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Received June 6, 1996

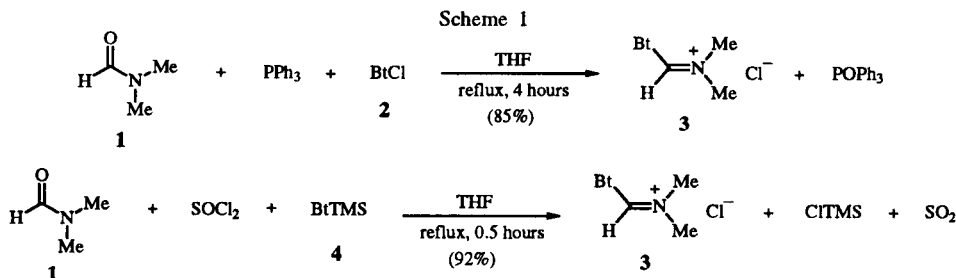
N,N-Dimethylaminobenzotriazolylcarbene (**5**) reacted with phenyl isocyanate in a [1+2+2] cycloaddition and then with nucleophiles to generate various hydantoins **10** in a one-pot procedure. It was also found that this novel carbene reacted with *trans*-dibenzoyl ethylene (**11**) in a [1+4] cycloaddition, generating 2-dimethylamino-3-benzoyl-5-phenylfuran (**13**) and 2-phenyl-3-[benzotriazol-1-yl]-4-benzoylfuran (**14**) whose structures were confirmed by ¹H-¹³C long range correlations as well as the structure of furan **14** being confirmed by X-ray crystallography.

J. Heterocyclic Chem., **33**, 1935 (1996).

Introduction.

Carbenes connected directly to heteroatoms (*N*, *O*, *S*, etc.) are of enduring interest [1-4]. Among these so-called "nucleophilic carbenes", aminocarbenes are of unique high stability and low reactivity [2,5], as evidenced recently by their isolation and X-ray structure determination [6-9].

Treatment of compound **3** with triethylamine in refluxing benzene led to the expected dimeric compounds **6** and **7** which can be explained by the formation of the corresponding aminocarbene followed by reaction with the salt **3** to generate the dimeric products (Scheme 2).



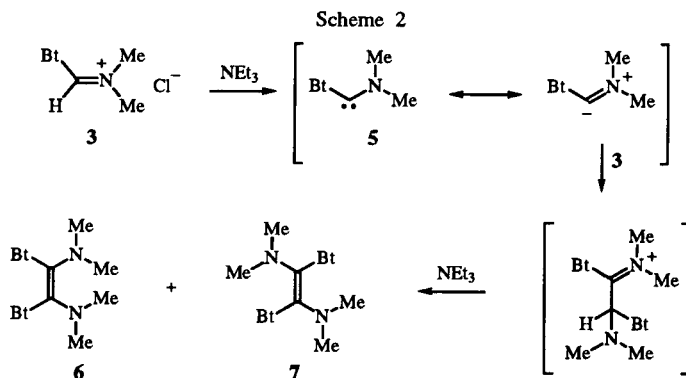
Heterocyclic aminocarbenes have been found to react with electrophiles including aldehydes, benzoyl halides, alkyl halides, phenyl isothiocyanate, and cyclopentanone [10-12]. However, to our knowledge the few reported reactions of *acyclic* nucleophilic carbenes are limited to [1+2+2] cycloadditions with aryl isocyanates and isothiocyanates [13] and [1+4] cycloadditions with tetrazines [14].

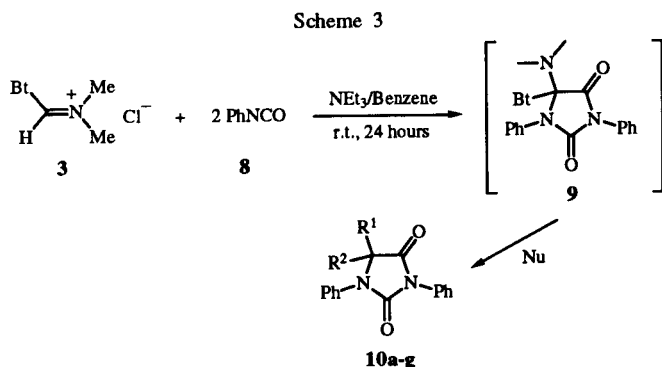
We report herein the generation of a new acyclic aminocarbene, *N,N*-dimethylaminobenzotriazolylcarbene, by deprotonation of *N,N*-dimethylaminobenzotriazolylmethyleniminium chloride under mild conditions, and trapping in a [1+4] cycloaddition with *trans*-dibenzoyl ethylene and with phenyl isocyanate in reactions which demonstrate some synthetic utility in approaching the hydantoin system.

