2-propanol bath was replaced with an ice/water bath and stirred for another 5 h. The cap of the Teflon bottle was removed to allow HF to slowly evaporate. The residue was adsorbed onto silica gel, placed on top of a silica gel column, and eluted with a hexane/benzene mixture (80:20), yielding 0.12 g of a yellow solid which was recrystallized from methanol, mp 80–81 °C: ^{1}H NMR δ 7.91–7.97 (m, 2 H), 7.87 (d, 1 H), 7.73 (d, 1 H), 7.50–7.58 (m, 2 H), 7.34–7.39 (m, 2 H), 3.46 (t, 2 H), 3.10 (t, 2 H), 1.99–2.10 (m, 2 H), 1.88–1.99 (m, 2 H); MS, *m/e* (relative intensity) 256 (M$^+$, 100), 254 (23), 228 (36), 226 (22); high resolution MS, *m/e* calcd 256.1252, found 256.1247.

Benz[*a*]aceanthrylene (5). Hydrocarbon **19** (0.3 g) was dissolved in 60 mL of dry benzene. To this solution was added 0.7 g of DDQ and the mixture was refluxed for 2 h. The solution was allowed to cool and adsorbed onto silica gel, placed on top of a silica gel column, and eluted with benzene. The nonpolar fraction was applied to preparative TLC plates (1 mm) and developed with a hexane/benzene mixture (4:1). The major component was crystallized from ethanol, giving 0.23 g of yellow crytalline needles; mp 144.5–146 °C (lit.[21] mp 145–146 °C); UV λ_{max} (EtOH) 215, 258; ^{1}H NMR δ 7.36–7.52 (m, 3 H), 7.60–7.67 (m, 2 H), 7.96–8.00 (m, 3 H), 8.11 (d, 1 H), 8.36 (d, 1 H), 8.42 (s, 1 H), 8.72 (d, 1 H); MS, *m/e* (relative intensity) 252 (M$^+$, 100), 249 (41), 125 (18), 113 (11); high resolution MS, *m/e* calcd 252.0939, found 252.0927.

Acknowledgment. We gratefully acknowledge the generous financial support of this work by the Natural Science and Engineering Research Council of Canada, as well as the Ontario Ministry of Environment ARB.

The Structure of the Products from the Reaction of 4-Phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione with Alcohols

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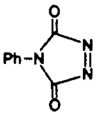
Received August 11, 1986

The title azo compound (1) reacts with alcohols to give 1-(alkoxycarbonyl)-2-(*N*-phenylcarbamoyl)-4-phenyl-1,2,4-triazolidine-3,5-diones (2), the structures originally assigned to them. The X-ray diffraction analysis of the butyl compound **2c** is described, together with details of its synthesis from 1 and from the parent urazole 7.

Ten years ago in a preliminary communication[1] and later in a full paper,[2] we described the formation of 1-(alkoxycarbonyl)-2-(*N*-phenylcarbamoyl)-4-phenyl-1,2,4-triazolidine-3,5-diones (**2**) from the interaction of two molecules of 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (**1**) and one of alcohol, with the loss of one molecule of nitrogen. An independent synthesis of one of these, the methyl ester **2a**, was also reported.[2]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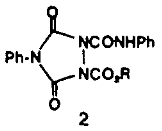
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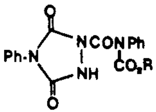
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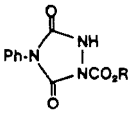
a R = Me
b R = Et
c R = n-Bu
d R = i-Pr
e R = c-C$_5$H$_9$
f R = CH$_2$Ph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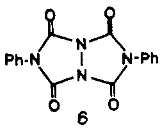
$PhNHCO_2R$

5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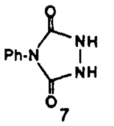
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Table I. Selected X-ray Crystallographic Parameters for 2c

bond lengths, Å		bond angles, deg		Σ[a]
N(1)–N(2)	1.407 (3)	N(2)–N(1)–C(5)	108.4 (2)	
N(1)–C(5)	1.408 (4)	N(2)–N(1)–C(6)	115.1 (2)	348.2 (4)
N(1)–C(6)	1.427 (5)	C(5)–N(1)–C(6)	124.7 (2)	
N(2)–C(3)	1.395 (5)			
N(2)–C(13)	1.457 (4)	N(1)–N(2)–C(3)	108.7 (2)	
C(3)–N(4)	1.389 (4)	N(1)–N(2)–C(13)	114.0 (2)	346.8 (4)
C(3)–O(22)	1.197 (4)	C(3)–N(2)–C(13)	124.1 (2)	
N(4)–C(5)	1.383 (5)			
N(4)–C(23)	1.429 (5)	C(3)–N(4)–C(5)	112.1 (2)	
C(5)–O(29)	1.199 (3)	C(3)–N(4)–C(23)	124.1 (2)	359.8 (4)
		C(5)–N(4)–C(23)	123.6 (2)	

[a] The sum of bond angles about each of the three nitrogens in the heterocyclic ring is included to show the degree of nonplanarity at N(1) and N(2).

