Tetrahedron Letters No.32, pp. 3085-3088, 1967. Pergamon Press Ltd. Printed in Great Britain.

CYCLOPROPANONES. VI.

REACTION OF CYCLOPROPANONE WITH AMINES[*]

Nicholas J. Turro[**] and Willis B. Hammond[***]
Chemistry Department, Columbia University
New York, New York 10027

(Received 23 May 1967)

Wasserman and Clagett[1] have reported that the reaction of 1-ethoxy-1-hydroxycyclopropane with aniline at room temperature yields 1,1-dianilinocyclopropane (6). These workers proposed that cyclopropanone (1) and 1-anilino-1-hydroxycyclopropane (3) may be intermediates in the formation of 6. The results reported here are pertinent to the above report and the general field of cyclopropanone and cyclopropane chemistry.[2-6]

Treatment of methylene chloride solutions[7] of cyclopropanone (1) with 1.0 equivalent of aniline at -78° results in immediate formation of a mixture of two compounds, 2 (33%) and 3 (66%). Treatment of 1 with two equivalents of aniline under similar conditions results in formation of 3 as major product (95%) and 2

---

[*]
(a) Presented in part at the 153th Meeting of the American Chemical Society, Miami, Florida, April, 1967.
(b) Part V: N.J. Turro and W.B. Hammond, _J. Am. Chem. Soc._, **89**, 1028 (1967).
(c) The generous support of the Air Force Office of Scientific Research (Grant AFOSR-1000-66) and the National Science Foundation (Grant NSF-GP-4280).

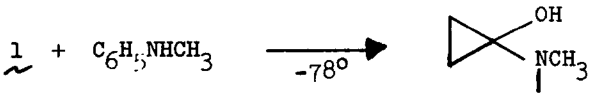
[**] Alfred P. Sloan Fellow, 1966-1968.

[***] National Science Predoctoral Fellow, 1964-1967.

as the minor product (< 1%). Compound 2 was identified as N,N-bis-(1-hydroxycyclopropyl)-aniline: nmr;[8] τ 2.6-3.2 (multiplet, 5H), 7.0 (singlet, 2H), and 8.8 (singlet, 8H)[9]; mass spectrum m/e 205 (M^{+}), 149 ($M^{+}-C_3H_4O$), 93 ($M^{+}-C_6H_8O_2$); infrared $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 3580 (sharp, -OH), 3420 (broad, OH). Compound 2 is slowly converted to 3 upon standing at room temperature in the presence of aniline.

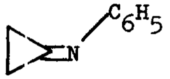
Compound 3 was identified by the following evidence as 1-anilino-1-hydroxycyclopropane: nmr, τ 8.95 (A_2B_2). Addition of ketene to 3 yields 1-(N-acetylanilino)-1-hydroxycyclopropane (5): nmr, τ 2.4-2.9 (multiplet, 5H), 8.05 (singlet, 3H), 9.0-9.3 (A_2B_2, 4H); infrared $\lambda_{max}^{CH_2Cl_2}$ 1680 cm^{-1}; mass spectrum m/e 191 (M^{+}), 149 ($M^{+}-C_2H_2O$), 135 ($M^{+}-C_3H_4O$). Pyrolysis (230°) of 3 converts it to propioanilide, while treatment of 3 with excess cyclopropanone converts it quantitatively to 2, confirming the structure of the latter. Treatment of 3 with excess aniline at room temperature for six days yields 1,1-dianilinocyclopropane[1] (c.a. 80%). [See Chart 1].

Reaction of 1 with N-methylaniline cannot produce a species analogous to 2; accordingly, addition of N-methylaniline to 1 at -78° results in smooth formation (~100%) of 1-(N-methylanilino)-1-hydroxycyclopropane (7): nmr, τ 2.5-3.0 (multiplet, 5H), 619 (singlet, 3H), 8.8-9.0 (A_2B_2, 4H); infrared $\lambda_{max}^{CH_2Cl_2}$ (cm^{-1}) 3575 (sharp, -OH) 3420 (broad, -OH) 1595, 1495 (aromatic); mass spectrum m/e 163 (M^{+}), 107 ($M^{+}-C_3H_4O$), 106 ($M^{+}-C_3H_5O$).