Results and Discussion.

N,N-Dimethylaminobenzotriazolylmethyleniminium chloride (**3**) can be prepared as a hygroscopic white solid in high yields by either of the two methods shown in Scheme 1.

The existence of new aminocarbene **5** was further evidenced by treating **5** with phenyl isocyanate in a typical carbene reaction [13], of [1+2+2] cycloaddition (Scheme 3). However, imidazolidinetrione **10** was isolated instead of the expected 5-dimethylamino-5-benzotriazolyl-1,3-diphenylhydantoin (**9**). The benzotriazolyl group is evidently easily





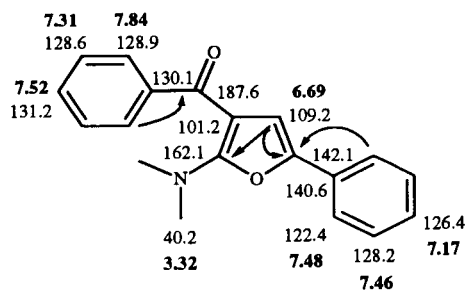
eliminated, and thus the proposed intermediate is hydrolyzed on work-up to the corresponding oxo-derivative.

Quenching this reaction with various nucleophiles enabled the one-pot synthesis of various 5-substituted hydantoin 10a-g (Table 1) in acceptable yields by using simple reagents under mild conditions.

Table 1
Preparation of Hydantoin 10

Entry (%)	Nu	R ¹	R ²	10	Yield
1	H ₂ O		oxo	a	67
2	propylamine		propylimino	b	54
3	NEt ₄ SH	H		c	35
4	MeOH	dimethylamino	MeO	d	57
5	Morpholine	dimethylamino	N-morpholinyl	e	48
6	NaBH ₄	dimethylamino	H	f	51
7	EtMgBr	dimethylamino	Et	g	56

Reaction of the new aminocarbene 5 with *trans*-dibenzoyl-ethylene gave a 15% yield of the 4-benzoyl-5-dimethylamino-2-phenylfuran (13) and a 6% yield of 3-benzotriazolyl-4-benzoyl-2-phenylfuran (14) after refluxing for 24 hours. The structures of furans 13 and 14 were assigned on the basis of the ¹H-¹³C direct and long range correlations and ¹³C chemical shifts. The chemical shifts and the relevant ¹H-¹³C long range correlations for compounds 13 and 14 are given in Figure 1. The structure of compound 14 was confirmed by X-ray



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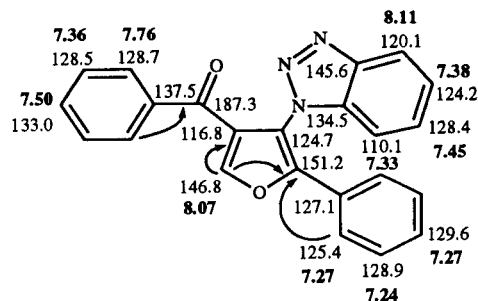
Figure 1

Table 2
Atomic coordinates (x10⁴) and equivalent isotropic displacement coefficients (Å²x10³)

