Tetrahedron Letters,Vol.23,No.17,pp 1747-1750,1982 0040-4039/82/171747-04$03.00/0
Printed in Creat Britain

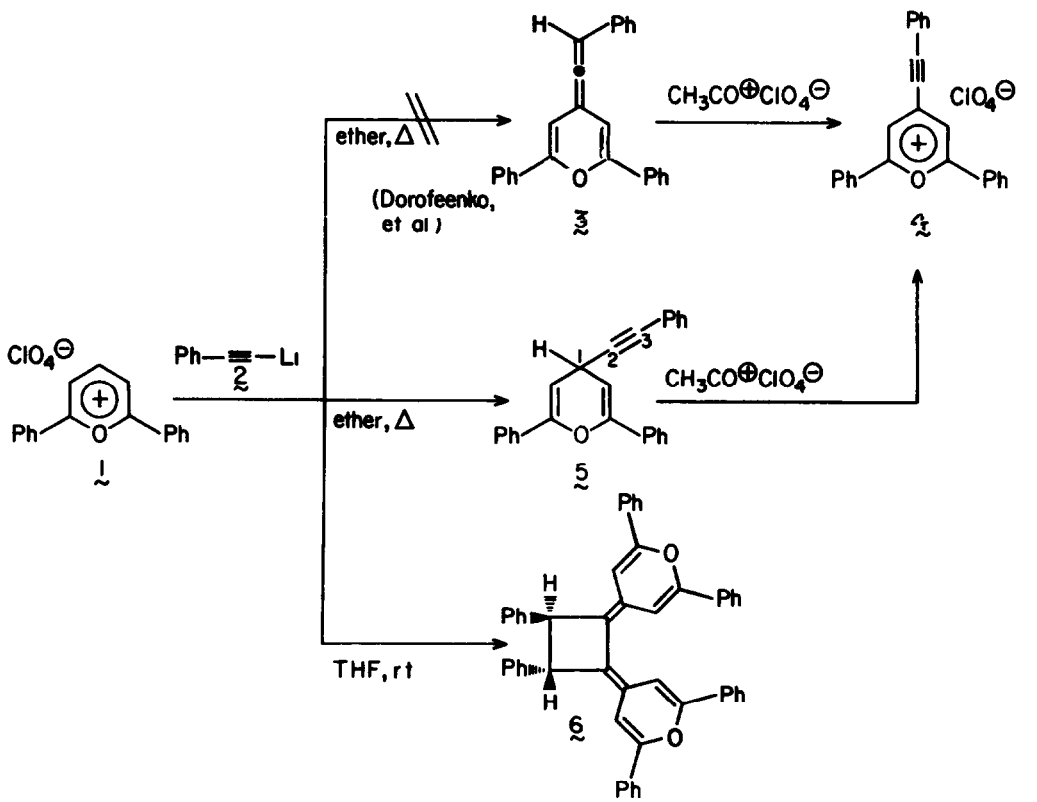
SYNTHESIS OF TRANS-1,2-DIPHENYL-3,4-BIS[4-(2,6-DIPHENYL-4H-PYRANYLIDENYL)]CYCLOBUTANE: CORRECTION AND STRUCTURE PROOF

Jeffrey J. Doney,* Chin H. Chen, and Henry R. Luss

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, USA

Summary: The reaction of phenyl lithium acetylide (2) with 2,6-diphenylpyrylium perchlorate (1) is solvent dependent. With diethyl ether as solvent, the isolated product differed from that previously reported and is reassigned as 2,6-diphenyl-4-phenylacetylenyl-4H-pyran (5). On the other hand, in THF the title compound (6) was obtained; its structure was confirmed by single-crystal x-ray crystallography.

Aside from our general interest in the synthesis of pyrans and thiopyrans,[1] efforts to understand the chemistry of acetylenic and allenic pyrans were



stimulated by a conflicting result. From the reaction of 2 with 1 in refluxing ether, Dorofeenko and co-workers[2] isolated a reddish-orange crystalline solid with a melting range of 136-138°C. Based solely upon infrared absorption peaks at 1950 cm^{-1} (ν_{as}) and 1050 cm^{-1} (ν_s), the Russian authors assigned allenic structure 3 to this product. Its subsequent treatment with 70% perchloric acid in acetic anhydride yielded a green crystalline product which was assigned as the perchlorate 4.

