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SYNTHESIS AND SOME PROPERTIES OF 1-PHENYL-2,2-DIMETHOXY-2(N-ALKOXYCARBONYLAMINO)-DIAZOETHANES.(*)

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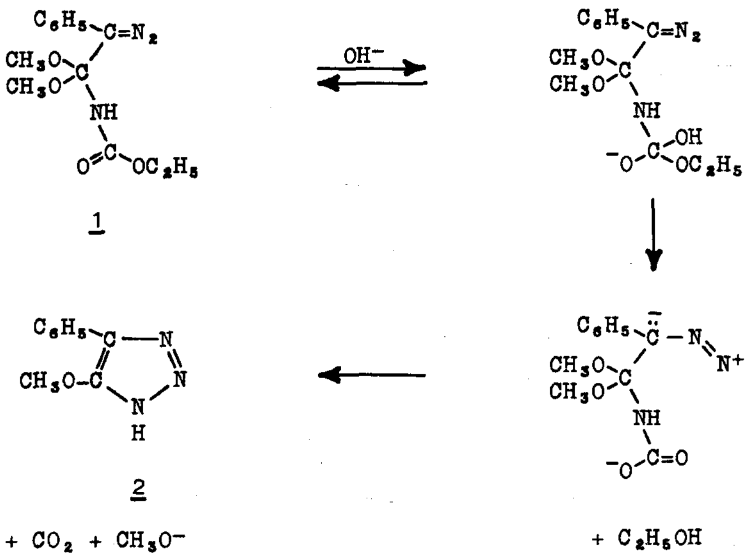
1,3-Dipolar addition of alkyl azidoformate onto ketene dialkylacetals and alkylketene dialkylacetals at 35° is immediately followed by the evolution from the intermediate unstable Δ^2-triazolines of nitrogen in approximately quantitative amounts. 2,4,4-Trialkoxy-Δ^2-oxazolines and N-alkoxycarbonyl-2-alkoxyimino-ethers are formed from 1-alkoxycarbonyl-5,5-dialkoxy-Δ^2-1,2,3-triazolines[1] and 4-alkyl-substituted triazolines[2,3], respectively.

We wish now to report that 1-alkoxycarbonyl-4-phenyl-5,5-dimethoxy-Δ^2-1,2,3-triazolines at 35° show a different behaviour, in that the ring opening is followed in this case by a proton shift to yield 1-phenyl-2,2-dimethoxy-2(N-alkoxycarbonylamino)-diazoethanes as the main products.

When ethyl azidoformate was heated with an excess of phenylketene dimethylacetal for 8 days at 35° and the reaction mixture chromatographed on neutral alumina[4](Woelm, grade IV activity), elution with increasing concentrations (up to 80%) of benzene in light petroleum gave fractions containing the hitherto unreported diazoethane $\underline{1}$, which were pooled and rechromatographed on Polyamid-SC 6 (Macherey-Nagel, light petroleum as the eluent) to give in pure form the red, thermally unstable, diazoethane $\underline{1}$ (yield ~ 40%)[5], m.p. 63-66°; $\lambda_{\max}^{\mathrm{CHCl_3}}$ mμ 285 (log ε 4.29), 480 (log ε 1.76); $\lambda_{\max}^{\mathrm{CCl_4}}$ μ 2.95 (>NH), 4.84 ($>C=N_2$), 5.74, 5.84 (-NH-COO-), 9.20-9.25 ($>C{<}^{O-C}_{O-C}$); nmr (CCl_4) τ 2.60--3.20 (5H, m, aromatic H), 3.91 (1H, s, NH), 6.01 (2H, q (7), methylenic H), 6.74 (6H, s, $2xOCH_3$), 8.90 (3H, t (7), methylic H).