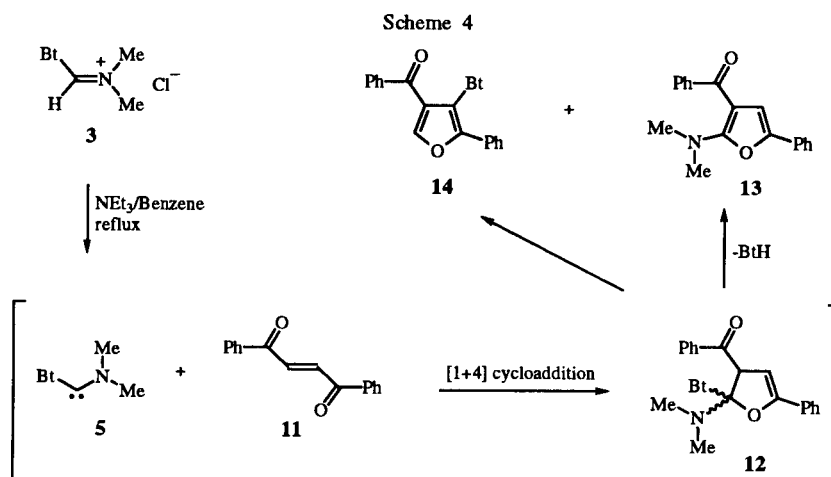
atom	x	y	z	U _{eq} [a]
O1	3099(2)	8757(1)	5096(1)	28(1)
C2	4878(2)	8233(1)	4704(1)	25(1)
C3	5738(2)	9168(1)	3688(1)	24(1)
C4	4427(2)	10329(1)	3399(1)	24(1)
C5	2874(2)	10008(1)	4305(1)	27(1)
C21	5388(2)	6864(1)	5394(1)	26(1)
C22	3826(2)	6021(2)	5946(1)	31(1)
C23	4287(3)	4716(2)	6573(1)	35(1)
C24	6309(3)	4233(2)	6648(2)	37(1)
C25	7866(3)	5065(2)	6110(2)	36(1)
C26	7424(2)	6367(2)	5490(1)	32(1)
N31	7572(2)	8987(1)	3012(1)	24(1)
N32	9450(2)	9026(1)	3302(1)	29(1)
N33	10864(2)	8804(1)	2554(1)	29(1)
C31	9919(2)	8627(1)	1759(1)	24(1)
C32	10735(2)	8367(1)	794(1)	29(1)
C33	9383(2)	8260(2)	155(1)	32(1)
C34	7239(2)	8416(2)	437(1)	31(1)
C35	6397(2)	8668(1)	1383(1)	27(1)
C36	7798(2)	8757(1)	2042(1)	22(1)
C40	4787(2)	11570(2)	2352(1)	26(1)
O4	6437(2)	11715(1)	1727(1)	41(1)
C41	3142(2)	12633(1)	2058(1)	26(1)
C42	3738(2)	13895(2)	1459(1)	31(1)
C43	2281(3)	14919(2)	1156(2)	36(1)
C44	210(3)	14700(2)	1425(2)	36(1)
C45	-383(2)	13455(2)	1992(2)	35(1)
C46	1060(2)	12423(2)	2311(1)	29(1)

[a] equivalent isotropic U defined as one third of the trace of the orthogonal U_{ij} tensor.

crystallography (Figure 2). The formation of the 4-benzoyl-5-dimethylamino-2-phenylfuran (13) can be easily explained by a carbene mechanism as shown (Scheme 4). Such [1+4] cycloadditions with unsaturated carbonyl compounds are common with isocyanides [15] and have occasionally been reported as side-reactions of the cyclopropanation of sulfoxonium ylides [16]. Hoffmann and co-workers have reported similar reactions of dimethoxycarbene with special heterodienes [17]. A stepwise ionic cycloaddition seems more likely than a



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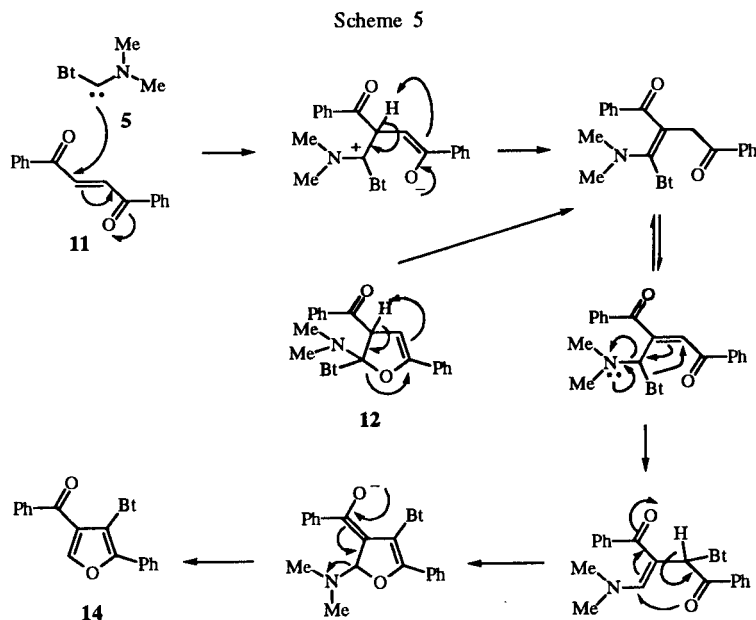
concerted mechanism in the light of orbital considerations and previous results on cycloaddition of nucleophilic carbenes [13,14,18,19].

