

## Furazan *N*-Oxides. Part 3.<sup>1,2</sup> Synthesis of Di-isocyanates from Strained Norbornane† Furazan *N*-Oxides

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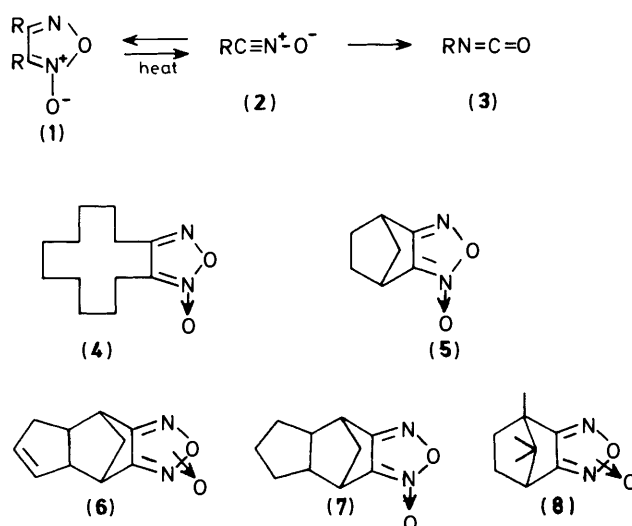
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Thermolysis, at *ca.* 110 °C, of the strained norbornane furazan *N*-oxides (5)—(8) in toluene, saturated with sulphur dioxide, affords the isomeric 1,3-di-isocyanatocyclopentanes (14)—(17). Product formation is explained by a mechanism involving cleavage of the furazan ring to cyclopentane-1,3-bis(nitrile oxides) [*e.g.* (9)], followed by 1,3-dipolar cycloaddition with SO<sub>2</sub> to form bis-1,3,2,4-dioxathiazol-2-ones [*e.g.* (12)]. Subsequent extrusion of SO<sub>2</sub> and rearrangement yields di-isocyanates [*e.g.* (14)] which were identified spectroscopically and by preparation of urethane and/or urea derivatives on reaction with alcohols and aniline. Compound (8) with aniline gives the cyclic biuret (20) rather than a bis-urea, the structure of the product being established by X-ray crystallography. In the absence of SO<sub>2</sub> polymeric furoxans are formed.

Furazan *N*-oxides (furoxans) (1) have often been regarded as unwanted dimers formed during the 1,3-dipolar cycloaddition reactions of nitrile oxides (2). However, it has recently been established<sup>3,4</sup> that they can undergo thermal cycloreversion thus providing a source of both compounds (2) and, by rearrangement, the isomeric isocyanates (3). The corresponding process for a bicyclic furoxan yields a bis(nitrile oxide) and a di-isocyanate; *e.g.* decamethylene di-isocyanate is formed from decamethylenefuroxan (4) at 240 °C. We have earlier reported<sup>1</sup> the synthesis of the norbornene- and dicyclopentadiene-derived furoxans, (5) and (6), from the parent cycloalkenes by treatment with dinitrogen trioxide followed by dehydration of the resulting nitronitroso adduct. We now describe the conversion of these furoxans and also the tricyclodecene and camphor analogues, (7) and (8), into the isomeric 1,3-di-isocyanatocyclopentanes.

### Results and Discussion

Simple disubstituted furoxans and unstrained bicyclic analogues such as (4) undergo cycloreversion to nitrile oxides at 200–250 °C, at which temperature the nitrile oxide to isocyanate rearrangement is rapid; hence the ready formation of decamethylene di-isocyanate from (4). In contrast the strained compounds (5)—(8) are much less stable and decompose at 60–100 °C; below the threshold apparently necessary for isocyanate generation.<sup>5a</sup> Thus heating norbornene furoxan (5) at 110 °C in toluene did not yield the required di-isocyanate (14). Instead the product was an amorphous white solid with an i.r. spectrum showing an intense peak at 1595 cm<sup>-1</sup> but no absorption in the region 2250–2270 cm<sup>-1</sup> characteristic of isocyanates. Peaks at *ca.* 1600 cm<sup>-1</sup> are typical of unstrained furoxans, and we therefore believe the product to be a polymeric furoxan of general structure (10), resulting from ring opening of the furoxan (5) to give cyclopentane-1,3-bis(nitrile oxide) (9) which may be expected to undergo intermolecular dimerisation at the nitrile oxide groups. Unhindered aliphatic nitrile oxides are reported<sup>5b</sup> to have short lifetimes even at room temperature. Further support for structure (10) is provided by examination of its mass spectrum. A major peak at 92 a.m.u. (C<sub>7</sub>H<sub>8</sub>) and a smaller one at 65 a.m.u. (C<sub>5</sub>H<sub>5</sub>) are consistent with de-



