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FURTHER INVESTIGATIONS ON THE REACTION BETWEEN PHENYLKETENE DIMETHYLACETAL AND ETHYL AZIDOFORMATE (*)

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In a previous paper[1] we reported the synthesis and some properties of 1-phenyl-2,2-dimethoxy-2(N-ethoxycarbonylamino)-diazoethane 4 and anticipated that the reaction of phenylketene dimethylacetal 1 with ethyl azidoformate 2, leading to 4, proceeds *via* 1-ethoxycarbonyl-4-phenyl-5,5-dimethoxy- Δ^2-1,2,3-triazoline 3. We have now obtained unequivocal evidence of the intermediate formation of the triazoline 3 and also evidence on triazoline 3 $\rightleftarrows$ diazoethane 4 mutual conversion.

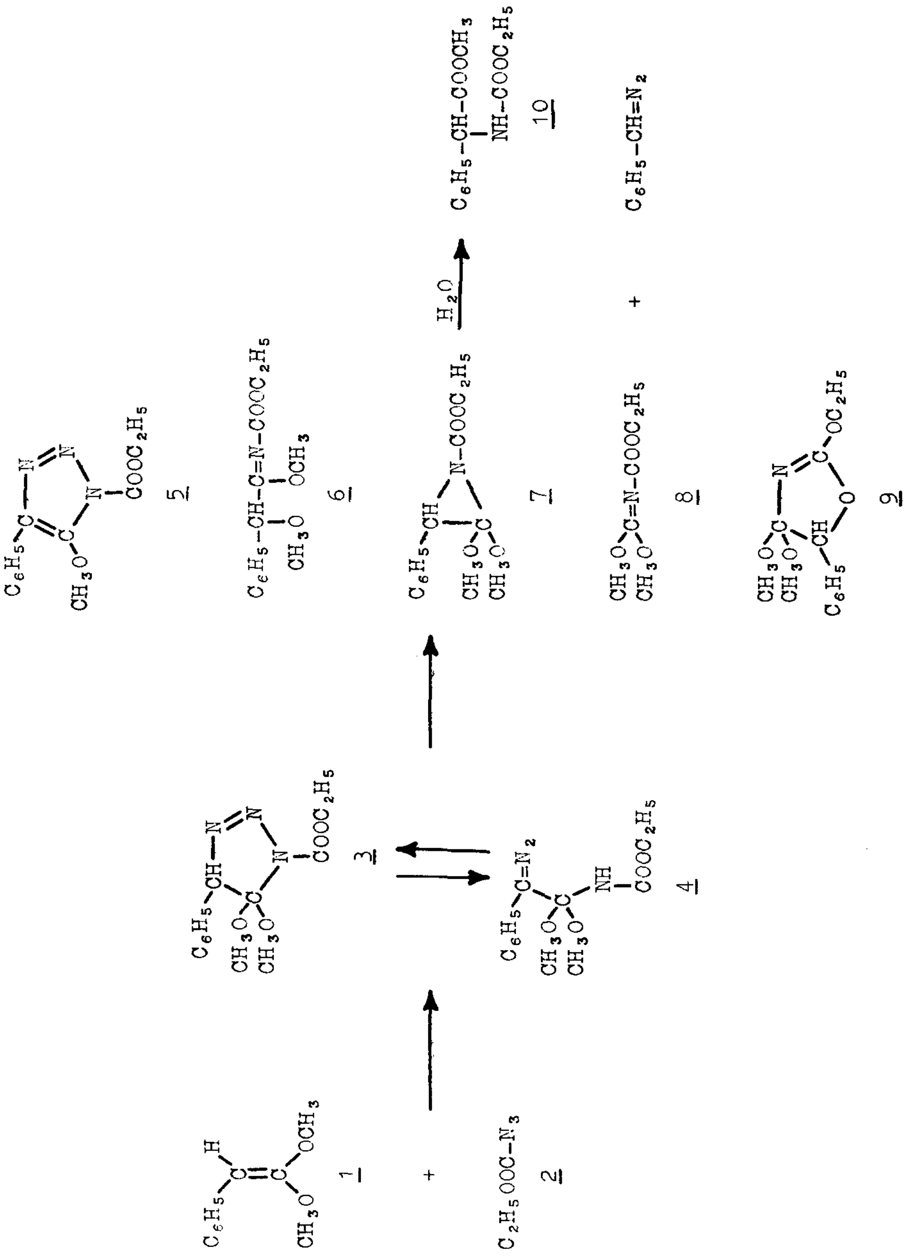
When a 1:1 mixture of phenylketene dimethylacetal 1 and ethyl azidoformate 2 was allowed to react at -15° for two months its NMR spectrum (CCl_4) showed, in addition to the signals of the starting materials, three singlets at τ 4.84 (1H; Ph-CH-N), 6.62 (3H; OCH_3), 7.16 (3H; OCH_3), a quartet at τ 5.73 (2H, (7), methylenic H) and a triplet at τ 8.63 (3H, (7), methylic H), all consistent with the structure of triazoline 3. This adduct, formed in ~ 30% yield, is not stable enough to be isolated. When ethyl azidoformate was removed under red. press. (0.5 mm) at room temperature and the remaining mixture (phenylketene acetal and triazoline) heated at 35°, its NMR spectrum gradually changed, developing new peaks whereas the signals assigned to triazoline 3 decreased in intensity. After the above mixture was kept 48 hr at this temperature, the analysis of its NMR spectrum[2] showed the presence of diazoethane 4[3,1], of triazole 5[3] and of imino-ether 6[3] in ca 1:1 molar ratio, and smaller quantities of imidocarbonate 8[4], oxazoline 9[3,5,6], benzalazine[3,7]. No spectral evidence has been obtained to support the presence in the reaction mixture of aziridine 7; however Al_2O_3 chromatography allowed the isolation of methyl N-ethoxycarbonyl-2-aminophenylacetate 10 which evidently is formed by hydrolysis of 7 during the separation procedure, as observed in similar cases[8].