The formation of 3-benzotriazolyl-4-benzoyl-2-phenylfuran (14), its structure confirmed by X-ray crystallography, was initially believed to have resulted from reaction of 4-benzoyl-5-dimethylamino-2-phenylfuran (13) with

free benzotriazole. This assumption was made on the basis that when monitoring the reaction by gcms, the peak corresponding to compound 14 appeared after 18 hours and was observed to increase in size while the peak corresponding to compound 13 decreased. However, this hypothesis was rejected because 13 was unchanged by refluxing in benzene with benzotriazole for 72 hours. Two

Table 3
Bond Lengths (Å) and angles (°) for 14

O1-C2	1.378(2)	O1-C5	1.353(2)	C2-C3	1.354(2)
C2-C21	1.457(2)	C3-N31	1.418(2)	C3-C4	1.437(2)
C4-C5	1.359(2)	C4-C40	1.474(2)	C21-C22	1.396(2)
C21-C26	1.400(2)	C22-C23	1.381(2)	C23-C24	1.386(2)
C24-C25	1.385(2)	C25-C26	1.375(2)	N31-C36	1.356(2)
N31-N32	1.373(2)	N32-N33	1.307(2)	N33-C31	1.378(2)
C31-C32	1.398(2)	C31-C36	1.401(2)	C32-C33	1.363(2)
C33-C34	1.418(2)	C34-C35	1.376(2)	C35-C36	1.397(2)
C40-O4	1.224(2)	C40-C41	1.491(2)	C41-C42	1.396(2)
C41-C46	1.397(2)	C42-C43	1.381(2)	C43-C44	1.392(2)
C44-C45	1.378(2)	C45-C46	1.382(2)		
C5-O1-C2	107.46(11)	C3-C2-O1	108.30(13)		
C3-C2-C21	134.45(14)	O1-C2-C21	117.20(13)		
C2-C3-N31	124.70(14)	C2-C3-C4	108.37(13)		
N31-C3-C4	126.86(13)	C5-C4-C3	104.38(13)		
C5-C4-C40	129.77(14)	C3-C4-C40	125.85(13)		
O1-C5-C4	111.45(13)	C22-C21-C26	119.06(14)		
C22-C21-C2	119.63(14)	C26-C21-C2	121.29(14)		
C23-C22-C21	120.3(2)	C22-C23-C24	120.1(2)		
C25-C24-C23	119.9(2)	C26-C25-C24	120.5(2)		
C25-C26-C21	120.1(2)	C36-N31-N32	110.36(11)		
C36-N31-C3	128.42(12)	N32-N31-C3	121.22(12)		
N33-N32-N31	108.42(12)	N32-N33-C31	108.33(12)		
N33-C31-C32	130.92(13)	N33-C31-C36	108.73(12)		
C32-C31-C36	120.35(13)	C33-C32-C31	117.08(14)		
C32-C33-C34	122.07(14)	C35-C34-C33	122.0(2)		
C34-C35-C36	115.39(14)	N31-C36-C35	132.75(13)		
N31-C36-C31	104.15(12)	C35-C36-C31	123.09(13)		
O4-C40-C4	119.46(14)	O4-C40-C41	120.59(14)		
C4-C40-C41	119.96(13)	C42-C41-C46	119.05(14)		
C42-C41-C40	117.65(13)	C46-C41-C40	123.25(14)		
C43-C42-C41	120.2(2)	C42-C43-C44	120.3(2)		
C45-C44-C43	119.7(2)	C44-C45-C46	120.6(2)		
C45-C46-C41	120.2(2)				



possible routes for the formation of compound **14** are shown in Scheme 5.

Figure 2 shows a perspective view and atom labeling of the X-ray crystal structure of **14**, which confirms the structure and substitution pattern in the furan ring. Tables 2 and 3 list atom coordinates and bonding geometries. Each of the aromatic ring systems is planar to within 0.01 Å, with the furan ring inclined to the meanplanes of the C2-phenyl, C3-benzotriazole, and C4-phenyl ring planes at angles of 34.7 (1), 81.2 (1) and 36.3 (1)°, respectively. The mutually orthogonal orientation of the furan and benzotriazole rings results in an interesting packing of the molecules within the crystal lattice. The intramolecu-

lar bonding geometry shows no unusual features, and there are no intermolecular contacts between non-hydrogen atoms of less than 3.2 Å.

Conclusions.

N,N-Dimethylaminobenzotriazolylcarbene (**5**) can be generated by deprotonation of *N,N*-dimethylaminobenzotriazolylmethyleniminium chloride (**3**) under mild conditions. Carbene **5** can be trapped with *trans*-dibenzoyl ethylene in a [1+4] cycloaddition. Reaction with phenyl isocyanate followed by different work-up reagents gives hydantoins with various functionalities at 5-position in one-pot processes which provides a useful approach to this system.

