# Reaction of Hexamethylbicyclo[2,2,0]hexadiene with Cyanogen Azide and Benzenesulphonyl Azide

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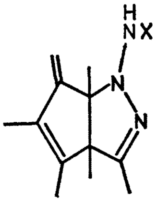
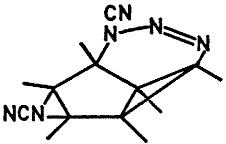
*Summary* Reaction of hexamethylbicyclo[2,2,0]hexadiene with cyanogen azide is time- and temperature-dependent and produces three distinct skeletal systems.

OWING to its unique structural characteristics and also to its present availability, hexamethylbicyclo[2,2,0]hexadiene has featured in a number of recent reports.[1] In particular, its nucleophilic behaviour has been examined extensively by employing such electrophiles as *N*-sulphonylcarbamate,[2] chlorosulphonyl isocyanate,[3] and a variety of Brønsted acids.[4] Although in each case the hydrocarbon undergoes rapid skeletal rearrangement the seemingly similar dipolar electrophiles lead to radically different tricyclic products. This surprising result prompts us to detail our own observations on the reaction of hexamethylbicyclo[2,2,0]hexadiene with cyanogen azide,[5] a powerful dipolar electrophile.[6]

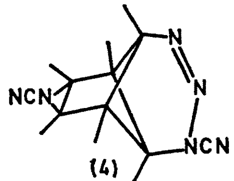
Prolonged contact (*ca.* 10 hr) at ambient temperature of cyanogen azide with a substantial excess of hexamethylbicyclo[2,2,0]hexadiene in ethyl acetate leads, in *ca.* 30% yield, to a single 1:1 adduct without overall loss of molecular nitrogen. This crystalline substance,‡ $C_{13}H_{18}N_4$, m.p. 149—150°, has $\nu_{max}$ (KBr): prominent peaks at 3300 (N–H), 2220 (CN), 1650, and 1620 $cm^{-1}$; $\tau$ ($CDCl_3$): sharp singlets at 8·12, 8·17, 8·24 (9 H), 8·55 (3 H), and 8·68 (3 H), an AB quartet (*J* 2·5 Hz) with doublet components at 5·03 (1 H) and 5·16 (1 H) and a broad signal at 4·33 due to a single, readily exchangeable ($D_2O$) proton; $\lambda_{max}$ ($C_6H_{12}$) 220 nm ($\epsilon$ 16,600) and 255 (8200). Its mass spectrum (20 ev) contains a parent ion (*P*) at *m/e* 230 (38%) and prominent lines at *m/e* 215 ($P - CH_3$) (100%) and 189 ($P$ − NHCN) (14%). The product thus contains five methyl groups and one *exo*-methylene function (n.m.r.), a conjugated diene system (u.v.), and a cyanamido-entity (m.s., i.r.). Furthermore, on treatment with molecular hydrogen (Pd–C) at 50 lb./in.$^2$ it underwent efficient (79% yield) and specific hydrogenolysis to produce trimethylpyrazole, identical (m.p., n.m.r., i.r.) with authentic material.[7] We conclude on the basis of *all* the information at hand that (**1a**) represents the most likely structure for the product.



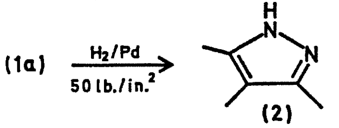
(1a) X = CN
(1b) X = $SO_2Ph$



(3)



(4)



(2)

In striking contrast to these results, extended treatment (*ca.* 10 hr) of hexamethylbicyclo[2,2,0]hexadiene with cyanogen azide in ethyl acetate at *ca.* 0° leads to an entirely different substance, $C_{14}H_{18}N_6$,‡ in *ca.* 23% yield.§ This product, though moderately stable as a solid is quite labile in solution, its decomposition being especially rapid in media of high dielectric constant. Its i.r. spectrum shows prominent peaks (KBr) at 2210 (CN), 1690, and 1650 $cm^{-1}$; n.m.r. $\tau$ ($CDCl_3$): sharp singlets at 7·73 (3H), 7·97, 7·99 (6 H), 8·16 (3 H), 8·60 (3 H), and 8·77 (3 H); mass spectrum (20 ev): parent ion (*P*) at *m/e* 270 (23%) and *m/e* 175 (100%). The molecule thus lacks an NH function (i.r.) and is entirely unsymmetrical (n.m.r.). We believe that structure (**3**) best accommodates the data.

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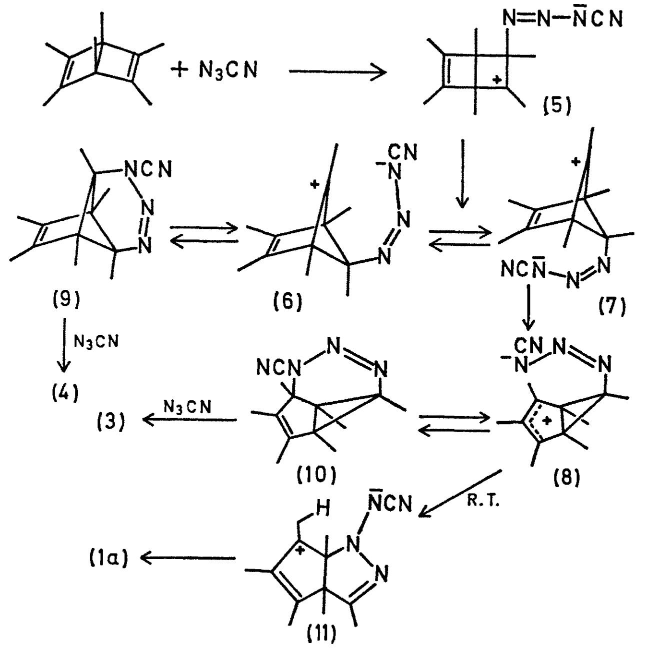
† National Science Foundation Trainee, 1969—70.