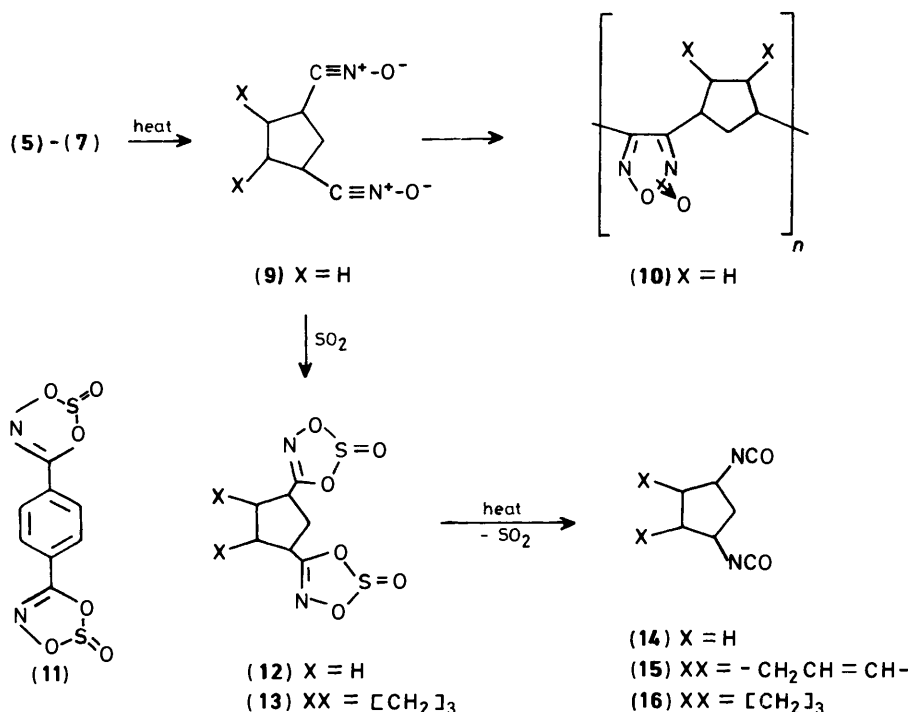
polymerisation and loss of N<sub>2</sub>O<sub>2</sub>, an established fragmentation pathway for furoxans under ionising radiation.<sup>6</sup>

In order to achieve the conversion of such strained furoxans into the isomeric di-isocyanates it was therefore necessary to intercept the bis(nitrile oxide) before polymerisation could take place. The approach selected is based on the work of Burk and Carlos<sup>7</sup> who found that treatment of terephthalonitrile di-*N*-oxide with sulphur dioxide yielded the bis(dioxathiazole) (11), from which *p*-phenylene di-isocyanate could be generated by thermal expulsion of SO<sub>2</sub> and rearrangement.

A solution of norbornene furoxan (5) in toluene was saturated with sulphur dioxide and the mixture was heated under reflux for 0.5 h. Removal of the solvent and SO<sub>2</sub> left an oil from which 1,3-di-isocyanatocyclopentane (14), (72%) was isolated by distillation. The product was identified from its spectroscopic data [*v*<sub>max</sub>, 2260 cm<sup>-1</sup>; *δ*<sub>c</sub>, 122.5 p.p.m. (NCO); *m/z* 152 (*M*<sup>+</sup>)] and by the preparation of its bis-urea derivative on treatment with aniline. The proposed route (Scheme 1) involves initial cleavage of the oxadiazole at the O(1)–N(2) and C(3)–C(4) bonds, rapid 1,3-dipolar cycloaddition of the resulting bis(nitrile oxide) (9) with S=O of the sulphur dioxide to form the bis(dioxathiazolyl)cyclopentane (12), followed by thermal cycloreversion of the latter to yield di-isocyanate (14).

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‡ Norbornane here refers to bicyclo[2.2.1]heptane.



