

of the isodesmic reactions which is otherwise frequently used. A possible influence of different alkyl branching on the central C atom can be tested, on the basis of the variously substituted malonic diesters **1 a-c**.

Increments for the carboxy group,  $\Delta H_f^0(\text{g}) \text{CO}_2[2\text{C}]$ , and the O-bound carbon,  $\Delta H_f^0(\text{g}) \text{CH}_3^0[\text{CO}_2]$ ,  $\text{CH}_2^0[\text{CO}_2, \text{C}]$ , as well as for the ester-bearing alkyl groups,  $\Delta H_{\text{ester}} \text{CH}_3[\text{CO}_2]$ ,  $\text{CH}_2[\text{CO}_2, \text{C}]$ ,  $\text{CH}[\text{CO}_2, 2\text{C}]$ ,  $\text{C}[\text{CO}_2, 3\text{C}]$  could be calculated from the known  $\Delta H_f^0(\text{g})$  values of monocarboxylates<sup>[6]</sup> with the help of already known increments for alkanes,  $\Delta H_{\text{alkyl}}^{[5]}$  (Table 2). The increments for alkyl groups with two ester

Table 2. Increments in enthalpy of formation [kcal mol<sup>-1</sup>] for pure alkyl groups ( $\Delta H_{\text{alkyl}}$ ) and alkyl groups substituted by one ( $\Delta H_{\text{ester}}$ ), two ( $\Delta H_{\text{diester}}$ ), or three ( $\Delta H_{\text{triester}}$ ) [a] ester groups.

$\Delta H_{\text{alkyl}}^{[5]}$	$\Delta H_{\text{ester}}^{[b]}$	$\Delta H_{\text{diester}}^{[c]}$	$\Delta H_{\text{triester}}^{[d]}$
$\text{CH}_3 [C] - 10.05$	$[\text{CO}_2] \equiv - 10.05$	-	-
$\text{CH}_2 [2C] - 5.13$	$[\text{CO}_2, C] - 4.74$	$[2\text{CO}_2] - 1.57$	-
$\text{CH} [3C] - 2.16$	$[\text{CO}_2, 2C] - 1.92$	$[2\text{CO}_2, C] + 1.14$	$[3\text{CO}_2] + 7.74$
$\text{C} [4C] - 0.30$	$[\text{CO}_2, 3C] + 0.40$	$[2\text{CO}_2, 2C] + 3.02$	$[3\text{CO}_2, C] -$

[a] Neighboring atoms in square brackets. [b] From monocarboxylates [6] with  $\text{CO}_2[2\text{C}] - 77.34$ ,  $\text{CH}_3^0[\text{CO}_2] - 10.05$  and  $\text{CH}_2^0[\text{CO}_2, \text{C}] - 8.80$ . [c] From the malonic diesters **1 a-c** (Table 1). [d] From tricarboxylates **2** (Table 1).

groups as neighbors,  $\Delta H_{\text{diester}}$ , were determined from the new thermochemical data for the malonic diesters **1 a-c** (see Table 1), while the increments for CH with three ester groups as neighbors,  $\Delta H_{\text{triester}}$ , were determined from the data for **2** (Table 2). On introducing an ester substituent instead of an alkyl group the increments hardly change; the destabilization energy  $\Delta H_{\text{ester}} - \Delta H_{\text{alkyl}}$  lies between 0.2 and 0.7 kcal mol<sup>-1</sup> (Table 3). A second ester group, however, gives rise to

mine the extent of geminal effects and their dependence on the structure of some other substituents.

When discussing the CH-acidity of malonic esters and other geminally substituted compounds one must not only consider the stabilization of the anion but also the destabilization of the ground state as contributing to the acidity.

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**1a**, 108-59-8; **1b**, 609-02-9; **1c**, 6065-54-9; **2**, 6279-86-3; **3**, 7452-79-1; **4**, 3938-95-2.