Repeating the Russian procedure, we obtained a reddish-orange solid with an uncorrected melting range of 147.5-149°C. However, no significant (some weak second-order peaks were present) infrared absorption was present at 1950 cm^{-1}. Therefore, based on a ^1H NMR A_2X splitting pattern at δ 4.38 (t, 1, J_{XA} = 4 Hz) and 5.49 (d, 2, J_{AX} = 4 Hz), as well as ^{13}C NMR peaks at δ 25.25 (C1), 80.96 (C2), and 91.95 (C3), and the absence of a low-field peak expected for the allene center carbon,[3] we assign acetylene 5 as the correct structure. As expected, treatment of 5 with 70% perchloric acid in acetic anhydride yielded the same green crystalline product with a melting range of 179-181°C (Russian value, 177-179°C) and an

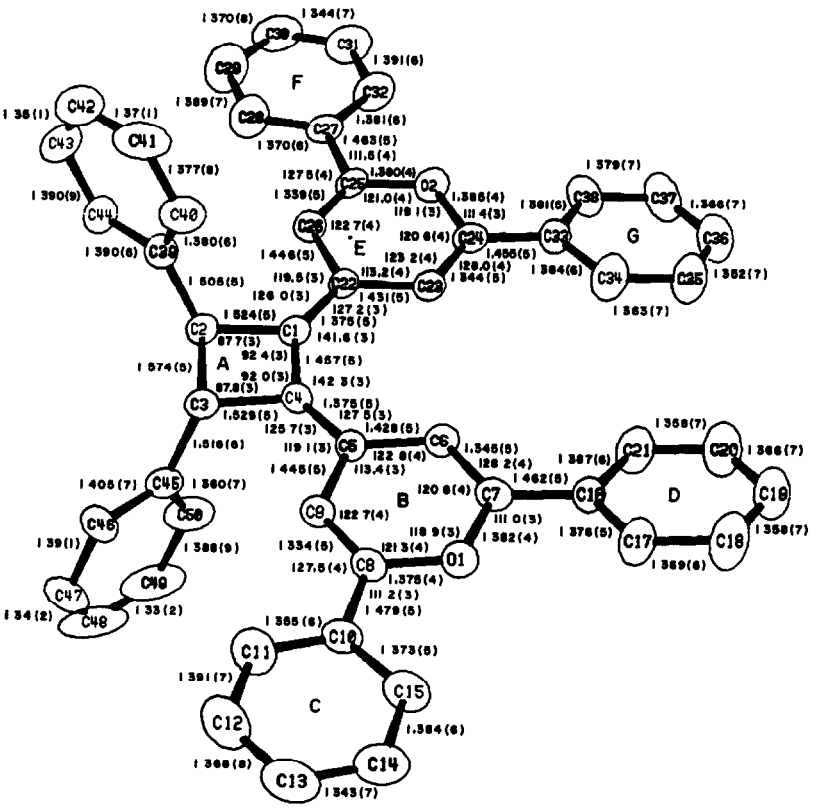


Figure 1. A plot of the molecule showing bond lengths and selected angles with estimated standard deviations in parentheses. Hydrogen atoms were omitted for clarity.

infrared spectrum with all the absorptions reported by the Russian authors for 4. Improvement of the procedure gave acetylene 5 of higher quality in 98% yield as a tan crystalline solid.[4]

Using tetrahydrofuran (THF) as solvent rather than diethyl ether and using the same reactants at room temperature gave a very different result. The title compound 6 was isolated stereochemically pure in 72% yield. We postulated that 6 is the result of, first, a 1,3 prototropic rearrangement[5] of 5 to generate the reactive allenic pyran 3 which, in turn, dimerizes via a 2+2 cycloaddition reaction[6] to form the cyclobutane ring. A less stable minor product (5-10%) that appears to be isomeric with 6, based on their similar mass spectra (m/e = 668, M^+ for $C_{50}H_{36}O_2$) and infrared spectra,[7] was also isolated. The structure, however, has not yet been fully determined.