EXPERIMENTAL

Melting points were determined using a Thomas Hoover capillary Melting Point Apparatus and are not corrected. The nmr spectra were recorded on a Varian Gemini-300 spectrometer using either deuteriochloroform or dimethyl sulfoxide- d_6 as solvent. The gcms instrument used was a Hewlett Packard 5890 Series II Gas Chromatography coupled to a 5972 Mass Selective Detector. Elemental analyses were performed on a Carlo Erba-1106 instrument. 1-Chlorobenzotriazole (**2**) [20] and 1-trimethylsilylbenzotriazole (**4**) [21] were prepared according to literature methods. Tetrahydrofuran and benzene were predried and freshly distilled from sodium and benzophenone. Dimethylformamide was dried over molecular sieves. Column chromatography was carried out on MCB silica gel (230-400 mesh).

X-ray Crystallography.

Intensity data were collected with a Nicolet P4s four-circle diffractometer by using monochromatized Mo K α ($\lambda = 0.710734$) radiation. The crystal used was a pale yellow block of

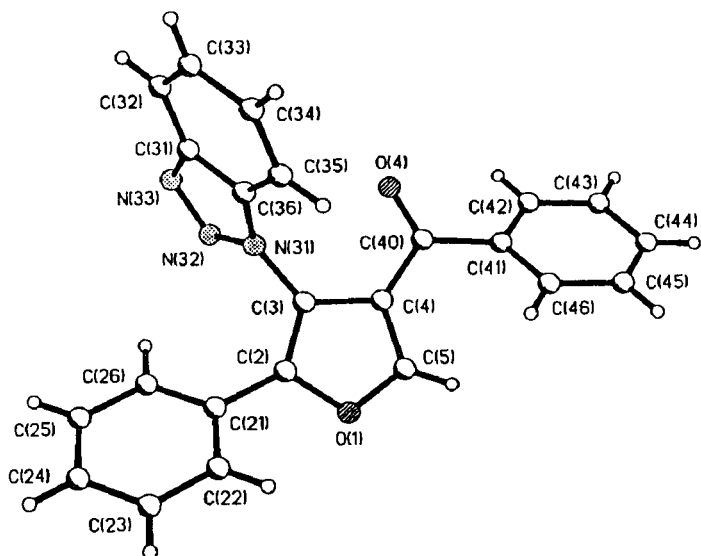


Figure 2. Perspective view and atom labeling of the X-ray structure of **14**.

dimensions 0.74 x 0.72 x 0.48 mm. Throughout data collections the intensities of the three standard reflections were monitored at regular intervals and the intensities were corrected for minor decay (<9%). The intensities were also corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods using SHELXS90 [22], and refined on F^2 by full-matrix least-squares procedures using SHELXL93 [23]. All non-hydrogen atoms were refined with anisotropic displacement coefficients. Hydrogen atoms were included in calculated positions with isotropic displacement coefficients equal to 1.3 times the isotropic equivalent of their carrier carbons. The function minimized was $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + 0.0742P^2]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$. A final difference map showed no features greater or less than $0.27\text{e}/\text{\AA}^3$. Final non-hydrogen atom coordinates, bond lengths and bond angles are listed in Tables 2 and 3. Tabulations of hydrogen atom coordinates, anisotropic thermal parameters, structure factors and equations of meanplanes are available as supplementary material from the author PJS.

Crystal Data for 14 -115°: $C_{23}H_{15}N_3O_2$, Mr = 365.4, triclinic, space group P-1, $a = 6.653(1)$, $b = 11.667(2)$, $c = 12.716(1)$ Å, $\alpha = 63.17(1)^\circ$, $\beta = 80.21(1)^\circ$, $\gamma = 82.12(1)^\circ$, $U = 865.9(2)$ Å³, $F(000) = 380$, $Z = 2$, $D_c = 1.401\text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 0.92\text{ cm}^{-1}$, ω scans, $2\theta_{\max} = 55^\circ$, 253 parameters, $S = 0.95$, $wR2 = 0.115$ for all 3831 data, $R1 = 0.044$ for 2775 data with $F_o > 4\sigma(F_o)$.

N,N-Dimethylaminobenzotriazolylmethyleniminium Chloride (3).

Procedure A.