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## Some Valenes of Benzannelated Five-Membered Heteroarenes – Synthesis and NMR Spectra\*\*

By Manfred Christl,\* Stefan Krimm and Arno Kraft

Dedicated to Professor Rolf Huisgen  
on the occasion of his 70th birthday

The chemical shifts of the C-atoms common to both three-membered rings of *endo,endo'*-bridged bicyclobutanes stretch over the unusually large range of  $\Delta\delta \approx 90$  ( $\delta = -13.4$  to  $75.5$ ).<sup>[1]</sup> In the valenes of naphthalene, 1,4-disubstituted phthalazines,<sup>[1a]</sup> and quinoxaline-2,3-dicarbonitrile<sup>[2]</sup> recently investigated by us the corresponding  $\delta$ -values lie between 42.4 and 48.6. We now present the first valenes of benzannelated five-membered heteroarenes and their NMR spectra.

The majority of the conventional methods for the synthesis of five-membered heteroarenes are unsuitable in the case of benzvalene-annelated derivatives. Thus, we were unable to dehydrogenate the benzvalene adducts of benzonitrile oxide and diphenyl nitrile imine.<sup>[3, 4a]</sup> We therefore carried out 1,3-dipolar cycloadditions<sup>[5]</sup> with benzvalenyl phenyl sulfone **1**.<sup>[6]</sup> This reacts with even more 1,3-dipolar compounds than does benzvalene.<sup>[3, 4]</sup> Moreover, the phenylsulfonyl

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Table 3. Destabilization of geminal di- and tricarboxylates from the difference in group increments in Table 2 [kcal mol<sup>-1</sup>]

	$\Delta H_{\text{ester}}^{[a]} - \Delta H_{\text{alkyl}}^{[d]}$	$\Delta H_{\text{diester}}^{[b]} - \Delta H_{\text{ester}}^{[a]}$	$\Delta H_{\text{triester}}^{[c]} - \Delta H_{\text{diester}}^{[b]}$	$\Delta\Delta H_{\text{gem}}$ [e]	$\Delta\Delta H_{\text{gem, gem}}$ [f]
$\text{CH}_2[x\text{CO}_2, (2-x)\text{C}]$	+ 0.39	+ 3.17	-	+ 2.78	-
$\text{CH}[x\text{CO}_2, (3-x)\text{C}]$	+ 0.24	+ 3.06	+ 6.60	+ 2.82	+ 3.54
$\text{C}[x\text{CO}_2, (4-x)\text{C}]$	+ 0.70	+ 2.62	-	+ 1.92	-

[a]  $x = 1$ . [b]  $x = 2$ . [c]  $x = 3$ . [d]  $x = 0$ . [e]  $(\Delta H_{\text{diester}} - \Delta H_{\text{ester}}) - (\Delta H_{\text{ester}} - \Delta H_{\text{alkyl}})$ . [f]  $(\Delta H_{\text{triester}} - \Delta H_{\text{diester}}) - (\Delta H_{\text{diester}} - \Delta H_{\text{ester}})$ .

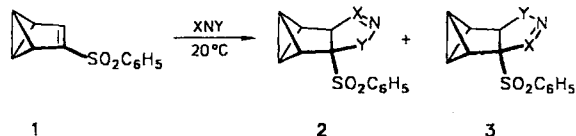
a significant destabilization: the destabilization energy  $\Delta H_{\text{diester}} - \Delta H_{\text{ester}}$  is 2.6 to 3.2 kcal mol<sup>-1</sup>. The corresponding destabilization by the third ester group ( $\Delta H_{\text{triester}} - \Delta H_{\text{diester}}$ ), with a value of 6.6 kcal mol<sup>-1</sup>, is substantial. The extra destabilization  $\Delta\Delta H_{\text{gem}} = \Delta H_{\text{diester}} - 2\Delta H_{\text{ester}} + \Delta H_{\text{alkyl}}$  and  $\Delta\Delta H_{\text{gem, gem}} = \Delta H_{\text{triester}} - 2\Delta H_{\text{diester}} + \Delta H_{\text{ester}}$ , i.e. the energy in excess of the additive destabilization energy is 1.9 to 2.8 kcal mol<sup>-1</sup> in the case of malonic diesters and 3.5 kcal mol<sup>-1</sup> in the case of tricarboxylates.

The classical anomeric effect is enhanced by alkyl groups on the central carbon atom.<sup>[2]</sup> The analogous dependence of the "inverse anomeric effect" on the degree of substitution is only slight in the case of the malonates.