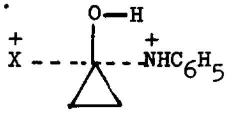


7

Some of these reactions appear to involve either the Schiff base[10] 8 of cyclopropanone or an S_N2 displacement,[11] 9. So far, attempts to synthesize 8 by dehydration of 3 have been unsuccessful.[12,13]



8



9

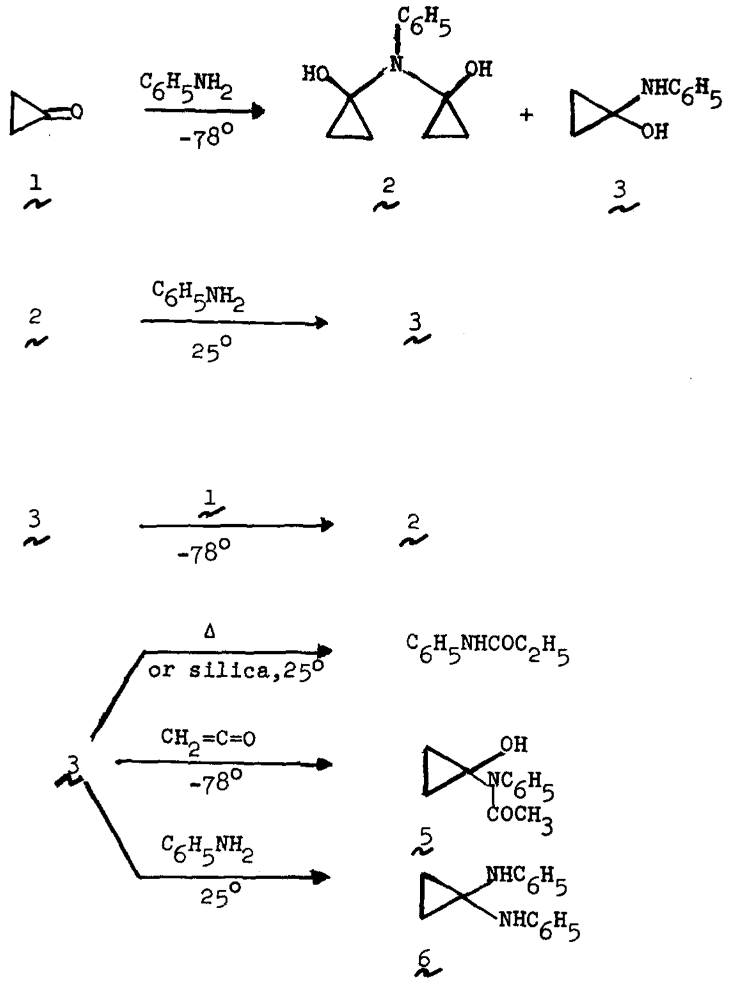


Chart I. Reaction of **1** with aniline and characterization of **2** and **3**.

The reactions of **1** with other nucleophiles will be the subject of forthcoming publications.

References

1. H.H. Wasserman and D.C. Clagett, *J. Am. Chem. Soc.*, **88**, 5368 (1966); D.C. Clagett, Ph.D. Dissertation, Yale University, New Haven, 1966.
2. J.F. Pazos and F.D. Greene, *J. Am. Chem. Soc.*, **89**, 1030 (1967).
3. D.C. Zecher and R. West, *ibid.*, **89**, 153 (1967).
4. S.E. Schoafsmo, H. Steinberg and J.T. de Boer, *Rec. Trav. Chim.*, **85**, 1170 (1966).
5. R.C. Cookson, M.J. Nye and G. Subrahmarryham, *J. Chem. Soc.*, *C*, 473 (1967).
6. M.Y. Lukina, *Russian Chem. Rev.* (Eng. Trans.), **31**, 419 (1962).
7. N.J. Turro and W.B. Hammond, *J. Am. Chem. Soc.*, **88**, 3672 (1966).
8. All nmr spectra taken on a Varian A-60 instrument in methylene chloride, TMS external standard. Yields are based on nmr analysis employing CH_2Cl_2 as internal standard.
9. This singlet transforms into an A_2B_2 multiplet when pyridine is added. The remainder of the spectrum is not substantially modified.
10. No authentic examples of such compounds have been reported. However, a recent report indicates that Schiff bases of tetramethylcyclopropanone may be generated as intermediates: H.U. Hostettler, *Helv. Chim. Acta*, **49**, 2417 (1967).
11. J.D. Roberts and V. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).
12. The following reagents were employed to effect dehydration:
    1) dicyclohexylcarbodiimide and pyridine in methylene chloride at reflux for one day.
    2) reflux in benzene for 18 hours.
    3) reflux in benzene with a trace of p-toluene sulfuric acid for 2 1/2 hours.
13. The addition of alkylamines to **1** has recently been reported: W.J.M. Van Tilborg, S.E. Schoafsma, H. Steinberg and Th. J. de Boer, *Rec. Trav. Chim.*, **86**, 417 (1967).