A solution of 100 mmol (7.4 g) of DMF and 100 mmol (26.2 g) of triphenylphosphine in 100 ml of dry THF was treated with a solution of 100 mmol (15.4 g) of 1-chlorobenzotriazole 2 in 40 ml of dry THF, dropwise. The mixture was then refluxed for 4 hours before cooling and quickly filtering off the resulting precipitate, which was washed once with 40 ml of dry THF to give product 3 as a white solid (17.9 g, 85%).

Procedure B.

To a solution of 8 ml (55.2 mmol, 10.7 g) of 1-trimethylsilylbenzotriazole 4, 4 ml (55.2 mmol, 4.0 g) of DMF and 100 ml of dry THF was added 4 ml (55.2 mmol, 6.6 g) of thionyl chloride, dropwise. The mixture was then refluxed 30 minutes before cooling and quickly filtering off the resulting precipitate, which was washed once with 40 ml of dry THF to give product 3 as a white solid (10.6 g, 92%).

Anal. Calcd. for $C_9H_{11}ClN_4$ (210.5): C, 51.41; H, 5.28; N, 26.66. Found: C, 51.18; H, 5.24; N, 26.67.

Cis- and *trans*-1,2-[1-Benzotriazolyl]-1,2-dimethylaminoethylene (6) and (7).

Compound 3 (1.06 g, 5 mmol) in 20 ml of dry benzene was refluxed in the presence of an equimolar of triethylamine under a nitrogen atmosphere overnight. The mixture was then washed with water (2 x 20 ml), dried over anhydrous magnesium sulfate, filtered and then evaporated to dryness to give an oily residue which was subjected to column chromatography. From the column it was possible to obtain some fractions that contained pure 6 (oil) and 7 (oil) the other fractions being mixtures of the two geometrical isomers with an overall yield of 45%. The ¹H-nmr of the reaction mixture showed that the ratio between 6 and 7 was about 1:1.

Compound 6 had ¹H-nmr (deuteriochloroform): δ 2.83 (s, 12H), 7.19 (t, $J = 7.2$ Hz, 2H), 7.36 (t, $J = 8.1$ Hz, 2H), 7.55 (d, $J = 8.3$ Hz, 2H), 7.77 (d, $J = 9.2$ Hz, 2H); ¹³C-nmr (deuteriochloroform): δ 40.7, 110.3, 119.5, 124.1, 125.2, 127.9, 132.9, 145.0.

Anal. Calcd. for $C_{18}H_{20}N_8$ (348): C, 62.04; H, 5.79; N, 32.17. Found: C, 62.11; H, 5.69; N, 31.90.

Compound 7 had ¹H-nmr (deuteriochloroform): δ 2.22 (s, 12H), 7.47 (t, $J = 8.2$ Hz, 2H), 7.58 (t, $J = 8.1$ Hz, 2H), 7.73 (d, $J = 8.2$ Hz, 2H), 8.16 (d, $J = 8.3$ Hz, 2H); ¹³C-nmr (deuteriochloroform): δ 40.2, 111.0, 120.2, 124.5, 125.3, 128.3, 133.6, 146.0.

Anal. Calcd. for $C_{18}H_{20}N_8$ (348): C, 62.04; H, 5.79; N, 32.17. Found: C, 62.28; H, 5.76; N, 31.88.

General Procedure for the Synthesis of 5-Substituted-1,3-Diphenylhydantoins 10.

A mixture of 1.06 g (5 mmol) of 3, 1.19 g (10 mmol) of phenyl isocyanate and 1.01 g (10 mmol) of triethylamine in 20 ml of dry benzene was stirred 24 hours at room temperature. This was then quenched with the corresponding nucleophile to give the products 10.

1,3-Diphenylimidazolidinetrione (10a).

The reaction mixture was then quenched with water (20 ml), heated to reflux, cooled and extracted with diethyl ether (30 ml). The organic extracts were washed with water (2 x 40 ml), dried over anhydrous magnesium sulfate, filtered and evaporated to dryness to give an oily residue. This was then treated with ethanol and refrigerated to crystallize out the product 10a as a white solid (67%), mp 204° (lit [24] 206-207°); ¹H-nmr (deuteriochloroform): δ 7.40-7.60 (m, 10H); ¹³C-nmr (deuteriochloroform): δ 125.8, 129.3, 129.5, 129.7, 151.8, 155.0; gcms: $m/z = 266$ (M^+ , calcd. for $C_{15}H_{10}N_2O_3$: 266).

5-Propylimino-1,3-diphenylhydantoin (10b).