The confirmation of the presumed inverse anomeric destabilization in the case of **1** and **2** indicates that the concept under discussion is a generally valid one. We shall next deter-

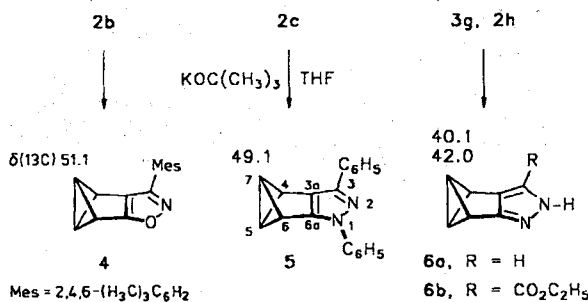
function introduced with **1** serves as leaving group in the elimination required en route to the target molecules.

Two nitrile oxides, diphenyl nitrile imine, (4-nitrophenyl)-phenyl nitrile ylide, two azides and two diazoalkanes afforded the dihydroheteroarenes **2** and **3**. Benzotrifluoride,<sup>[5b]</sup> diphenyl nitrile imine<sup>[5b]</sup> and 4-nitrophenyl phenyl nitrile



ylide<sup>[5c]</sup> were slowly generated in situ from their hydrogen chloride adducts, with triethylamine, while the other 1,3-dipolar compounds were used as such. Data on the reaction conditions, yields and isomeric ratios are listed in Table 1. The regioselectivity compares with that of known 1,3-dipolar cycloadditions of vinyl sulfones.

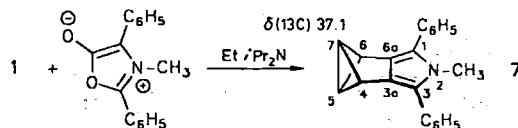
Since the phenylsulfonyl function is only a moderately good leaving group the elimination of phenylsulfonic acid<sup>[8]</sup> from **2** and **3** did not succeed in all cases. With potassium *tert*-butoxide in tetrahydrofuran at 20 °C we obtained the isoxazole **4** (5 h, 77% yield) from **2b**, and the pyrazoles **5** (5 h, 23%), **6a** (1 h, 29%) and **6b** (25 h, 68%), respectively, from **2c**, **3g** and **2h**.<sup>[7]</sup> There is no doubt about the structure of **5**, whereas in the case of **6a**, **b** tautomeric forms also have to be taken into consideration; however, on the basis of the <sup>13</sup>C-NMR spectra we prefer the structures **6**.



The success of these aromatizations seems to be dependent, *inter alia*, on the acidity of the protons that have to be split off. Thus, on using the mixture **2c**, **3c**, the reaction of **2c** proceeded smoothly, while **3c** remained unchanged and could then be readily isolated in isomerically pure form. In

the case of **3e** the elimination reaction leading to the valene of phenylbenzotriazole was not complete, and attempted separation of product and unconsumed starting material met without success.

3-Methyl-2,4-diphenyloxazolium-5-olate *N*-methyl-diphenyl munchedone underwent reaction with **1** in dichloromethane, but the expected product was not obtained. In contrast, in the presence of ethyldiisopropylamine the desired pyrrole **7**<sup>[7]</sup> was immediately formed in 41% yield. Presumably, after cycloaddition and elimination of CO<sub>2</sub>, the phenylsulfonate ion splits off at the stage of the transient azomethine ylide.<sup>[5d]</sup> The cationic precursor of **7** then transfers a proton even to the weak base ethyldiisopropylamine.



Starting from *cis*-3,4-dibenzoyltricyclo[3.1.0.0<sup>2,6</sup>]hexane<sup>[1a]</sup> **8** and tricyclo[3.1.0.0<sup>2,6</sup>]hexanedione<sup>[2]</sup> **9** there are several conceivable possibilities for the synthesis of the desired type of compound. However, only two reactions have thus far met with success: those to the thiophenes **10** (20% yield) and **11** (9%)<sup>[7]</sup> from **8** and Lawesson's reagent (toluene, triethylamine, 22 °C, 7 d) and from **9** and bisphenacylthioether (KOH in methanol, 20 °C, 18 h), respectively. The latter reaction provided the glycol product first, which was dehydrated with thionyl chloride in pyridine (0 °C, 1.5 h). 3,4-Diaminothiophene converted **9**, in analogy to known reactions,<sup>[2]</sup> into **12** (27%),<sup>[7]</sup> the valene of thieno[3,4-*b*]quinoxaline.