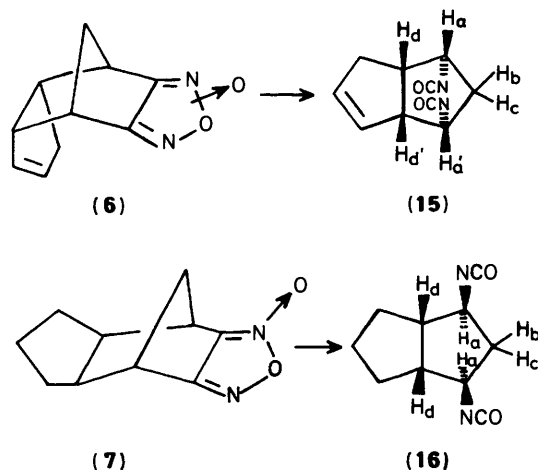
Scheme 1.

by extrusion of SO<sub>2</sub> and rearrangement. The S=O bond of sulphur dioxide is reported to be a reactive dipolarophile towards nitrile oxides even at room temperature, and the formation of isocyanates from 1,3,2,4-dioxathiazol-2-ones at 100–150 °C is well established.<sup>7</sup> The tricyclodecene-derived furoxans, (6) and (7), reacted similarly yielding, respectively, 6,8-di-isocyanatobicyclo[3.3.0]oct-2-ene (15) (78%) and the dihydro compound (16) (55%). Treatment with aniline and methanol gave the corresponding urea and urethane derivatives, respectively.

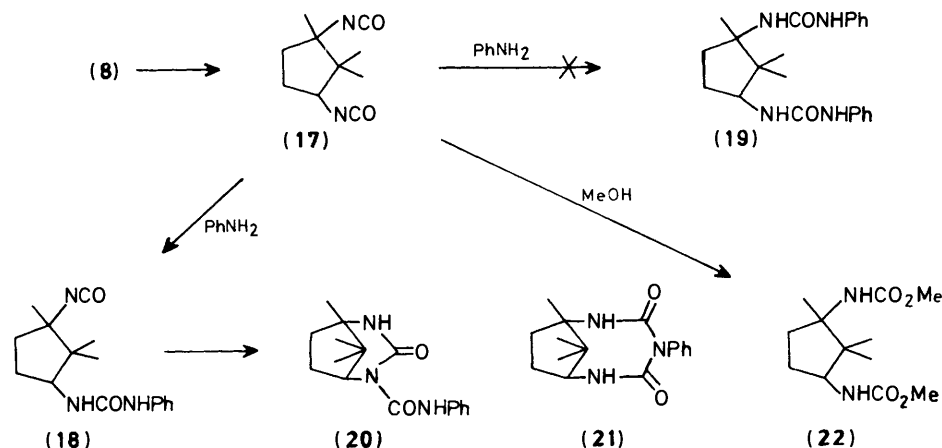
In order to confirm the involvement of dioxathiazolones as intermediates in the isomerisation process, compound (7) was treated with SO<sub>2</sub> in toluene at room temperature and the reaction was monitored by i.r. spectroscopy. After one week a strong peak had appeared at 1245 cm<sup>-1</sup>, characteristic of dioxathiazolones.<sup>7</sup> Its intensity subsequently decreased as the isocyanate absorption at 2260 cm<sup>-1</sup> reached its maximum. Furthermore, when the solution was treated with aqueous iron(III) chloride a deep purple colour was formed, consistent with hydrolysis of compound (13) to bicyclo[3.3.0]octane-2,4-dihydroxamic acid and formation of its Fe<sup>3+</sup> complex.<sup>8</sup>

Detailed examination of the <sup>1</sup>H n.m.r. spectra of compounds (15) and (16) allows their stereochemistry to be determined. As it had previously been established<sup>1</sup> that the propenylene group in the furoxan (6) is *endo*, it was anticipated that for the resulting di-isocyanate (15) the CH<sub>2</sub>CH=CH<sub>2</sub> chain would be arranged *cis* to the isocyanato substituents, which themselves must of necessity be *cis* to each other. The observed splitting patterns (*J*<sub>ab</sub> ≈ *J*<sub>a'b</sub> = 10.2 Hz; *J*<sub>ad</sub> ≈ *J*<sub>a'd</sub> = 8.1 Hz; *J*<sub>a'c</sub> ≈ *J*<sub>ac</sub> = 5.5 Hz) for the protons H<sub>a</sub> and H<sub>a'</sub> adjacent to the isocyanates are in accord with this expectation. Similar arguments for compound (16) for which *J*<sub>ab</sub> ≈ *J*<sub>ad</sub> = 5.5 Hz and *J*<sub>ac</sub> = 8.1 Hz confirm that the trimethylene group is *trans* to the isocyanates, consistent with the *exo*-geometry for the furoxan (7).