The reaction mixture was cooled to 0° before adding a solution of propylamine (10 mmol) in 3 ml of dry benzene, dropwise. This was then stirred at room temperature for 30 minutes before cooling to 0° and filtering off the resulting precipitate. Evaporation of the filtrate gave an oil which was subjected to column chromatography to give the product 10b as an oil in 54% yield; ¹H-nmr (deuteriochloroform): δ 0.99 (t, $J = 7.4$ Hz, 3H), 1.71 (sextet, $J = 7.1$ Hz, 2H), 4.16 (t, $J = 7.0$ Hz, 2H), 7.35-7.60 (m, 10H); ¹³C-nmr (deuteriochloroform): δ 11.8, 24.5, 51.6, 126.1, 127.1, 128.1, 128.6, 128.9, 129.2, 130.4, 131.9, 140.3, 152.1, 154.1; gcms: $m/z = 307$ (M^+ , calcd for $C_{18}H_{17}N_3O_2$: 307); hrms: M^+ , calcd. for $C_{18}H_{17}N_3O_2 = 307.1321$. Found: 307.1321.

1,3-Diphenylhydantoin (10c).

The reaction mixture was quenched with tetraethylammonium hydrogen sulfide (20 mmol) and then stirred overnight. This was then cooled to 0°, filtered and then diluted with diethyl ether (30 ml) before washing with water (2 x 40 ml), drying over anhydrous magnesium sulfate, filtering and evaporating to dryness. The resulting product was subjected to column chromatography to give the solid product 10c in 35% yield, mp 136° (lit [25] 135°); ¹H-nmr (deuteriochloroform): δ 4.40 (s, 2H), 7.13-7.21 (m, 1H), 7.35-7.52 (m, 7H), 7.60 (d, $J = 7.7$ Hz, 2H); ¹³C-nmr (deuteriochloroform): δ 49.6, 118.5, 124.5, 126.2, 128.3, 129.0, 129.3, 131.2, 137.4, 153.0, 167.2; gcms: $m/z = 252$ (M^+ , calcd for $C_{15}H_{12}N_2O_2$: 252).

5-Methoxy-5-dimethylamino-1,3-diphenylhydantoin (**10d**).

The reaction mixture was quenched with methanol (2 ml) and then heated to reflux before cooling to 0° and filtering off the resulting precipitate. Evaporation of the filtrate gave an oily residue which was treated with methanol and refrigerated to crystallize out the product **10d** as a white solid (57%), mp 140° (lit [26] 140°); ¹H-nmr (deuteriochloroform): δ 2.55 (s, 6H), 3.49 (s, 3H), 7.23-7.31 (m, 1H), 7.37-7.54 (m, 7H), 7.73 (d, J = 8.5 Hz, 2H); ¹³C-nmr (deuteriochloroform): δ 37.5, 51.8, 101.2, 124.3, 126.3, 126.5, 128.5, 128.9, 129.1, 130.7, 134.3, 152.8, 166.7.

5-(*N*-Morpholinyl)-5-dimethylamino-1,3-diphenylhydantoin (**10e**).

The reaction mixture was quenched with morpholine (2 ml) and then heated to reflux before cooling to 0° and filtering off the resulting precipitate. Evaporation of the filtrate gave an oily residue which was treated with methanol and refrigerated to crystallize out the product **10e** as a white solid (48%), mp 194°; ¹H-nmr (deuteriochloroform): δ 2.42 (s, 6H), 2.60-2.72 (m, 2H), 3.02-3.13 (m, 2H), 3.70-3.83 (m, 4H), 7.28-7.36 (m, 1H), 7.36-7.55 (m, 7H), 7.59 (d, J = 8.2 Hz, 2H); ¹³C-nmr (deuteriochloroform): δ 37.8, 46.8, 67.0, 95.5, 126.3, 126.7, 127.4, 128.4, 129.0, 131.1, 136.0, 153.4, 167.7.

Anal. Calcd. for C₂₁H₂₄N₄O₃ (380): C, 66.28; H, 6.36; N, 14.73. Found: C, 66.49; H, 6.36; N, 14.81.

5-Dimethylamino-1,3-diphenylhydantoin (**10f**).

The reaction mixture was cooled to 0° and 20 mmoles of sodium borohydride was added. The mixture was slowly heated to reflux before cooling to 0° and quenching with water (20 ml), dropwise. The organic phase was diluted with diethyl ether (30 ml) and washed with water (2 x 40 ml) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by column chromatography gave the product as an oil which was triturated with hexane to crystallize out the product **10f** as a white solid in a 51% yield, mp 113°; ¹H nmr (deuteriochloroform): δ 2.53 (s, 6H), 5.22 (s, 1H), 7.22-7.30 (m, 1H), 7.36-7.53 (m, 7H), 7.60 (d, J = 7.6 Hz, 2H); ¹³C-nmr (deuteriochloroform): δ 39.0, 77.2, 122.6, 125.8, 126.3, 128.4, 129.1, 131.2, 136.2, 153.0, 168.6.

