Summary A synthesis of mixed alkyl-carbohydrate carbonates from monosaccharides, tris(dimethylamino)phosphine, and dialkyl azodicarboxylates is described.

THE betaines (**1**)[1,2] formed from trivalent organophosphorus compounds and dialkyl azodicarboxylates are highly reactive intermediates easily undergoing reactions with various substrates, *e.g.* carboxylic acids,[3] malononitrile, and alcohols,[4] *etc.* Of particular interest is the reaction of (**1**; $R^1 = Et$, $R^2 = Ph$) with alcohols in the presence of imides, leading in one step to substituted imides.[5] This reaction appears to be a convenient preparative method for conversion of alcohols into amines.[5,6]


(**1**)

$$\underset{R^2_3P^+}{R^1O_2C\text{-}\underset{|}{N}}\text{—}\bar{N}\text{-}CO_2R^1$$

We report a new reaction involving betaine-type intermediates (**1**) and hydroxylic compounds. When monosaccharide derivatives containing "isolated" hydroxy-groups were treated in THF solution at room temperature with equimolar amounts of tris(dimethylamino)phosphine and dialkyl azodicarboxylate, mixed carbonates (**3**) were obtained in good yields.



$$R^1O_2C\text{-}N{=}N\text{-}CO_2R^1 + (Me_2N)_3P \rightarrow R^1O_2C\text{-}\underset{(Me_2N)_3P^+}{\underset{|}{N}}-\bar{N}\text{-}CO_2R^1 + R^2OH \rightarrow R^1O_2C\text{-}\underset{(Me_2N)_3P^+}{\underset{|}{N}}\text{-}NH\text{-}\overset{OR^2}{\overset{|}{\underset{O^-}{\underset{|}{C}}}}\text{-}OR^1 \quad (\mathbf{2}) \rightarrow R^2O\text{-}CO\text{-}OR^1 \quad (\mathbf{3})$$

R^2 = carbohydrate

The mechanism of the formation of carbonates from (**1**) ($R^2 = NMe_2$) is not clear at present. It seems however that a second betaine (**2**) formed from (**1**) and monosaccharide might be involved in the reaction.

In some cases compounds of type (**4**) were obtained.

$$R^1O_2C\text{–}NR\text{–}NH\text{–}CO_2R^1$$

(**4**)

The following carbonates have been obtained:† 1-*O*-ethoxycarbonyl-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose, yield 40% (51%)‡, 1-*O*-butoxycarbonyl-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose, 45% (35%), 3-*O*-ethoxycarbonyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, 77%, 6-*O*-ethoxycarbonyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose,§ 65% (5%), and 6-*O*-butoxycarbonyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose 65% (5%).

We feel that this method can be competitive, at least in some cases, with the classical one employing alkyl chloroformates and bases.[7]

(*Received*, 4*th February* 1974; *Com.* 151.)

---

† Correct elemental analyses were obtained for all products. The i.r. and n.m.r. spectra were in agreement with the assigned structures. The yields refer to isolated compounds.

‡ The figures in parentheses refer to the yields of the corresponding 1,2-dialkoxycarbonylhydrazino-compounds (**4**).

§ A sample of 6-*O*-ethoxycarbonyl-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose prepared from the substrate and ethyl chloroformate in pyridine was identical (i.r., n.m.r., mixed m.p.) with that obtained by the method described.

[1] D. C. Morrison, *J. Org. Chem.*, 1958, **23**, 1072.
[2] E. Brunn and R. Huisgen, *Angew. Chem.*, 1969, **81**, 534.
[3] O. Mitsunobu and M. Yamada, *Bull. Chem. Soc. Japan*, 1967, **40**, 2380.
[4] M. Wada and O. Mitsunobu, *Tetrahedron Letters*, 1972, 1279.
[5] O. Mitsunobu, M. Wada, and T. Sano, *J. Amer. Chem. Soc.*, 1972, **94**, 675.
[6] A. Zamojski, W. A. Szarek, and J. K. N. Jones, *Carbohydrate Res.*, 1972, **23**, 460.
[7] L. Hough, J. E. Priddle, and R. S. Theobald, *Adv. Carbohydrate Chem.*, 1960, **15**, 91.