Similar treatment of the camphor-derived furoxan (8) with sulphur dioxide in toluene under reflux afforded the expected diisocyanate (17) (77%). In this case the two isocyanate groups



show different reactivity (Scheme 2). Heating with excess of aniline in ether under reflux afforded a white solid which showed strong i.r. absorptions at 3370 and 1690 cm<sup>-1</sup> (NHCO) and also at 2260 cm<sup>-1</sup> (NCO). From these data and its <sup>1</sup>H n.m.r. and mass spectrum (*m/z* 287) the product was identified as the monourea-monoisocyanate derivative (18). Thermolysis of diisocyanate (17) at 110–115 °C with aniline did not give the expected bis-urea (19) but instead gave a product with formula C<sub>16</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>, *m/z* 287, and i.r. peaks at 3290 and 1690 cm<sup>-1</sup> (NHCO) but none at 2260 cm<sup>-1</sup>. Two structures were considered: the cyclic biurets (20) and (21) formed by intramolecular reaction between the residual isocyanato group in compound (18) and the N(1)-H or N(3)-H of the 3-phenylureido substituent. The i.r. data are consistent with both arrangements but the absence of a 7–8 Hz coupling to the adjacent CH in the <sup>1</sup>H n.m.r. peak at δ<sub>H</sub> 5.62, a coupling which is clearly resolved for the other phenylurea derivatives [*e.g.* that



Scheme 2.

derived from (14)], was taken as evidence for structure (20). Unequivocal proof for this arrangement was obtained by single-crystal *X*-ray structure analysis. A view of the *X*-ray molecular structure of compound (20) with the atom-labelling scheme and with hydrogen atoms omitted is shown in the Figure. The atomic co-ordinates are given in Table 1 and selected torsion angles in Table 2. Listings of bond lengths, bond angles, thermal parameters, and atomic co-ordinates for all atoms have been deposited as supplementary material. The atoms of the biuret grouping N(2), C(1), O(1), N(1), C(2), O(2), N(3), C(3) are nearly but not exactly coplanar (maximum deviation 0.16 Å; see also torsion angles in Table 2); the phenyl ring is twisted 40° from this plane. There is an intramolecular hydrogen bond (2.57 Å) involving N(3)–H and O(1).

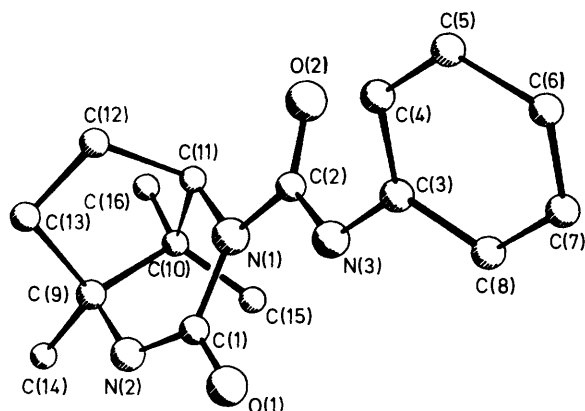


Figure. *X*-Ray molecular structure of cyclic biuret (20) showing atom labelling

In contrast to its behaviour with aniline, reaction of diisocyanate (17) with methanol in the presence of triethylamine yielded the dicarbamate (22).

From these results it is evident that the use of sulphur dioxide allows strained furoxans to be converted easily into the isomeric diisocyanates. The route is of particular value for those furoxans, such as (6) which are accessible from readily available cycloalkenes. A straightforward and inexpensive route is thus provided from these cycloalkenes to diisocyanates suitable for polyurethane formation.<sup>9</sup>

Table 1. Atomic co-ordinates for cyclic biuret (20) (estimated standard deviations *ca.* 0.002)

Atom	<i>x</i>	<i>y</i>	<i>z</i>
O(1)	0.2639	0.7969	0.3812
O(2)	0.1399	0.8875	0.6113
N(1)	0.1021	0.8150	0.4403
N(2)	0.0614	0.7028	0.2818
N(3)	0.3179	0.8937	0.5730
C(1)	0.1513	0.7704	0.3693
C(2)	0.1862	0.8672	0.5473
C(3)	0.4191	0.9440	0.6803
C(4)	0.4429	0.9130	0.7925
C(5)	0.5465	0.9627	0.8962
C(6)	0.6342	1.0460	0.8921
C(7)	0.6091	1.0764	0.7822
C(8)	0.5052	1.0268	0.6758
C(9)	−0.0841	0.6713	0.2566
C(10)	−0.1409	0.7767	0.2803
C(11)	−0.0425	0.7852	0.4161
C(12)	−0.0406	0.6667	0.4588
C(13)	−0.0576	0.5913	0.3639
C(14)	−0.1659	0.6214	0.1303
C(15)	−0.1455	0.8770	0.2097
C(16)	−0.2952	0.7546	0.2533