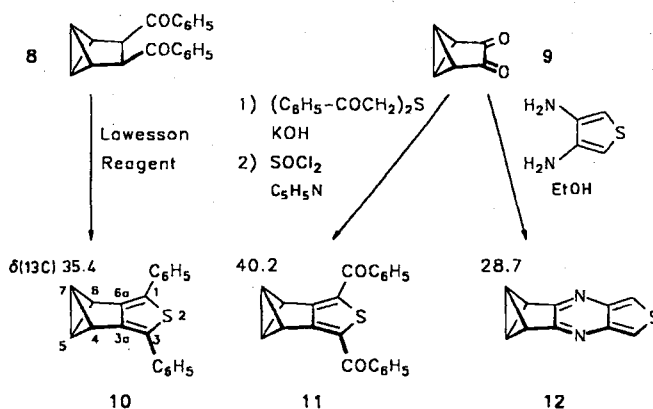


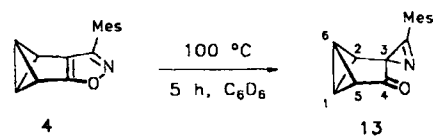
Table 1. Reactions of **1** with two nitrile oxides, diphenyl nitrile imine, 4-nitrophenyl phenyl nitrile ylide, two azides, and two diazoalkanes leading to the isomers **2** and **3**.

2, 3	1,3-Dipole XNY	Solvent	Time	X	Y	Yield [%]	Ratio 2:3
a	C <sub>6</sub> H <sub>5</sub> -CNO	CH <sub>2</sub> Cl <sub>2</sub>	6 h	C-C <sub>6</sub> H <sub>5</sub>	O	76	>95: 5
b	Mes-CNO	CHCl <sub>3</sub>	16 h	C-Mes	O	78	>95: 5
c	C <sub>6</sub> H <sub>5</sub> -CNN-C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>6</sub>	32 h	C-C <sub>6</sub> H <sub>5</sub>	N-C <sub>6</sub> H <sub>5</sub>	97	66:34
d	C <sub>6</sub> H <sub>5</sub> -CNCH-C <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	26 h	C-C <sub>6</sub> H <sub>5</sub>	CH-C <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub>	27	>95: 5
e	C <sub>6</sub> H <sub>5</sub> -N <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	7 d	N	N-C <sub>6</sub> H <sub>5</sub>	25	< 5:95
f	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -N <sub>3</sub>	CH <sub>2</sub> Cl <sub>2</sub>	5 d	N	N-C <sub>6</sub> H <sub>4</sub> -4-NO <sub>2</sub>	25	< 5:95
g	CH <sub>2</sub> N <sub>2</sub>	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O	[a]	N	CH <sub>2</sub>	96	15:85[b]
h	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> C-CHN <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	2 d	C-CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	NH	46	>95:5

[a] First 4 h at 0 °C then 2 d at 20 °C. [b] **2g** was not isolated but only characterized NMR spectroscopically.

The  $^{13}\text{C}$ -NMR chemical shifts of the bicyclobutane bridgehead atoms of the valenes are quoted alongside the formulas. They generally lie at considerably lower field than the values of the dihydro derivatives **2** and **3**. Especially noteworthy are the differences between the heteroarenes which are formally benzvalene derivatives, and those which can be derived from bismethylenetricyclo[3.1.0.0<sup>2,6</sup>]hexane.<sup>[9]</sup> Thus, **4** and **5**, with  $\delta = 51.1$  and  $49.1$ , respectively, show the furthest downfield shifts of all tricyclo[3.1.0.0<sup>2,6</sup>]hexane derivatives, whereas the corresponding signals of **7**, **10** and **11** with  $\delta = 37.1$ ,  $35.4$  and  $40.2$  lie at considerably higher field. A comparison of the  $\delta$  values of the pyrazoles **6** ( $\delta = 40.1$ ,  $42.0$ ) and **5** accordingly supports the proposed structure **6**. The expansion of the aromatic system in **12** leads to a further upfield shift to  $\delta = 28.7$ . In comparison to the corresponding absorption of the valene in which the thiophene moiety of **12** is replaced by a benzene ring,<sup>[21]</sup> a shielding of  $\Delta\delta = 6.2$  is observed in **12** which is possibly due to stronger double bond localization.