A recent publication describing the reactions of **1** with a variety of solvents, including alcohols, implicitly questions our findings.[3] Compounds **2** were not isolated. Structural isomers of **2**, the 1-[*N*-phenyl-*N*-(alkoxycarbonyl)carbamoyl]-4-phenyl-1,2,4-triazolidine-3,5-diones (**3**), were postulated as reactive intermediates, which with excess of alcohol were presumed to give the alkoxycarbonyl derivatives **4** and the urethanes **5**, products isolated from the reactions. From the decomposition of **1** with equimolar methanol, repeated crystallization of the reaction residues gave a small amount (2%) of a compound $C_{17}H_{14}N_4O_5$ to which structure **3a** was assigned. IR, ^{1}H NMR, and MS data were obtained, but insufficient material was available to study its reactivity.

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(1) Dao, L. H.; Mackay, D. *J. Chem. Soc., Chem. Commun.* **1976**, 326.
(2) Dao, L. H.; Mackay, D. *Can. J. Chem.* **1979**, *57*, 2727.
(3) Izydore, R. A.; Johnson, H. E.; Horton, R. T. *J. Org. Chem.* **1985**, *50*, 4589.

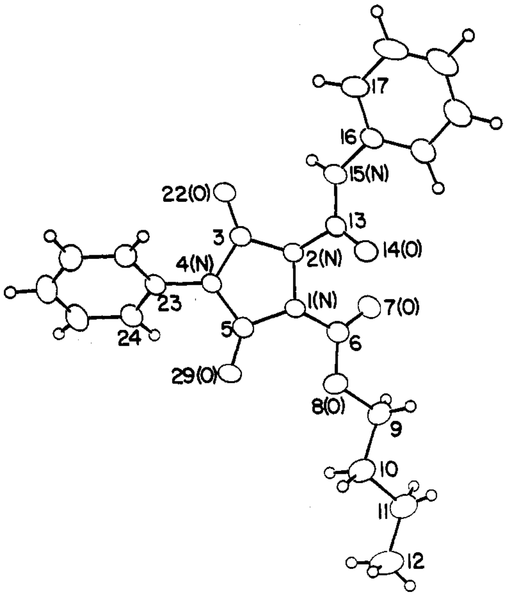

Figure 1. ORTEP diagram of the *N*-butyl compound **2c**.

Since then a paper has been published describing the mechanism of the conversion of **1** into the deaza dimer **6** under the influence of various catalysts.[4] Reactions with alcohols were also briefly studied. In the presence of methanol, sodium iodide, for example, catalyzed the conversion of **1** into a product $C_{17}H_{14}N_4O_5$, for which the structure **2a** was preferred over **3a**. It was not further investigated since its structure was of no consequence to the main focus of the work.

We wish to dispel any ambiguity whatsoever surrounding the identity of the compounds isolated by us in our earlier work:[1,2] *they have the structure* **2**, *originally assigned to them.*

Explicit details of the preparation of the *n*-butyl compound **2c** from both the azo compound **1** and the phenylurazole **7** are provided, the proof of structure being confirmed by the X-ray crystal determination (Figure 1 and Table I). Our choice of **2c** was dictated by the fact that it readily gave crystals suitable for X-ray analysis.

Compounds **2** are in fact stable substances. Samples stored at ambient temperature since the time of the original research[1] (**2a,c,e**) have ^{1}H NMR spectra unchanged in the intervening years.

That these compounds (**2a,c,e**) are structural analogues follows from the virtual superimposability of the complex aromatic regions of their 250-MHz ^{1}H NMR spectra. The spectra of all other compounds described here have equally complex but distinctively different aromatic regions.

The synthesis of **2c** from the azo compound was carried out either in an excess of *n*-butyl alcohol, alone or in benzene, or in an equimolar mixture with the alcohol in benzene solution. In each case, pure product crystallized from the solution on standing. Isolated yields were in the range of 60–70%.

The mother liquors from these crystallizations contained, as well as **2c**, small amounts of the alkoxycarbonyl derivative **4c** and the urethane **5c**, as well as two other unidentified compounds containing butoxycarbonyl groups. All corresponding triplets for the OCH_2 and the CH_3 protons in each of **2c**, **4c**, **5c**, and the two unidentified products were unambiguously distinguishable from one another at 250 MHz. An authentic sample of each known compound was added in turn to the NMR solutions of the mixture for confirmation of identity.