Table 2. Selected torsion angles (°) for cyclic biuret (20)

C(4)–C(3)–N(3)–C(2)	42
C(3)–N(3)–C(2)–N(1)	−178
N(3)–C(2)–N(1)–C(1)	12
C(2)–N(1)–C(1)–N(2)	166
N(1)–C(1)–N(2)–C(9)	−1

## Experimental

Mass spectra (70 eV ionisation potential) were measured using an AEI MS 902 instrument. Bruker WH 360 and Varian HA 100, Bruker WP 200 and Varian CFT 20, and Perkin-Elmer 257 spectrometers were used to record <sup>1</sup>H, <sup>13</sup>C n.m.r. and i.r. spectra respectively. 4,5,6,7-Tetrahydro-4,7-methanobenzo-[1,2,5]oxadiazole 1-oxide (norbornene furoxan) (5), 4a,5,7a,8-tetrahydro-4,8-methano-4*H*-indeno[5,6-*c*][1,2,5]oxadiazole 1- and 3-oxide (dicyclopentadiene furoxans) (6), 4a,5,6,7,7a,8-hexahydro-4,8-methano-4*H*-indeno[5,6-*c*][1,2,5]oxadiazole 1-

oxide (tricyclodecene furoxan) (7), and 4,5,6,7-tetrahydro-4,8,8-trimethyl-4,7-methanobenzo[1,2,5]oxadiazole 1- and 3-oxide (camphor furoxans) (8) were prepared as previously described;<sup>1</sup> **HAZARD WARNING:** Some strained furoxans have been found to decompose explosively if heated neat at temperatures as low as 80 °C. We strongly recommend that they be handled in solution.

**Thermolysis of Norbornene Furoxan, (5), in the Absence of Sulphur Dioxide.**—A solution of norbornene furoxan (1.00 g, 6.6 mmol) in dry toluene (25 ml) was heated under reflux for 2 h. After the mixture had cooled, the resulting precipitate was filtered off and dried to form a compound, presumed to be a polymer such as (10), as an amorphous white solid (0.73 g) [Found: C, 55.1; H, 5.4; N, 18.6. Calc. for  $(C_7H_8N_2O_2)_n$ : C, 55.3; H, 5.3; N, 18.4%;  $\nu_{\max}$  (Nujol) 1595  $\text{cm}^{-1}$  (furoxan N-oxide);  $m/z$  (%) 92 (38), 91 (45), 68 (2), and 65 (5).

**Synthesis of Di-isocyanates (14), (15), (16), and (17).**—The general method was to heat under reflux a solution of the furoxan in toluene saturated with sulphur dioxide, as described below for the conversion of norbornene furoxan (5) into 1,3-di-isocyanatocyclopentane (14). After removal of the solvent and  $\text{SO}_2$  the crude products were purified by vacuum distillation.

**1,3-Di-isocyanatocyclopentane (14).** A solution of norbornene furoxan (1.05 g, 6.9 mmol) in dry toluene (50 ml) was saturated with sulphur dioxide and the mixture was heated under reflux for 0.5 h. After the mixture had cooled, and  $\text{SO}_2$  had been removed by the passage of a stream of dry nitrogen, the solvent was evaporated off under reduced pressure to leave a pale yellow oil. Vacuum distillation (40–42 °C; 0.05 mmHg) yielded 1,3-di-isocyanatocyclopentane (14) (0.76 g, 72%) as a liquid (Found: C, 55.0; H, 5.2; N, 18.4.  $C_7H_8N_2O_2$  requires C, 55.3; H, 5.3; N, 18.4%;  $\nu_{\max}$  (thin film) 2260  $\text{cm}^{-1}$  (NCO);  $\delta_H$  ( $\text{CDCl}_3$ ; 100 MHz) 3.85–4.10 (2 H, m, 1- and 3-H), 2.28 (1 H, dt, 2-H), and 1.7–2.1 [5 H, m, 2-H and  $(\text{CH}_2)_2$ ];  $\delta_C$  ( $\text{CDCl}_3$ ; 20 MHz) 122.5 (2  $\times$  NCO), 53.3 (2  $\times$  CHNCO), 43.7 ( $\text{CH}_2$ ), and 33.7 p.p.m. (2  $\times$   $\text{CH}_2$ );  $m/z$  152 ( $M^+$ ).