The majority of the valenes synthesized underwent isomerization under more or less energetic conditions to the benzannulated heteroarenes. In the case of **6b** and **7** this took place at  $100 - 150^\circ\text{C}$  in  $\text{C}_6\text{D}_6$ , in the case of **10** and **11** during



attempts at chromatographic purification. The isoxazole **4**, on the other hand, was converted into the acylazirine **13** (67% yield) upon heating.<sup>[17]</sup> Reactions of this type have already been reported, but thermally initiated ones generally do not terminate at the stage of the acylazirine.<sup>[10]</sup>

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**1**, 51991-05-0; **2a**, 126664-51-5; **2b**, 126664-52-6; **2c**, 126664-53-7; **2d**, 126664-54-8; **2e**, 126664-55-9; **2f**, 126664-56-0; **2g**, 126664-57-1; **2h**, 126664-58-2; **3a**, 126664-59-3; **3b**, 126664-60-6; **3c**, 126664-61-7; **3d**, 126664-62-8; **3e**, 126664-63-9; **3f**, 126664-64-0; **3g**, 126664-65-1; **3h**, 126664-66-2; **4**, 126664-67-3; **5**, 126664-68-4; **6a**, 126664-69-5; **6b**, 126664-70-8; **7**, 126664-71-9; **8**, 96598-12-8; **9**, 85358-63-0; **10**, 126664-72-0; **11**, 126664-73-1; **12**, 126664-74-2; **13**, 126664-75-3; bisphenylacetylthioether, 2461-80-5; 2,4,6-triphenyl benzonitrile *N*-oxide, 2904-57-6; diphenyl nitrile imine, 15409-32-2; 4-nitrophenyl phenyl nitrile ylide, 10494-67-4; 5-hydroxy-3-methyl-2,4-diphenyl oxazolium hydroxide, inner salt, 13712-75-9; benzonitrile oxide, 873-67-6; phenyl azide, 622-37-7; *p*-nitrophenyl azide, 1516-60-5; diazomethane, 334-88-3; ethyl diazoacetate, 623-73-4; 3,4-diaminothiophene, 78637-85-1.

Table 2. Selected physical data of **2-7** and **10-13**: 200- and 400-MHz  $^1\text{H}$ -NMR and 50- and 100-MHz  $^{13}\text{C}$ -NMR spectra in  $\text{CDCl}_3$  ( $\delta$  values, coupling constants in Hz), IR (KBr,  $\text{cm}^{-1}$ ).

