

employing zinc chloride as condensing agent, has given in our case two products. One, obtained in low yield (8%), is identical with the 1,2:3,4-di-*O*-benzylidene- $\alpha$ -D-galactose described by the above-mentioned authors; the major product of the reaction is 4,6-*O*-benzylidene-D-galactose (yield 52%), m.p. 190-191°,  $[\alpha]_D^{25} + 118.5^\circ$  (methanol).

Our 1,2:3,4-di-*O*-benzylidene- $\alpha$ -D-galactose had m.p. 173-174°,  $[\alpha]_D^{25} - 50.4^\circ$  (methanol),  $-78.1^\circ$  (pyridine), in good agreement with the values reported by Pacák and Černý. That the primary hydroxyl is free follows from its transformation into 6-*O*-benzoyl-1,2:3,4-di-*O*-benzylidene- $\alpha$ -D-galactose, m.p. 144-145°,  $[\alpha]_D^{25} - 114.6^\circ$  (chloroform) and into 1,2:3,4-di-*O*-benzylidene-6-*O*-methyl- $\alpha$ -D-galactose, m.p. 130-131°,  $[\alpha]_D^{25} - 81.4^\circ$  (chloroform). On hydrolysis the benzoylated product gave the 6-*O*-benzoyl-D-galactose, m.p. 134-135°,  $[\alpha]_D^{25} + 79.8^\circ$  (24 hr., pyridine) previously described by Zinner *et al.*;<sup>3</sup> the methylated compound produced the known 6-*O*-methyl-D-galactose, m.p. 128-130°,  $[\alpha]_D^{25} + 74.3^\circ$  (6 hr.).<sup>4</sup>

Proof for the structure of the 4,6-*O*-benzylidene-D-galactose follows from the facts that, (a) oxidation with periodate gave a consumption of two moles of the reagent and no production of formaldehyde; (b) methylation afforded, the known methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl- $\beta$ -D-galactoside, m.p. 142-143°,  $[\alpha]_D^{25} + 17.5^\circ$ .<sup>5</sup>

The high yield of the 4,6-*O*-benzylidene-D-galactose is explained because the hydroxyls at C(4) and C(6) are the most favoured for the condensation with benzaldehyde; the new 1,3-dioxan ring formed is condensed *cis* to the pyranose ring and the resulting product presumably has a double chair, O-inside conformation, with the phenyl group equatorial. The  $\beta$ -anomer, with the equatorial hydroxyl in C(1)

should predominate and this seems to be confirmed by the preparation, by methylation, of the galactoside mentioned above, although on the other hand, benzoylation under the usual conditions employed for D-galactose, gave only the  $\alpha$ -anomer.

The following sequence of reactions was applied: 4,6-*O*-benzylidene-D-galactose, treated with benzoyl chloride in pyridine at 0°, gave 1,2,3-tri-*O*-benzoyl-4,6-*O*-benzylidene- $\alpha$ -D-galactose, m.p. 171-172°,  $[\alpha]_D^{25} + 226.2^\circ$  (chloroform). This compound on hydrolysis, produced 1,2,3-tri-*O*-benzoyl- $\alpha$ -D-galactose, m.p. 75-78°,  $[\alpha]_D^{25} + 237.1^\circ$  (chloroform) which on further benzoylation yielded the known 1,2,3,4,6-penta-*O*-benzoyl- $\alpha$ -D-galactose, m.p. 158-159°,  $[\alpha]_D^{25} + 186.6^\circ$ .<sup>6</sup>

We were unable to condense 4,6-*O*-benzylidene-D-galactose with another molecule of benzaldehyde, under the action of zinc chloride, and the original product was recovered in 88% yield.

Correct analyses were obtained for all new substances. We thank the Consejo Nacional de Investigaciones Científicas y Técnicas for a grant.

Received June 25, 1962

#### References

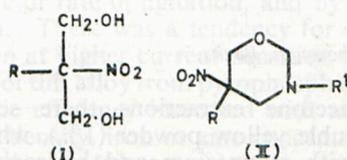
- 1 Pacák, J. & Černý, M., *Coll. Czech. Chem. Commun.*, 1961, **22**, 2212
- 2 For the case of D-glucose, see Gros, E. G., Ondetti, M. A., Sproviero, J. O., Deulofeu, V. & Deferrari, J. O., *J. org. Chem.*, 1962, **27**, 924
- 3 Zinner, H., Wessely, K., Bock, W., Rieckhoff, K., Strandt, F. & Nimmich, W., *Chem. Ber.*, 1957, **90**, 500
- 4 Pacsu, E. & Trister, S. M., *J. Amer. chem. Soc.*, 1940, **62**, 2301
- 5 Oldham, J. W. H. & Bell, D. J., *ibid.*, 1938, **60**, 323
- 6 Deferrari, J. O. & Deulofeu, V., *J. org. Chem.*, 1952, **17**, 1097

## By-products and the Mechanism of Formation of 5-Nitrotetrahydro-1,3-oxazine Derivatives

By Z. Eckstein, P. Gluźniński, D. Gürne, J. Plenkiewicz and T. Urbański

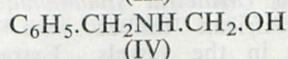
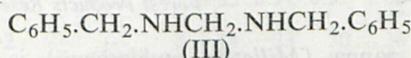
Institute of Technology (Politechnika), Department of Organic Technology II, Warsaw 10, Poland

By condensing 2-alkyl derivatives of 2-nitropropane-1,3-diol (I) with formaldehyde and halogenated benzylamine in aqueous alcohol we tried to obtain 5-nitrotetrahydro-1,3-oxazine derivatives (II, R = alkyl, R<sup>1</sup> = CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>X, where X = halogen)<sup>1</sup>:



However, instead of the expected products (II) compounds were formed containing no NO<sub>2</sub> group (as

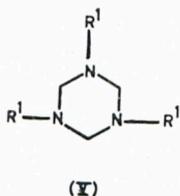
shown by infrared spectral measurements). The products appeared to be identical with the by-product obtained by Urbański and Gürne<sup>2</sup> in the course of preparation of 5-nitro-5-hydroxymethyl-3-benzyltetrahydro-1,3-oxazine and also by reaction of benzylamine with formaldehyde. It was then considered that the product has structure (III) suggested by Kempff.<sup>3</sup>



As we find in the present work, the condensation product of benzylamine and formaldehyde described

by Henry<sup>4</sup> as *N*-hydroxymethylbenzylamine (IV) is also identical with compound (III) (mixed m.p., infrared spectrum).

The infrared spectra of these compounds showed no bands, which could be assigned to NH or OH vibrations. We prepared several analogous products from aliphatic amines and formaldehyde. All of them gave similar infrared spectra. We identified our compounds as 1,3,5-tribenzylhexahydro-*s*-triazine derivatives (V), described partly by Graymore.<sup>5</sup>

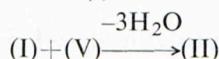


The structures of these compounds were established by Kahovec<sup>6</sup> through Raman spectral measurements.

Elucidation of the role of these compounds in the synthesis of the 5-nitrotetrahydro-1,3-oxazine ring starting from 2-nitropropane diol is of particular interest. This would also throw some light on the mechanism of the  $\alpha$ -amino-methylation reaction known in some cases as the Mannich reaction.

It seems probable that the first step of the reaction of primary aliphatic amines and formaldehyde in the presence of compounds containing active hydrogen atoms is the formation of the hexahydro-*s*-triazine ring (V). Then the compounds (V) react with the nucleophilic component to give tetrahydro-1,3-oxazines and other compounds typical for the  $\alpha$ -amino-methylation reaction. In other words the compounds (V) seem to be the source of formaldehyde and primary amine.

To prove this suggestion we investigated the reaction between compounds (V) and derivatives of 2-nitropropane-1,3-diol (I) in the molar ratio 1 : 3 :



The reaction occurred in benzene, toluene, or xylene with azeotropic removal of water. The tetrahydro-1,3-oxazine derivatives (II) were identified

by their infrared spectra compared with those of compounds prepared by conventional methods.

When tris-hydroxymethyl-nitromethane is used as a component in this reaction, the evolution of nitrogen dioxide occurred steadily at the end of the reaction and small amounts of tarry products were formed.

Satisfactory yields and analysis for various compounds with structure (II) and (V) have been obtained, and their physical properties will be given in our full report.<sup>7</sup>

It seems that regarding this preliminary communication a correction has to be made in those papers which reported the use of "*N*-hydroxymethyl-derivatives" for synthesis of tetrahydro-1,3-oxazine.<sup>8-10</sup> However, in the light of the results described in the present paper the part played by compound (V) in the Mannich reaction was demonstrated by our previous work.<sup>10</sup>

Recently Burke and co-workers<sup>11</sup> mentioned an application of 1,3,5-tribenzylhexahydro-*s*-triazine (V,  $R^1 = C_6H_5$ ) as a donor of amine in the reaction of hydroquinone with formaldehyde to yield benzoxazine derivatives. All these facts seem to confirm the prominent role of compounds (V) in Mannich reactions in cases when primary aliphatic amines and formaldehyde react with compounds possessing active hydrogen atoms.

Received April 24, 1962

#### References

- Eckstein, Z., Gluziński, P., Hofman, W. & Urbański, T., *J. chem. Soc.*, 1961, 489
- Urbański, T. & Gürne, D., *Roczniki Chem.*, 1954, **28**, 175
- Kempff, A., *Liebigs Ann.*, 1890, **256**, 220
- Henry, L., *Bull. soc. chim. Belg.*, 1895, **13**, 157; *Bull. acad. roy. Belg.*, 1897, **33**, 115
- Graymore, J., *J. chem. Soc.*, 1932, 1353; 1935, 865; 1947, 1116
- Kahovec, L., *Z. phys. Chem.*, 1939, **B43**, 364
- Eckstein, Z., Gluziński, P., Pleniewicz, J. & Urbański, T., *Bull. acad. polon. sci., sér. chim.*, in the press
- Senkus, M., U.S. Pat. No. 2,447,822 (1949); *J. Amer. chem. Soc.*, 1950, **72**, 2968
- Eckstein, Z., Sobótka, W. & Urbański, T., *Roczniki Chem.*, 1956, **30**, 133
- Gürne, D. & Urbański, T., *ibid.*, 1957, **31**, 855, 869
- Burke, W. J., Hammer, C. R. & Weatherbee, C., *J. org. Chem.*, 1961, **26**, 4403

## The Colouring Matter from *Millettia stuhlmannii*

By B. J. Hawthorne

*British Celanese Ltd., Putteridge Bury, Luton, Beds.*

and

J. W. W. Morgan

*Forest Products Research Laboratory, Princes Risborough, Bucks.*

Panga panga (*Millettia stuhlmannii*) is a dark brown East African timber with characteristic yellow streaks in the vessels. Extraction of the comminuted heartwood by boiling light petroleum removed a wax (0.3%); then from successive hot

ether and acetone extractions there separated a sparingly soluble yellow powder (1%), which gave a red colour with magnesium and hydrochloric acid. The product crystallised from methanol as small bright yellow needles,  $C_{15}H_{10}O_7 \cdot CH_3OH$ , (decom-