The Structure of the Cyclo-adduct from *exo*-3-Phenyl-3,4,5-triazatricyclo[5,2,1,$0^{2,6}$]dec-4-ene and *p*-Bromophenyl Isocyanate[1]

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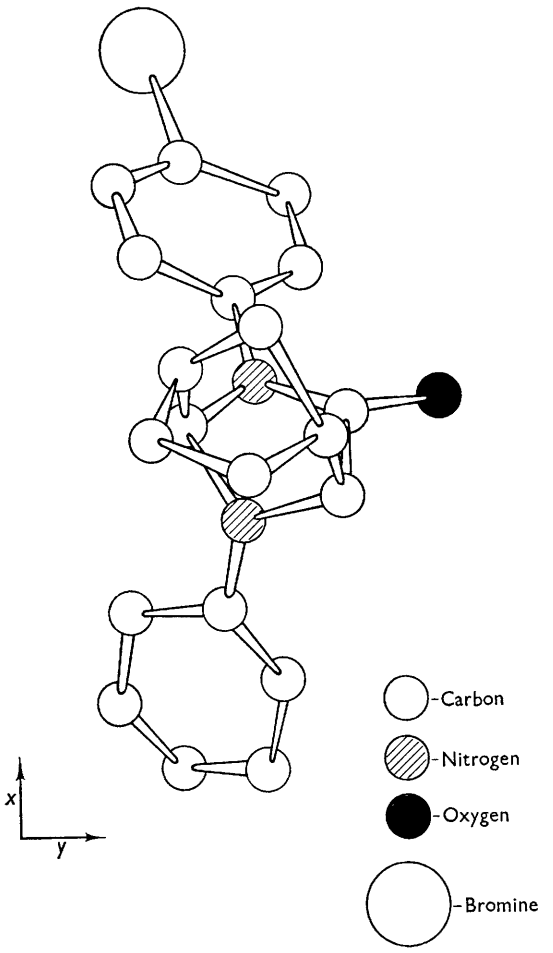
HEATING the adduct from phenyl azide and norbornene, *exo*-3-phenyl-3,4,5-triazatricyclo[5,2,1,$0^{2,6}$]-dec-4-ene (I), with phenyl isocyanate gives nitrogen and an adduct, $C_{20}H_{20}N_2O$, originally formulated as the urea (II) produced through a "1,3-dipolar cycloaddition" reaction.[2,3] More recently structure (II) for the product was shown to be untenable,[4] and the product was assigned the unusual heterocyclic structure (IIIa).[5,6] This structural proposal accommodated all available spectroscopic and chemical information and afforded a basis for rationalizing the formation of new degradation products obtained by other workers.[7] Nevertheless, the structural assignment has been characterized as "speculative"[7]; the so-called unorthodox reaction of triazoline (I) with phenyl isocyanate and the final structural elucidation of the product have been said to require further investigation.[7]

We now report a complete *X*-ray single-crystal structure determination for a heavy-atom derivative of the adduct (IIIa). The triazoline (I) and *p*-bromophenyl isocyanate at 160° gave an adduct $C_{20}H_{19}BrN_2O$, m.p. 176—178°, which crystallized as fine needles belonging to the monoclinic system with $a = 18{\cdot}27 \pm 0{\cdot}02$, $b = 6{\cdot}34 = 0{\cdot}01$, $c = 15{\cdot}16 \pm 0{\cdot}02$ Å, and $\beta = 106°30' \pm 12'$. The cell parameters were determined on a precession camera using Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). The space group is $P2_1/c$ with four molecules of $C_{20}H_{19}BrN_2O$ in the unit cell.

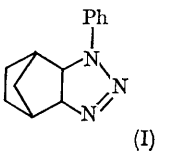


FIGURE

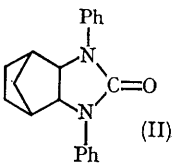
Stereographic projection of the molecule into the ab*-plane.*

Three-dimensional intensity data were recorded on equi-inclination Weissenberg photographs (Cu-K_α, $\lambda = 1{\cdot}5418$ Å) and estimated visually. A total of 1658 independent structure amplitudes was obtained. The signs of the structure amplitudes were obtained by the heavy-atom method,[8] and subsequent refinement has reduced the crystallographic R-factor to 0·14. The molecular structure is clearly established as (IIIb); a perspective drawing of the molecule projected onto the *ab*-plane is shown in the Figure. The bond lengths and angles agree well with expected values. Full crystallographic details will be published at a later date.

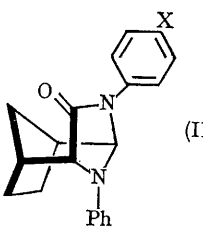
Thus the structure of the product from the "unorthodox"[7] reaction of triazoline (I) and aryl isocyanates is definitely (III), in confirmation of the earlier assignment.[5,6]



(I)



(II)



(III) a; X = H
b; X = Br

(*Received, May 2nd,* 1966; *Com.* 293.)

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