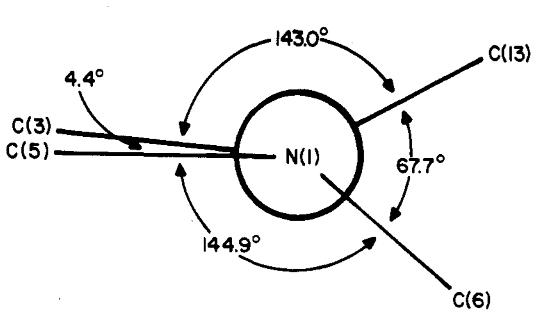

Figure 2. Newman projection along the N_1–N_2 bond of compound **2c** showing the pyramidal nature of these atoms.

The synthesis of **2c** was also achieved from the parent urazole **7**. With *n*-butyl chloroformate in pyridine it gave **4c**, which then gave **2c** by reaction with phenyl isocyanate. This order of acylation of **7**, unlike the reverse order, leaves little doubt that the product is **2c** and not **3c**.

The crystal used in the X-ray determination was obtained by slow evaporation of a chloroform solution of a sample of **2c** obtained from the azo compound. Companion crystals from this crystallization, in admixture with **2c** derived from **7** through **4c**, gave a ^{1}H NMR spectrum identical with that obtained from either product alone. Similarly the ^{13}C NMR spectrum of the mixture gave unique resonances for 14 of the 16 different carbon atoms in the molecule (two phenyl resonances in each ring being unresolved).

Selected bond lengths and angles for the crystal of **2c** are given in Table I. The conformation in the crystal is chiral, N_1 and N_2 being slightly pyramidal (1*S*,2*R* in Figure 1). The dihedral angles around the N_1–N_2 bond are shown in Figure 2. The carbamoyl and urethane groups are about as far separated as possible, and there is no intramolecular hydrogen bonding between them. The heterocyclic ring and its N_4 atom are both planar (Table I). The torsion angle between this ring and the phenyl ring is 51.14°: interaction of the N_4 lone pair electrons with the carbonyl groups is evidently more important than that with the phenyl ring.

An investigation of the mechanism of the reaction of the azo compound with alcohols and efforts to isolate the two unidentified products in these reactions are well in hand.[5]

Experimental Section

n-Butyl alcohol was spectrophotometric grade purchased from Fisher Scientific Co. The azo compound **1** was obtained by oxidation of the phenylurazole **7** with dinitrogen tetraoxide[6] or *tert*-butyl hypochlorite,[7] product from either route giving the same results. Melting points are uncorrected. Elemental analyses were done by Guelph Chemical Laboratories Ltd., Guelph, ON.

Use of High Resolution NMR Spectroscopy in Analysis of Reaction Products from 1 and *n*-Butyl Alcohol. With use of a Bruker AM-250 spectrometer each of the major product **2c**,

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(4) Borhani, D. W.; Greene, F. D. *J. Org. Chem.* **1986**, *51*, 1563.

(5) To date, these investigations have focused mainly on the reaction with methanol. Intermediates corresponding to A and B (see Experimental Section) in the present work have been observed, along with small amounts of other methoxy-containing products. Both intermediates decompose, at least one of them (that corresponding to B, which has been isolated but not characterized) proceeding to **2a**.

One of the methoxy containing products has an absorption at δ 4.00 (±0.02, the variation depending on concentration and solution complexity, as described in the Experimental Section), which corresponds with the value reported for **3a**. Efforts are being made to obtain crystals of both this compound and the methoxy analogue of B, with a view to X-ray analysis.

(6) Stickler, J. C.; Pirkle, W. H. *J. Org. Chem.* **1966**, *31*, 3444.