A portion of the product (0.31 g, 2.0 mmol) dissolved in dry ether (10 ml) was treated at room temperature with aniline (0.50 g, 5.4 mmol). After 1 h the resulting precipitate was filtered off, washed with ether, and recrystallised from ethanol to yield 1,3-bis-(3-phenylureido)cyclopentane (0.70 g, 96%) as a white crystalline solid, m.p. 259 °C (from EtOH) (Found: C, 67.4; H, 6.7; N, 16.4.  $C_{19}H_{22}N_4O_2$  requires C, 67.5; H, 6.5; N, 16.6%;  $\nu_{\max}$  3314 and 1560 (NH), and 1660  $\text{cm}^{-1}$  (C=O);  $\delta_H$  ( $\text{CDCl}_3$ ; 80 MHz) 8.29 (2 H, s, NH), 6.7–7.5 (10 H, m, 2  $\times$  Ph), 6.23 (2 H, d,  $J$  7 Hz, NH), and 3.7–4.2 and 1.0–2.5 (8 H, m, 2  $\times$  CH and 3  $\times$   $\text{CH}_2$ );  $m/z$  338 ( $M^+$ ).

**6,8-Di-isocyanatobicyclo[3.3.0]oct-2-ene (15).** This was similarly prepared (78%) from dicyclopentadiene furoxan and was isolated as an oil, b.p. 85–90 °C at 0.1 mmHg (Found: C, 62.8; H, 5.4; N, 14.8.  $C_{10}H_{10}N_2O_2$  requires C, 63.2; H, 5.7; N, 14.6%;  $\nu_{\max}$  (thin film) 2260  $\text{cm}^{-1}$  (NCO);  $\delta_H$  ( $\text{CDCl}_3$ ; 360 MHz) 4.93 (1 H, dq, =CH), 5.62 (1 H, dq, =CH), 3.95 (1 H, ddd,  $J_{ab}$  10.3,  $J_{ad}$  8.0,  $J_{ac}$  5.5 Hz,  $H_a$ ), 3.84 (1 H, ddd,  $J_{ab}$  10.1,  $J_{ad}$  8.0,  $J_{ac}$  5.6 Hz,  $H_a$ ), 3.39 (1 H, m,  $H_d$ ), 2.89 (1 H, m,  $H_d$ ), 2.54 (2 H, m, 4- $H_2$ ), 2.19 (1 H, dt,  $J_{cb}$  11.8,  $J_{ca}$  5.6 Hz,  $H_c$ ), and 1.73 (1 H, dt,  $J_{bc}$  11.8,  $J_{ba}$  10.3 Hz,  $H_b$ );  $\delta_C$  ( $\text{CDCl}_3$ ; 50 MHz) 134.3 and 128.0 (=CH), 122.7 and 122.2 (NCO), 54.2 (2  $\times$  CHNCO), 53.8 and 43.6 (2  $\times$  CH), and 40.0 and 34.9 (2  $\times$   $\text{CH}_2$ );  $m/z$  190 ( $M^+$ ).

Treatment with an excess of methanol and a few drops of triethylamine afforded dimethyl bicyclo[3.3.0]oct-2-ene-6,8-dicarbamate (89%) as crystals, m.p. 185–188 °C (from EtOH) (Found: C, 57.4; H, 7.3; N, 11.0.  $C_{12}H_{18}N_2O_4$  requires C, 57.6; H, 7.1; N, 11.0%;  $\nu_{\max}$  (Nujol) 3300 (NH) and 1695  $\text{cm}^{-1}$  (C=O);  $\delta_H$  ( $\text{CDCl}_3$ ; 80 MHz) 5.86 (1 H, m, =CH), 4.40 (1 H, m,

=CH), 4.75 (1 H, d, NH), 4.65 (1 H, d, NH), 1.0–4.2 (8 H, m, 4  $\times$   $\text{CH}_2$  and 2  $\times$   $\text{CH}_2$ ), and 3.64 (6 H, s, 2  $\times$  Me);  $m/z$  254 ( $M^+$ ).

