Tetrahedron Letters No. 17, pp 1635 - 1636, 1972. Pergamon Press. Printed in Great Britain.

THE 2:1 DIPHENYLKETENE: 1,1-DIPHENYLETHYLENE ADDUCT[1]

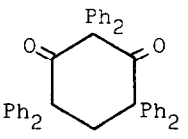
John E. Baldwin, Michael F. Breckinridge, and Donald S. Johnson

Department of Chemistry, University of Oregon,

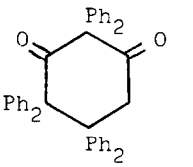
Eugene, Oregon 97403

(Received in USA 23 February 1972; received in UK for publication 16 March 1972)

The 2:1 adduct from diphenylketene and 1,1-diphenylethylene was originally prepared and assigned structure I by Staudinger and Suter.[2] A reinvestigation by Farooq and Abraham, which included a partial degradation of the molecule, led to the revised formulation II.[3]

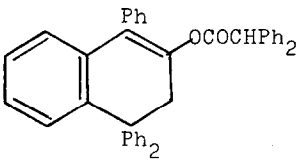


I

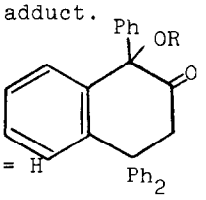


II

Spectroscopic evidence we obtained for the adduct in an earlier study[4] was sufficient to exclude both proposals I and II; the infrared band at 1745 cm^{-1} and the nmr singlets at τ 5.10 (1H) and 6.55 (2H) prompted our consideration of the enol ester structure III for the 2:1 adduct.



III



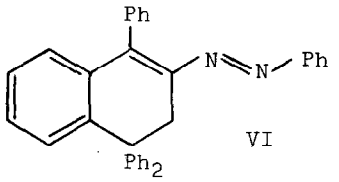
IV, R = H

V, R = Ac

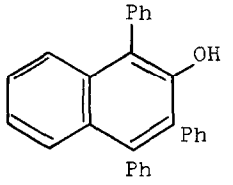
The irreconcilable conflict between structure III and the published results on the degradation of the adduct was removed through repetition of that degradation: structural and molecular formulas for all degradation products in the previous study[3] except diphenylacetic acid were found to be incorrect.

Basic hydrolysis or lithium aluminum hydride reduction of the 2:1 adduct

gives the hydroxyketone IV,[5,6] mp 195° [$\bar{\nu}$ 3450, 1725 cm^{-1}; nmr nonaromatic protons at τ 5.6 (1H, s, -OH), 6.0 (1H, d, J = 14 Hz), and 6.8 (1H, d, J = 14 Hz)] as well as diphenylacetic acid or 2,2-diphenylethanol. The hydroxyketone forms an acetate V, mp 167°, and a dehydrated phenylhydrazone derivative VI, mp 276° [2H nmr singlet at τ 5.1].



VI



VII

Dehydration of IV with hydrogen chloride in refluxing acetic acid gives 1,3,4-triphenyl-2-naphthol VII, mp 232°, identical with an authentic sample prepared from the diazonium salt of 1,3,4-triphenyl-2-aminonaphthalene[7] through hydrolysis with 50% sulfuric acid.

We are continuing work on the structure of the hydrocarbon with mp 97-98° claimed by Farooq and Abraham[3] to be 1,1,4,4-tetraphenyl-1-butene, and the mechanistic aspects of the thermal reaction sequence leading to the 2:1 adduct III.

NOTES AND REFERENCES

1. This work was supported by the National Science Foundation through GP-23021.

2. H. Staudinger and E. Suter, Ber. deutsch. Chem. Gesellschaft, 53, 1092 (1920).

3. M. O. Farooq and N. A. Abraham, Bull. Soc. Chim. Fr., 832 (1958).

4. J. E. Baldwin and J. A. Kapecki, J. Amer. Chem. Soc., 92, 4868 (1970).

5. Molecular formulas for compounds III through VII have been confirmed through analysis or mass spectrometry.

6. Compounds III and IV gave been assigned accurate structures by Heller and co-workers in an independent study: J. S. Hastings, H. G. Heller, and R. M. Megit, The Chemical Society Autumn Meeting, University of York, September 27-30, 1971, Abstract A25.

7. C. F. Allen, A. Bell, and C. W. Gates, Jr., J. Org. Chem., 8, 373 (1943).