Anal. Calcd. for C₁₇H₁₇N₃O₂ (295): C, 69.12; H, 5.81; N, 14.23. Found: C, 69.16; H, 5.69; N, 14.33.

5-Ethyl-5-dimethylamino-1,3-diphenylhydantoin (**10g**).

The reaction mixture was cooled to 0° and then quenched with ethylmagnesium bromide (11 mmoles) in diethyl ether. The mixture was allowed to warm to room temperature and stirred for one hour before quenching with water (20 ml), dropwise. The mixture was filtered and the organic phase was diluted with diethyl ether (30 ml) and washed with water (2 x 40 ml) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by column chromatography gave the product as an oil which was triturated with hexane to crystallize out the product **10g** as a white solid in a 56% yield, mp 110°; ¹H nmr (deuteriochloroform): δ 0.89 (t, J = 7.4 Hz, 3H), 1.85 (overlapping dq, 13.9, 7.4 Hz, 1H), 2.37 (overlapping dq, J = 13.9, 7.2 Hz, 1H), 2.58 (s, 6H), 7.24-7.31 (m, 1H), 7.35-7.53 (m, 7H), 7.75 (d, J = 8.5 Hz, 2H); ¹³C-nmr (deuteriochloroform): δ 7.85, 24.9, 38.1, 84.7, 125.2, 126.3, 126.5, 128.2, 128.8, 129.0, 131.2, 135.2, 154.0, 171.0.

Anal. Calcd. for C₁₉H₂₁N₃O₂ (323): C, 70.55; H, 6.55; N, 13.00. Found: C, 70.56; H, 6.56; N, 13.04.

Procedure for Compounds **13** and **14**.

A solution of *N,N*-dimethylaminobenzotriazolymethyleniminium **3** (1.06 g, 5 mmoles), 1.18 g (5 mmoles) *trans*-dibenzoyl ethylene, triethylamine (1.01 g, 10 mmoles) in dry benzene (20 ml) was refluxed for 24 hours. After diluting with diethyl ether (30 ml), the mixture was washed with 10% sodium carbonate (40 ml) and water (40 ml) and dried over anhydrous magnesium sulfate. Evaporation of the solvent followed by column chromatography gave **13** in 15% and **14** in 6% yield.

2-Dimethylamino-3-benzoyl-5-phenylfuran (**13**).

This compound was obtained as an oil; ¹H-nmr (deuteriochloroform): δ 3.24 (s, 6H), 6.71 (s, 1H), 7.18 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.4 Hz, 2H), 7.43-7.57 (m, 5H), 7.85 (d, J = 6.4 Hz, 2H); ¹³C-nmr (deuteriochloroform): δ 40.3, 101.3, 109.2, 122.4, 126.4, 128.2, 128.6, 128.9, 130.2, 131.2, 140.6, 142.2, 162.2, 187.7; gcms: *m/z* = 291 (M⁺, calcd. for C₁₉H₁₇NO₃: 291).

Anal. Calcd. for C₁₉H₁₇NO₂ (291): C, 78.32; H, 5.89; N, 4.81. Found: C, 77.98; H, 5.79; N, 4.79.

2-Phenyl-3-[benzotriazol-1-yl]-4-benzoylfuran (**14**).

This compound was obtained as a pale yellow solid, mp 175-177°; ¹H-nmr (deuteriochloroform): δ 7.21-7.54 (m, 11H), 7.76 (d, J = 7.2 Hz, 2H), 8.07 (s, 1H), 8.11 (d, J = 8.1 Hz, 1H); ¹³C-nmr (deuteriochloroform): δ 110.1, 116.8, 120.1, 124.2, 124.7, 125.4, 127.1, 128.4, 128.4, 128.8, 128.9, 129.6, 133.1, 134.5, 137.5, 145.6, 146.8, 151.2, 187.4; gcms: *m/z* = 365 (M⁺, calcd. for C₂₃H₁₅N₃O₂: 365).

Anal. Calcd. for C₂₃H₁₅N₃O₂ (365): C, 75.59; H, 4.14; N, 11.51. Found: C, 75.56; H, 4.07; N, 11.53.

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