**2,4-Di-isocyanatobicyclo[3.3.0]octane (16).** This was similarly prepared (55%) from tricyclodecene furoxan and was isolated as an oil, b.p. 95–110 °C at 0.6 mmHg (Found:  $M^+$ , 192.091 02.  $C_{10}H_{12}N_2O_2$  requires  $M$ , 192.089 87)  $\nu_{\max}$  (thin film) 2250  $\text{cm}^{-1}$  (NCO);  $\delta_H$  ( $\text{CDCl}_3$ ; 100 MHz) 3.44 (2 H, dt,  $J_{ac}$  8.2,  $J_{ab} \approx J_{ad}$  5.5 Hz,  $H_a$ ), 2.5–2.7 (2 H, m,  $H_d$ ), 2.23 (1 H, dt,  $J_{bc}$  12.1,  $J_{ba}$  5.5 Hz,  $H_b$ ), 1.81 (1 H, dt,  $J_{cb}$  12.1,  $J_{ca}$  8.2 Hz,  $H_c$ ), and 0.8–2.3 (6 H, m, 3  $\times$   $\text{CH}_2$ );  $\delta_C$  ( $\text{CDCl}_3$ ; 20 MHz) 122.5 (2  $\times$  NCO), 58.7 (2  $\times$  CHNCO), 52.1 (2  $\times$  CH), and 42.8, 31.5, and 25.6 p.p.m. (4  $\times$   $\text{CH}_2$ );  $m/z$  192 ( $M^+$ ).

Treatment with aniline yielded 2,4-bis-(3-phenylureido)bicyclo[3.3.0]octane, m.p. 258–260 °C (from EtOH) (Found: C, 69.5; H, 7.1; N, 15.1.  $C_{22}H_{26}N_4O_2$  requires C, 69.8; H, 6.9; N, 14.8%;  $\nu_{\max}$  (Nujol) 3300 and 1555 (NH), and 1650  $\text{cm}^{-1}$  (C=O);  $\delta_H$  [( $\text{CD}_3$ ) $_2$ SO; 80 MHz] 8.3 (2 H, s, NH), 6.8–7.5 (10 H, m, 2  $\times$  Ph), 6.20 (2 H, d, NH), and 3.3–3.8 and 1.1–2.6 (12 H, m, 4  $\times$  CH and 4  $\times$   $\text{CH}_2$ );  $m/z$  378 ( $M^+$ ).

**1,3-Di-isocyanato-1,2,2-trimethylcyclopentane (17).** This was similarly prepared (77%) from camphor furoxan and was isolated as a pale yellow oil, b.p. 46 °C at 2 mmHg (Found:  $M^+$ , 194.105 67.  $C_{10}H_{14}N_2O_2$  requires  $M$ , 194.105 52);  $\nu_{\max}$  (thin film) 2260  $\text{cm}^{-1}$  (NCO);  $\delta_H$  ( $\text{CDCl}_3$ ; 100 MHz) 3.60 (1 H, t, CHNCO), 1.6–2.3 (4 H, m, 2  $\times$   $\text{CH}_2$ ), 1.26 (3 H, s, Me), 1.01 (3 H, s, Me), and 0.88 (3 H, s, Me);  $\delta_C$  ( $\text{CDCl}_3$ ; 20 MHz) 122.5 and 122.4 (NCO), 67.8 (CNCO), 62.4 (CHNCO), 48.6 ( $\text{CMe}_2$ ), 37.8 and 29.8 (2  $\times$   $\text{CH}_2$ ), and 25.4, 22.2, and 19.3 p.p.m. (Me);  $m/z$  194 ( $M^+$ ).

A portion of the product (0.20 g, 1.0 mmol) dissolved in ether (15 ml) was treated with aniline (0.57 g, 6.1 mmol) and the mixture was heated under reflux for 0.5 h and then cooled to afford compound (18) as a white solid (0.15 g), m.p. 182–183 °C (Found: C, 67.0; H, 7.5; N, 14.5.  $C_{16}H_{21}N_3O_2$  requires C, 66.9; H, 7.4; N, 14.6%;  $\nu_{\max}$  (Nujol) 3370 (NH), 2260 (NCO), and 1690  $\text{cm}^{-1}$  (C=O);  $\delta_H$  [( $\text{CD}_3$ ) $_2$ SO; 100 MHz] 8.23 (1 H, s, NH), 6.7–7.4 (5 H, m, Ph), 5.88 (1 H, d,  $J$  7 Hz, NH), 3.8–4.0 (1 H, m, 9-H), 1.6–2.2 (4 H, m, 2  $\times$   $\text{CH}_2$ ), 1.28 (3 H, s, Me), 0.86 (3 H, s, Me), and 0.85 (3 H, s, Me);  $m/z$  287.