(7) Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R.; Watts, C. T. In *Organic Syntheses*; Benson, R. E., Ed.; Wiley: New York, 1971; Vol. 51, p 121.

the alkoxycarbonyl derivative **4c**, the urethane **5c**, and the two unknown compounds A and B was identifiable by its ^1H NMR spectrum in the presence of any or all of the others. Even the aromatic region was useful in these analyses, the patterns, though complex, being distinctively different for each compound. All four sets of butyl protons were fully resolved (C_1 and C_4 protons, triplets; C_3, 5 lines; C_4, 6 lines). The positions of the OCH_2 and CH_3 triplets were in general sufficient to identify all compounds, confirmation for known ones being obtained by spiking the solution. Individual shift values were slightly dependent on concentration or the presence of other compounds in solution, but no reversal of the shift positions of OCH_2 or CH_3 between compounds was observed as a result of these variations. Peak separations of 0.004 ppm (1.0 Hz) were detectable. Typical shifts for these triplets in dilute solutions of mixtures are

	2c	4c	5c	A	B
CH_3	0.94	0.93	0.95	0.82	0.81
OCH_2	4.44	4.38	4.16	4.17	4.14

Reaction of 1 with Excess *n*-Butyl Alcohol. (i) As Solvent. The azo compound (250 mg, 1.43 mmol) was added to stirred alcohol (2.5 mL) at room temperature. It dissolved with evolution of nitrogen and after 0.5 h the red color had faded to pale yellow. The solution was set aside unstirred, and crystals slowly began to separate. After 5 h a first crop of **2c** was collected by careful withdrawal of the supernatant, which was again set aside. The crystals were washed free of the last traces of the alcohol solution by using hexane and were pure (105 mg). From the alcohol supernatant three further crops of **2c** were similarly collected (for a total of 179 mg, 63%). The final alcohol soluble residue (50 mg) showed only traces of **2c** and product B, a small amount of **4c** and, the major products, A and **5c**. The hexane washings yielded material (48 mg) of which about half was **2c** (overall yield 71%), the balance being **5c** with lesser amounts of **4c** and A, and only a trace of B.

(ii) In Benzene. A mixture of **1** (250 mg, 1.43 mmol) in benzene (2 mL) and *n*-butyl alcohol (1 mL) was stirred for 0.5 h during which the azo compound dissolved and the red solution became yellow-orange. It was set aside and allowed to evaporate slowly to about half its original volume. The precipitate was separated by decantation, washed with hexane, and pumped to dryness to remove all traces of alcohol. The product (170 mg) was **2c** containing a trace (4%) of **5c**. The mother liquor and washings gave a residue (127 mg) which on digestion with warm chloroform (10 mL) gave insoluble urazole **7** (13 mg, identified by its IR spectrum). The chloroform solution was evaporated and its spectrum showed it to contain about 10% of **2c** (62% overall yield), about the same amount of **4c**, and rather more of A and B, with the major portion (40–50%) being **5c**.

Reaction of 1 with Equimolar *n*-Butyl Alcohol. The azo compound (175 mg, 1.00 mmol) was dissolved in benzene (10 mL) and *n*-butyl alcohol (92 μL, 1.00 mmol) was added. The red color slowly faded and gave place to a pale yellow in about 2 days, and the solution was then allowed to evaporate to about half its volume. The crystalline fraction of pure **2c** (116 mg, 59%) was collected and washed with cold benzene, and the filtrate and washings were evaporated (83 mg) and analyzed. Half was **2c** (overall yield ca 80%), and about one-third was **5c**, with the balance being mainly **4c** and traces of A and B. From this fraction by crystallization from chloroform–2,2,4-trimethylpentane further **2c** (14 mg, 66% total isolated yield) was obtained.

1-(Butoxycarbonyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (4c). *n*-Butyl chloroformate (363 μL, 2.86 mmol) was added slowly to pyridine (5 mL) at −70 °C, which was then allowed to warm to room temperature. Powdered urazole **7** (500 mg, 2.82 mmol) was added and slowly dissolved on shaking. The solution was kept at room temperature for 2 days and the pyridine was evaporated off. Water followed by dilute HCl was added and the precipitate collected and washed with water (405 mg, 52%). The ^1H NMR spectrum showed it to be completely pure. It could be recrystallized from benzene–2,2,4-trimethylpentane or aqueous MeOH, a sample from the latter having mp 117–118 °C: IR spectra in the solid phase showed a wide variation in the NH and CO regions, depending on whether the product had been recrystallized or what solvent it had been recrystallized from, and were not of diagnostic value; ^1H NMR δ ($CDCl_3$) 8.9 (NH, extremely broad), 7.49–7.45 (5 H, Ph, dominated by a singlet), 4.38 (2 H, OCH_2, t, $J = 6.6$ Hz), 1.74 (2 H, β-CH_2, 5 lines), 1.44 (γ-CH_2, 6 lines), 0.93 (3 H, CH_3, t, $J = 7.3$ Hz); ^{13}C NMR δ ($CDCl_3$) 150.5, 147.1, 145.8 (3 CO), 130.1, 128.9, 128.5, 125.7 (Ph), 68.3 (OCH_2), 30.1 (β-CH_2), 18.5 (γ-CH_2), 13.3 (CH_3). Anal. Calcd for $C_{13}H_{15}N_3O_4$: C, 56.31; H, 5.45; N, 15.16. Found: C, 56.73; H, 5.23; N, 15.25.

