CRYSTAL STRUCTURE OF THE PHOTOCYCLOADDUCT OF 1-[4'-BROMOPHENYL]-2-PHENYL-3-ETHOXYCARBONYL-Δ^2-PYRROLINE-4,5-DIONE WITH BUTADIENE[1]

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The structure of the cycloadduct of 1-[4'-bromophenyl]-2-phenyl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione with butadiene was determined by X-ray analysis using a heavy atom method.

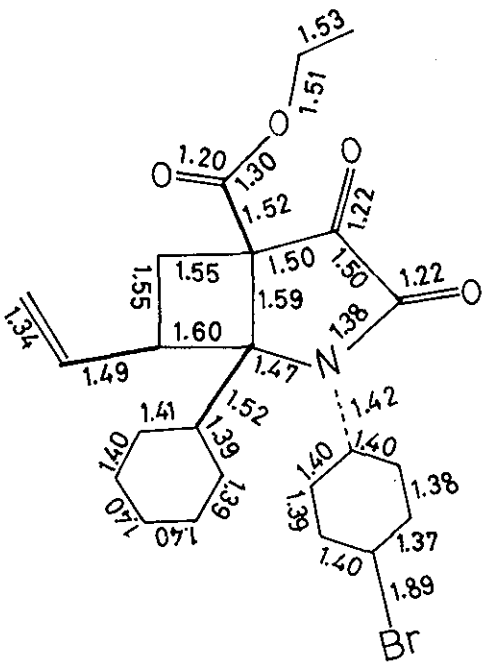
In a preceding paper we showed that the both thermal and photolytic cycloadditions of 2-phenyl-3-ethoxy-carbonyl-Δ^2-pyrroline-4,5-dione with butadiene gave the same [2+2] cyclo-adduct[2]. In order to determine the regio- and stereochemistry of the adduct, we undertook the X-ray analysis of the photoadduct

of 1-[4'-bromophenyl]-2-phenyl-3-ethoxycarbonyl-Δ^2-pyrroline-4,5-dione with butadiene. The desired cycloadduct was obtained in about 20% yield on irradiation of the mixture of the two reactants in dioxane-ether (1:1) at -10°C for 60 min and formed the single crystals (m.p. 193-195°) by crystallization from methanol.

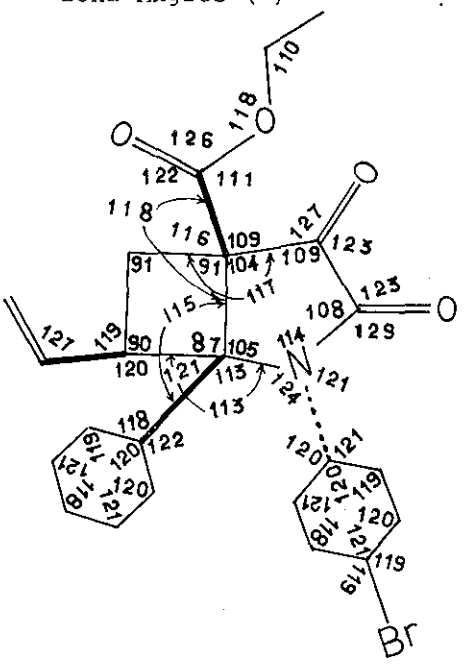
The crystals are colorless prisms. The cell dimensions were obtained by means of the least-squares method. The crystal data were collected on a Rigaku Denki Computer-controlled four-circle diffractometer, using CuKα radiation. All the intensities were obtained from a crystal with dimension 0.30X0.25X0.25mm. Reflections with 2θ values up to 140° of (hkl), (hk$\bar{l}$), ($\bar{h}$kl), and ($\bar{h}$k$\bar{l}$) were measured by ω-2θ scanning technique at a scan rate of 2° per minute. The scan rang of ω for each reflection was calculated by the fomula $\omega=0.90^\circ+0.15^\circ\tan\theta$ and the backgrounds were measured at both ends of the scan range for 10.0 seconds. The intensity data were corrected for the background count and for the usual Lorentz and polarization effects. A total of 2329 independent non-zero reflections were measured visually.

The crystal belongs to the triclinic system, with two fomula units in a cell with dimensions of; a=11.566, b=12.238, c=8.228Å, α=96.98, β=103.45, γ=104.90°. The space group is P$\bar{1}$. The structure has been determined by the Patterson synthesis, a series of Fourier syntheses, and the least-squares method. The final R value is 0.0788 for 2292 observed reflection.

Bond Distances (Å)



Bond Angles (°)



From the determined structure of the cycloadduct, we can see that the bonds of C_1-C_5 (1.59 Å) and C_1-C_7 (1.60 Å) are unusually lengthened compaired with normal carbon-carbon single bond distance (∿1.53 Å). This suggests the high reactivity of the cycloadduct about the concerned bonds. In fact the fission of these carbon-cabon single bonds participates in the 1,3-sigmatropy of the 1,2-cycloadduct[2] and in the formation of dihydroazatropolone[3].

REFERENCES

1 Dioxopyrrolines VII. Part VI. T. Sano and Y. Tsuda, Heterocycles, the preceding paper.

2 See Part VI.

3 Dioxopyrrolines II. T. Sano and Y. Tsuda, Heterocycles, 1976, 4, 1229.

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