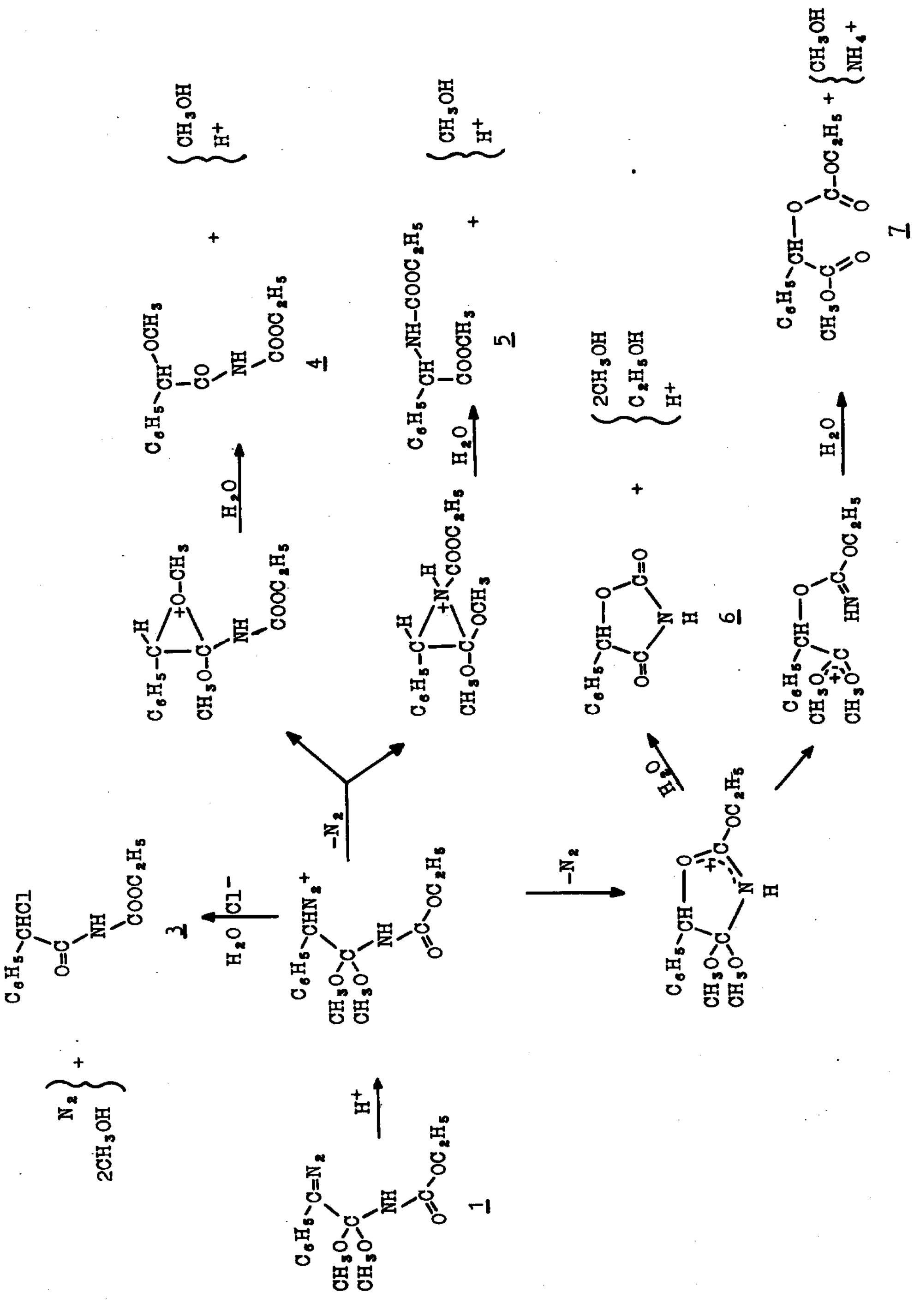
Treatment of diazoethane 1 with 1% methanolic KOH at room temperature afforded triazole 2 (~ 97%)[5] probably according to the following mechanism:



The reaction is actually a special case of decomposition of N-alkylcarbamic acids obtained from alkaline hydrolysis of aliphatic carbamate esters[6].

Treatment of diazoethane 1 in dioxane solution with 1/3 equivalent of 1N hydrochloric acid at room temperature led to a complex mixture, which was separated by chromatography (SiO_2) into 3 (~ 6%)[5], 4 (~ 30%)[5], 5 (~ 2%)[5], 6 (~ 27%)[7], 7 (~ 18%)[5]. We interpret our results in term of the mechanism presented in Scheme I where the key step is the attack of H^+ at the diazo carbon atom[8].

SCHEME I.



A more detailed discussion will be reported in near future.

REFERENCES and NOTES

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[1] R. Scarpati, M.L. Graziano and R.A. Nicolaus, Gazz. Chim. Ital. 99, 1339 (1969).

[2] R. Scarpati, M.L. Graziano and R.A. Nicolaus, Gazz. Chim. Ital. 100, 665 (1970).

[3] M.L. Graziano and R. Scarpati, Gazz. Chim. Ital., in press.

[4] Because of the sensitivity of diazoethane 1 to hydrolysis, chromatography was practiced at a higher rate than usual.

[5] All the new compounds described in this paper gave satisfactory elemental analyses; IR and NMR spectra are consistent with the proposed structures.

[6] M.L. Bender and R.B. Homer, J. Org. Chem. 30, 3975 (1965).

[7] W. Traube and R.A. Ascher, Ber. 46, 2082 (1913).

[8] G.W. Cowell and A. Ledwith, Quart. Rev. 24, 119 (1970).