1-(Butoxycarbonyl)-2-(*N*-phenylcarbamoyl)-4-phenyl-1,2,4-triazolidine-3,5-dione (2c) from 4c and Comparison with 2c Derived from 1. To **4c** (554 mg, 2.00 mmol) in methylene chloride (1.5 mL) was added a solution of phenyl isocyanate (262 mg, 2.20 mmol) in methylene chloride (0.5 mL). The clear solution was kept stoppered for 2 days and then allowed to evaporate, and the solid residue was stirred with hexane (10 mL). The product (0.75 g) was shown by its ^1H NMR spectrum to be mainly **2c**, but contained 10–15% of the starting material. Crystallization by slow evaporation from chloroform solution gave two successive crops of pure product (480 mg, 61%).

Compound **2c** derived from the azo compound was similarly given a final purification by crystallization from chloroform. Crystals prepared by each route (melting point variable[8]) had identical high resolution ^1H NMR spectra; admixture of these two NMR solutions caused no change in the spectrum. A mixture of the crystals from both sources gave a ^{13}C NMR spectrum showing only four carbonyl and only four butyl carbon resonances and six of the eight possible phenyl resonances: ^1H NMR δ ($CDCl_3$) 9.04 (NH), 7.5–7.1 (10 H, 2 Ph, complex), 4.44 (2 H, OCH_2, t, $J = 6.5$ Hz), 1.77 (2 H, β-CH_2, 5 lines), 1.47 (2 H, γ-CH_2, 6 lines), 0.94 (3 H, CH_3, t, $J = 7.3$ Hz); ^{13}C NMR δ ($CDCl_3$) 150.1, 148.3, 146.4, 145.3 (4 CO), 136.1, 129.5, 129.2, 126.0, 125.1, 120.0 (2 Ph, 2 pairs of lines overlapping), 69.5 (OCH_2), 30.4 (β-CH_2), 18.8 (γ-CH_2), 13.6 (CH_3).

X-ray Analysis of 2c. Crystal Data: $C_{20}H_{20}N_4O_5$, M_r, 396.41; orthorhombic, $a = 8.329$ (1), $b = 12.920$ (2), and $c = 18.199$ (3) Å, $V = 1958.4$ (6) Å^3; space group $Pca2_1$; $Z = 4$; $\rho_c = 1.344$ g cm^{-3}; $F(000) = 832$; $\lambda = 0.71069$ Å; t = 294 ± 1 K; μ(Mo Kα) = 1.07 cm^{-1}.

Data were collected on a crystal of dimensions 0.28 × 0.30 × 0.37 mm grown from $CDCl_3$ using θ–2θ scans ($3.2 \leq 2\theta \leq 52°$) with a variable scan speed of 3.45–29.30 min^{-1} and a scan width of 1.0° below Kα_1 to 1.0° above Kα_2 on a Syntex P2_1 diffractometer. From a total of 2004 measured reflections, 1364 with $I \geq 3\sigma(I)$ were considered observed and were used in the structure refinement. The structure was solved by direct methods (MULTAN 80) and refined by full-matrix least-squares methods. The refinement converged at R and R_w values of 0.029 and 0.030, respectively [$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2\}^{1/2}$; $w^{-1} = 2.22 - 0.0554|F_o + 0.00124|F_o|^2$]. Maximum residuals were 0.13 e Å^{-3}. Atomic coordinates (Table S1), anisotropic thermal parameters (Table S2), and bond lengths and angles (Table S3) are available as supplementary material. Structure factors are available from the authors.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council for support of this work and a postgraduate scholarship (to I.D.W.).

Registry No. 1, 4233-33-4; 2c, 60290-36-0; 4c, 106501-67-1; 5c, 1538-74-5; 7, 15988-11-1; butyl alcohol, 71-36-3; phenyl isocyanate, 103-71-9.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **2c** (4 pages); table of observed and calculated structure factors for **2c** (8 pages). Ordering information is given on any current masthead page.

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[8] In capillary tubes only very broad melting ranges are observed for **2c**, likely due to the slow release of phenyl isocyanate with the gradual formation of solid **4c**. The sharp mp originally reported for **2c**[2] is not reproducible and is a result of the use of a hot stage melting apparatus for its determination. In the confined space between the glass plates the escape of liquid phenyl isocyanate is impeded and liquefaction of the sample can occur very rapidly. While the mp is sharp, however, it is very dependent on crystal size and may lie as much as 10° on either side of the reported value.[2]