‡ Satisfactory elemental analyses were obtained for *all* new compounds isolated.

Finally, brief contact (*ca.* 20 min) of hexamethylbicyclo[2,2,0]hexadiene with cyanogen azide in ethyl acetate at 0° leads to the exclusive formation, in *ca.* 15% yield,§ of yet another compound of formula $C_{14}H_{18}N_6$, m.p. 160—161°, $\nu_{max}$ (KBr): prominent absorptions at 2250 (CN) and 1590 cm$^{-1}$; n.m.r. $\tau$ ($CDCl_3$): sharp singlets at 8·15 (6 H), 8·32 (3 H), 8·47 (3 H), and 9·35 (6 H); $\lambda_{max}$ end-absorption only; mass spectrum (20 ev): parent ion (*P*) at *m/e* 270 (< 0·5%) and prominent lines at *m/e* 242 (*P* — $N_2$) (16%), 175 (33%), and 136 (100%). Obviously, this third compound lacks an NH group (i.r.) and possesses an element of symmetry (two pairs of equivalent methyls by n.m.r.). Structure (**4**) best accommodates the results.



SCHEME

Compounds (**3**) and (**4**) neither interconvert under the reaction conditions, nor is either of them formed on reaction of (**1a**) with cyanogen azide. Conversely, the precursors to these products appear to be intricately, albeit irreversibly, related to one another. Specifically, we find that: (i) only (**4**) is formed when a portion of a mixture, derived from brief contact (*ca.* 20 min), at 0°, of cyanogen azide with a large excess of hexamethylbicyclo[2,2,0]hexadiene in ethyl acetate is treated with an excess of azide; (ii) both (**3**) and (**4**) are formed, in a 3·5:1 ratio, when a second portion of the reaction mixture is allowed to "age" (*ca.* 5 hr) at 0° before quenching with additional azide; and (iii) (**1a**) is the sole product on allowing a further portion of the original mixture to "age" (*ca.* 5 hr) at room temperature. Furthermore, isomerization proceeds most readily in media of high dielectric constant.¶**

The results presented here and closely related information concerning the course of low-temperature protonation[4] of hexamethylbicyclo[2,2,0]hexadiene suggest the self-consistent mechanistic interpretation summarized in the Scheme. In this, the product of initial electrophilic addition (**5**) is shown to isomerize rapidly to one or both of the two stereoisomeric ions (**6**) and (**7**). Furthermore, analogy with low-temperature protonation requires that these two ions exist in a state of rapid interconversion and that leakage to ion (**8**) be a relatively slow process. Nevertheless this latter ion is expected to be formed irreversibly from (**7**), so that eventually (**9**) ought to isomerize completely to (**10**). At ambient temperatures (**8**) may then undergo an irreversible vinyl–cyclopropane-type rearrangement to ion (**11**) which is in turn ideally suited to generate (**1a**) by internal proton transfer through a reasonable six-membered transition state. Addition of an excess of cyanogen azide during the very early stages of the low temperature reaction should produce (**4**), while quenching with azide of an "aged" low-temperature mixture ought to lead predominantly to (**3**). Because of the rapid interconversion between (**6**) and (**7**) depicted here, it would be totally meaningless to comment on the stereochemical course of the initial addition, *i.e.*, the stereochemistry of this process may not be deduced from the structural details of the skeletally rearranged products.

Benzenesulphonyl azide, being less electrophilic than cyanogen azide, reacts with the hydrocarbon only on prolonged contact (*ca.* 48 hr) at an elevated temperature (*ca.* 50°) to produce a compound $C_{18}H_{23}N_3SO_2$, m.p. 139—140°.‡ This material was characterized as (**1b**) on the basis of spectral data; $\nu_{max}$ (KBr) prominent absorption at 3250 (NH), 1660, and 1610 cm$^{-1}$; n.m.r. $\tau$ ($CDCl_3$): sharp singlets at 8·57 (3 H), 8·79 (3 H), 8·86 (3 H), 9·08 (3 H), and 9·33 (3 H), an AB quartet (*J* 2·0 Hz) with doublet components centred at 4·93 (1 H) and 5·73 (1 H), a broad singlet at 4·50 (1 H), and a complex multiplet at 2·0—2·7 (5 H).

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§ Optimum yield obtained on employing a two-fold excess of azide.

¶ For example, on changing the solvent from ethyl acetate (ε 6·02) to dichloromethane (ε 9·08) "run" (*ii*) produces (**3**) exclusively.

** To date, all our attempts to isolate and characterize the direct precursor of either (**3**) or (**4**) have been unsuccessful.

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