When the above phenylketene acetal-triazoline mixture was heated at 90° (2 hr) conspicuous evolution of nitrogen was observed. Inspection of the NMR spectrum of the reaction mixture[9] showed the presence of imino-ether 6[10,6] and imidocarbonate 8 as the main products and of very little quantities of triazole 5 (molar ratio 5:6 ca 1:10), oxazoline 9, benzalazine. Moreover, the presence of aziridine 7 was deduced through the isolation of its hydrolysis product 10 by Al_2O_3 chromatography.

Diazoethane 4, heated at 35° (80 days, without solvent), gave a mixture which, on the basis of its NMR spectrum, resulted to comprise the starting material (~ 70%), triazole 5 and imino-ether 6 in ca 1:1 molar ratio, and oxazoline 9; very small quantities of 7 and 8 were also present.

When diazoethane 4 was heated at 90° (24 hr, without solvent) triazole 5 was formed as the main product, which was isolated by chromatography on silica gel[6] (yield ~ 65%); all of the by-products (6, 7, 8, 9) were present in small quantities (molar ratio 5:6 ca 10:1).

The above results point out a mutual conversion between triazoline 3 and diazoethane 4: in fact, by heating 3 and 4 at 90°, 5 and 6 are obtained in a molar ratio of 10:1 and 1:10 respectively, whereas at 35°, the molar ratio is about the same. This indicates that imino-ether 6 is formed through the triazoline 3, whereas triazole 5 derives from diazoethane 4, at least in part, without preliminary conversion into triazoline 3. As to the origin of 7 and 8,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they are likely formed through triazoline 3 in agreement with the behaviour of 1-phenyl-4,4-dialkyl-5,5-dimethoxy- Δ^2-1,2,3-triazolines[8] which at 120° decompose to give 2-substituted N-phenyl-2-methoxyacetimino methylethers, dimethyl phenylimidocarbonate and 1-phenyl-2,2-dialkyl-3,3-dimethoxyaziridines.

REFERENCES and NOTES

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[1] R. Scarpati and M.L. Graziano, *Tetrahedron Letters*, 1971, 2085.

[2] The same peaks were observed when the reaction was performed directly at 35°.

[3] Identification was made possible by comparision with NMR spectrum of the pure compound.

[4] Identification was made possible by comparision with the previously reported NMR spectrum of the compound 8 (R. Scarpati, M.L. Graziano and R.A. Nicolaus, *Gazz. Chim. Ital.* **99**, 1339 (1969)) and by chromatographyc isolation of its product of hydrolysis (methoxycarbonyluretan).

[5] Oxazoline was isolated by chromatography on neutral Al_2O_3 and on polyamide.

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

[7] Benzalazine is probably formed from phenyldiazomethane (G.W. Cowell and A. Ledwith, *Quart. Rev.* **24**, 119 (1970)).

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

[9] The same peaks were observed when the reaction was performed directly at 90°.

[10] Isolated from the reaction mixture by distillation under red. press..