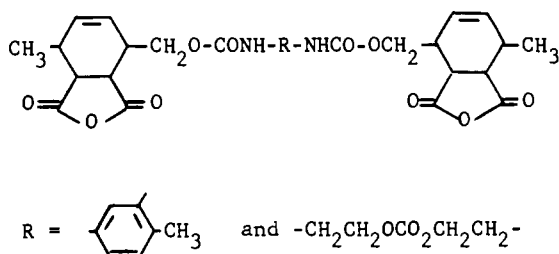


Some Novel Dianhydrides

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SEVERAL NOVEL DIANHYDRIDES were prepared by the reaction of maleic anhydride with bis-dienes derived from the condensation of 2,4-hexadienol (sorbyl alcohol) with diisocyanates.



EXPERIMENTAL

Bis-(2,4-hexadienoxyformamido)ethyl carbonate. To a solution of 49 grams (0.5 mole) of 2,4-hexadienol, 0.25 grams of dibutyltin diacetate in 200 ml. of dry benzene was added 50 grams (0.25 mole) of bis(2-isocyanatoethyl) carbonate at 30° C., all temperatures are uncorrected, during 30 minutes. The precipitated solid was removed by filtration, washed with benzene to remove unreacted starting material and dried at about 10 mm. Hg and ambient temperature under reduced pressure to give a 95 per cent yield of a fine white powder. Extensive polymer formation occurred on attempted crystallization from hot ethanol and when the melting point was sought using the capillary tube resistance-heated metal block. *Anal.* Calcd. for $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_7$: C, 57.56; H, 7.12; N, 7.06. Found: C, 55.40; H, 6.63; N, 6.22.

Infrared spectrum is consistent with assigned structure with maxima at 3.0μ (NH), 5.72, 10.3 and 12.6μ (O—CO—O), 5.85, 6.5 and 8.0μ (—NHCO₂—) with alcohol impurity 9.7μ .

Bis-(2,4-hexadienyl) tolylene-2,4-dicarbamate. The same procedure as described above was employed using 2,4-tolylene diisocyanate to give a quantitative yield of fine white solid. *Anal.* Calcd. for $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_4$: C, 68.09; H, 7.07; N, 7.56. Found: C, 68.26; H, 6.99; N, 7.62.

Infrared spectrum was consistent with the assigned structure with maxima at 3.03μ (NH), 5.85, 6.5 and 8.05μ

(NHCO₂), 6.25 and 6.68μ (aromatic), 6.13μ (=C conj.), 10.1μ (C=C trans).

Bis-[2-(3-methyl-1-cyclohexene-4,5-dicarboxyanhydro)-methoxyformamido]ethyl carbonate. A mixture of 40 grams (0.1 mole) of bis-2-(2,4-hexadienoxyformamido)ethyl carbonate, 20 grams (0.2 mole) of maleic anhydride and 200 ml. of dry benzene was purged with nitrogen and warmed to reflux for three hours. The precipitate was removed, washed with benzene and dried under reduced pressure at about 10 mm. Hg and ambient temperature. There was obtained 41 grams, a 69 per cent yield, of a cream-colored solid whose analysis indicates it to be a slightly impure product. *Anal.* Calcd. for $\text{C}_{27}\text{H}_{32}\text{N}_2\text{O}_{13}$: C, 54.73; H, 5.44; N, 4.73. Found: C, 56.46; H, 5.58; N, 4.38.

Infrared spectrum is consistent with the assigned structure having maxima at 2.95 and 6.50μ (—NH carbamate), 5.40 and 5.60μ (CO—O—CO), 5.7 and 5.8μ (CO carbamate), 6.10 and 14.6μ (C=C cis).

Bis[(3-methyl-1-cyclohexene-4,5-dicarboxyanhydro)-methyl] tolylene-2,4-dicarbamate. To a mixture of 37 grams (0.10 mole) of bis(2,4-hexadienyl) tolylene-2,4-dicarbamate and 200 ml. of dry benzene at reflux temperature there was added 20 grams (0.2 mole) of maleic anhydride. The mixture was held at reflux for 1.5 hours and then cooled. The precipitate was removed and the filtrate evaporated in a rotating vacuum flask at ambient temperature at 10 mm. Hg to give a total of 55 grams, a 97 per cent yield, of impure solid product. The combined solids were taken up in hot benzene and filtered to remove a small amount of polymer. Evaporation of the benzene gave a light cream-colored solid. *Anal.* Calcd. for $\text{C}_{29}\text{H}_{30}\text{N}_2\text{O}_{10}$: C, 61.5; H, 5.34; N, 4.94. Found: C, 61.92; H, 5.66; N, 5.19.

Infrared maxima: 3.0 and 6.5μ (—NH, carbamate), 3.3, 6.18 and 6.24μ (phenyl), 5.40 and 5.60μ (CO—O—CO) and 8.15μ (C—O—C).

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