The single-crystal x-ray analysis of the cyclobutane 6,[8] with bond lengths and selected angles, is shown in Figure 1. The structure, excluding the C2 and C3 phenyl rings, is surprisingly planar. The least-squares planes through the individual rings (indicated in Fig. 1) enclose dihedral angles of 2.7, 2.7, 4.7, 13.7, 2.5, and 9.8° between planes A-B, A-E, B-C, B-D, E-F, and E-G, respectively. The cyclobutane ring is bent slightly along a line between C2 and C4, describing two planes enclosing a dihedral angle of 3.2°. Crowding in the molecule is alleviated by the opening (about 8°) of angles C1-C22-C23, C4-C1-C22, C1-C4-C5, and C4-C5-C6. Bonds C1-C22 and C4-C5 are about 0.04 Å longer than a normal $C_{sp^2}=C_{sp^2}$ double bond (1.34 Å),[9] and bonds C1-C4, C5-C6, C5-C9, C22-C23, and C22-C26 are correspondingly shorter than a normal $C_{sp^3}-C_{sp^3}$ single bond (1.48 Å).[9]

References

(1) C. H. Chen and G. A. Reynolds, J. Org. Chem. 45, 2449, 2453 (1980); G. A. Reynolds and C. H. Chen, ibid. 46, 184 (1981). C. H. Chen, G. A. Reynolds, and B. C. Cossar, ibid. 46, 2752 (1981).

(2) G. N. Dorofeenko et al., Zh. Org. Kim. Engl. Trans. 10, 2015 (1974); ibid. 9th Inter. Conf. on Organometallic Chem.; Sept. 12-16, 1977; Kyoto, Japan.

(3) J. W. Munson in "Allenes and Ketenes," 1st ed.; S. Patai, Ed.; Interscience, New York, 1980; Vol. I, pp. 165-186.

(4) After heating at reflux for 2 h (ref. 1), simply evaporate the mixture to dryness, wash successively with excess water and with a minimal amount of diethyl ether, and then dry under high vacuum.

(5) R. J. Bushby, Quarterly Reviews, 24, 585 (1970); W. D. Huntsman in "Allenes and Ketenes," 1st ed.; S. Patai, Ed.; Interscience, New York, 1980; Vol. I, pp. 522-558.

(6) J. O. Roberts and C. M. Sharts, Org. React. 12, 1 (1962); H. J. Bestman and R. W. Saalfrank, Angew. Chem. Int. Ed. Engl. 9, 367 (1970); E. V. Demlow and G. C. Ezimova, Tetrahedron Letters, 1265 (1972); T. J. Levek and E. K. Kiefer, J. Am. Chem. Soc. 98, 1875 (1976).

(7) The infrared spectra of 6 and its isomer are very similar and exhibit the same number of significant peaks, although most of the absorptions are shifted slightly.

(8) Crystals were obtained from the pyridine half of a water/pyridine diffusion cell. The crystal data, with cell parameters obtained from least-squares refinement of the setting angles for 25 reflections centered by the diffractometer, are: $C_{50}H_{36}O_2$, M_r = 668.8, triclinic, space group $P\bar{1}$ (confirmed by structure solution), a = 13.286(2), b = 14.229(3), c = 10.733(2) Å, α = 11.08(2), β = 97.16(2), γ = 74.33(1)°, V = 1822(1) Å^3, Z = 2, D_{calc} = 1.219 Mg m^{-3}, D_{obs} = 1.20 Mg m^{-3}. The intensities of 4739 reflections for 2θ < 45° were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation. Data were corrected for Lorentz and polarization effects. No absorption correction was necessary (μ = 0.79 cm^{-1}, Mo Kα). The structure was solved from a Patterson map and refined, with anisotropic thermal parameters for nonhydrogen atoms, by full-matrix least-squares.[10] Hydrogen atom positions were calculated and included in the final refinement cycles. Only 2568 reflections had I > σ(I) and were considered observed and used in the refinement which converged to R = 0.062.[11]

(9) M. Burke-Laing and M. Laing, Acta Cryst. B32, 3216 (1976).

(10) The programs used for this study were part of the Enraf-Nonius Structure Determination Package (SDP), Enraf-Nonius, Delft, Holland, 1975, revision 3-B, 1980.

(11) A list of atomic coordinates with thermal parameters have been deposited with the Cambridge Crystallographic Data Center. A list of structure factors has been deposited with the British Library, Lending Division.

(Received in USA 19 January 1982)