A further portion of the di-isocyanate (0.47 g, 4.7 mmol) in toluene was heated under reflux for 3 h with aniline. Removal of the solvent and excess of aniline and treatment of the resulting oil with ether yielded compound (20) as a white solid (0.27 g), m.p. 175–176 °C (from ethanol) (Found: C, 67.0; H, 7.4; N, 14.7.  $C_{16}H_{21}N_3O_2$  requires C, 66.9; H, 7.4; N, 14.6%;  $\nu_{\max}$  (Nujol) 3290 (NH) and 1690  $\text{cm}^{-1}$  (C=O);  $\delta_H$  ( $\text{CDCl}_3$ ; 100 MHz) 11.12 (1 H, s, NH), 6.6–7.3 (5 H, m, Ph), 5.62 (1 H, s, NH), 4.54 (1 H, d,  $J$  5 Hz, CH), 1.6–2.2 (4 H, m, 2  $\times$   $\text{CH}_2$ ), 1.10 (3 H, s, Me), 0.98 (3 H, s, Me), and 0.96 (3 H, s, Me);  $\delta_C$  ( $\text{CDCl}_3$ ; 20 MHz) 156.3 and 152.0 (C=O), 138.5 (aryl *ipso* C), 128.9, 123.3, and 119.8 (5  $\times$  aryl CH), 64.9 and 41.7 (quaternary C), 61.4 (CH), 39.9 and 30.1 (2  $\times$   $\text{CH}_2$ ), and 21.3, 17.1, and 16.9 p.p.m. (Me);  $m/z$  287.

A mixture of the di-isocyanate (0.39 g, 2.0 mmol) methanol (2 ml), and triethylamine (3 drops) in ether (25 ml) was heated under reflux for 30 h. Removal of the solvent afforded dimethyl 1,2,2-trimethylcyclopentane-1,3-dicarbamate (22) (78%) as a white crystalline solid, m.p. 145–146 °C (from toluene) (Found: C, 56.0; H, 8.7; N, 10.7.  $C_{12}H_{22}N_2O_4$  requires C, 55.8; H, 8.6; N, 10.8%;  $\nu_{\max}$  (Nujol) 3320 (NH) and 1695  $\text{cm}^{-1}$  (C=O);  $\delta_H$  ( $\text{CDCl}_3$ ; 100 MHz) 4.76 (1 H, d,  $J$  8 Hz, NH), 4.72 (1 H, s, NH), 3.8–4.1 (1 H, m, CH), 3.63 (3 H, s, OMe), 3.58 (3 H, s, OMe), 1.82–2.4 (4 H, m, 2  $\times$   $\text{CH}_2$ ), 1.29 (3 H, s, Me), 0.95 (3 H, s, Me), and 0.84 (3 H, s, Me);  $\delta_C$  ( $\text{CDCl}_3$ ; 20 MHz) 156.7 and 155.7 (C=O), 62.7 and 47.1 (quaternary C), 58.4 (CH), 51.8 and 51.3

(OMe), 34.5 and 27.6 ( $2 \times \text{CH}_2$ ), and 21.9 and 17.1 p.p.m. ( $3 \times \text{Me}$ );  $m/z$  258 ( $M^+$ ).

*X-Ray Crystal Structure Analysis of Cyclic Biuret (20).*—*Crystal data.*  $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_2$ ,  $M = 287.4$ , monoclinic,  $a = 11.08(2)$ ,  $b = 12.04(3)$ ,  $c = 13.27(3)$  Å,  $\beta = 121.1^\circ$ ,  $Z = 4$ ,  $D_c = 1.26 \text{ g cm}^{-3}$ , space group  $P2_1/c$ , Cu- $K_\alpha$  radiation. All crystals examined were multiple and of poor quality. Weissenberg photographs of the layers  $h0l$ — $h7l$  were of the best available crystal, and were measured by the S.E.R.C. microdensitometer service; layer scale factors were estimated from exposure times. The structure was solved by direct methods and refined, using SHELX; interlayer scale factors were refined in initial rounds; hydrogen atoms were included at stereochemically expected positions; positional and anisotropic vibrational parameters of non-hydrogen atoms were refined. Final  $R$  factor 0.091 for 728 observed reflections (excluding  $h2l$  where photographs were particularly poor, or 0.099 for 827 reflections if included). Atomic co-ordinates and selected torsion angles are shown in Tables 1 and 2. Bond lengths, bond angles, vibration parameters, and atomic co-ordinates including those of hydrogen atoms have been deposited as a Supplementary Publication [SUP. No. 56412 (5 pp)].\*

\* For details of the Supplementary Publications Scheme, see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 1*, 1986, issue 1. Tables of observed and calculated structure factors are available from the editorial office on request.

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