**2a**: m.p.  $137 - 139^\circ\text{C}$  - **2b**: m.p.  $173 - 176^\circ\text{C}$   
**2c**:  $^1\text{H}$  NMR:  $\delta = 2.19$  (dq,  $J_{5,7} = 8.2$ ,  $J_{5a,7} = J_{6,7} = 1.7$ ; 7-H), 2.66 (dq,  $J_{6,6} = 5.0$ ,  $J_{3a,4} = J_{4,5} = 1.7$ ; 4-H), 2.83 (m; 5-H), 3.21 (dt,  $J_{5,6} = 1.7$ ; 6-H), 4.43 (br.s; 3a-H), 6.97 - 7.95 (several m;  $3\text{C}_6\text{H}_5$ ). -  $^{13}\text{C}$  NMR:  $\delta = 3.6$  (d, C-7), 10.7 (d; C-5), 38.6, 39.2 (each d; C-4, -6), 64.3 (d; C-3a), 100.8 (s; C-6a), 117.8, 121.8, 125.7, 128.1, 128.4 - 129.2, 133.8 (each d, each *3o*-, *m*-, *p*-C); 131.1, 137.2, 143.5, 149.2 (each s; 3 *ipso*-C, C-3)  
**3c**: m.p.  $167 - 170^\circ\text{C}$ . -  $^1\text{H}$  NMR:  $\delta = 2.34$  (dq,  $J_{5,7} = 7.9$ ,  $J_{6,7} = J_{6a,7} = 1.7$ ; 7-H), 2.82 (m; 6-H), 2.84 (m; 5-H), 3.39 (dt,  $J_{6,6} = 4.9$ ,  $J_{6,5} = 1.7$ ; 4-H), 5.18 (br.s; 6a-H), 6.86 (tt; 1 *p*-H), 7.03 (m; 2 *o*-H), 7.18 - 7.52 (m; 10H), 7.81 (m; 2 *o*-H). -  $^{13}\text{C}$  NMR:  $\delta = 3.4$  (d; C-7), 8.9 (d; C-5), 38.9, 40.3 (each d; C-4, -6), 74.9 (d; C-6a), 90.8 (s; C-3a), 112.8, 126.8, 128.3, 128.6, 129.0, 129.2 (each d; *m*-, *o*-C), 120.0, 128.5, 133.9 (each d; *p*-C), 131.4, 137.9, 141.2, 142.7 (each s; 3 *ipso*-C, C-3)  
**2d**: m.p.  $216 - 219^\circ\text{C}$  - **3e**: m.p. =  $142 - 145^\circ\text{C}$  - **3f**: m.p. =  $215 - 217^\circ\text{C}$   
**3g**: m.p.  $121 - 124^\circ\text{C}$  (still contains a few % **2g**)  
**2h**: m.p.  $170^\circ\text{C}$  (decomp.). - IR:  $\tilde{\nu} = 3350$  (n-H), 1685 (C=O)  
**4**: m.p.  $104 - 107^\circ\text{C}$   
**5**: m.p.  $136 - 139^\circ\text{C}$ . -  $^1\text{H}$  NMR:  $\delta = 2.73$ , 2.84 (each dt,  $J_{6,6} = 4.6$ ,  $J_{6,5} = J_{5,6} = 1.5$ ; 4-, 6-H), 4.51 (t; 5.7-H), 7.22 (tt; *p*-H), 7.26 (tt; *p*-H), 7.37 (m; 2 *m*-H), 7.41 (m; 2 *m*-H), 7.67 (m; 2 *o*-H), 7.80 (m; 2 *o*-H). -  $^{13}\text{C}$  NMR:  $\delta = 31.7$ , 33.4 (each ddt,  $J_{C,H} = 175$ , 11, 3; C-4, -6), 49.1 (dd,  $J_{C,H} = 211$ , 4; C-5,7), 119.0 (dt; *o*-C), 125.8 (dt; *p*-C), 126.0 (dt; *o*-C), 127.4 (dt; *p*-C), 128.4 (dd; *m*-C), 129.2 (dd; *m*-C), 133.4 (particularly high intensity), 140.0, 144.2, 160.0 (each s; C-3, -3a, -6a, 2 *ipso*-C)  
**6a**: m.p.  $80 - 83^\circ\text{C}$  - IR:  $\tilde{\nu} = 3180$  (breit; N-H)  
**6b**: m.p.  $88 - 90^\circ\text{C}$  - IR:  $\tilde{\nu} = 3140$  (breit; N-H), 1710 (C=O)  
**7**: m.p.  $150 - 151^\circ\text{C}$  -  $^1\text{H}$  NMR:  $\delta = 2.68$  (t,  $J_{4,5} = 1.5$ ; 4-H), 3.39 (s;  $\text{CH}_3$ ), 3.87 (t; 5-H), 7.24 (tt; *p*-H), 7.41 (m; *m*-H), 7.45 (m; *o*-H). -  $^{13}\text{C}$  NMR:  $\delta = 32.4$  (ddt,  $J_{C,H} = 172$ , 11, 4; C-4), 34.7 (q,  $J_{C,H} = 138$ ;  $\text{CH}_3$ ), 37.1 (dd,  $J_{C,H} = 212$ , 5; C-5), 126.1 (dt; *p*-C), 128.1 (dt; *o*-C), 128.5 (dd; *m*-C), 130.1, 133.2, 135.6 (each s; C-1, -3a, *ipso*-C)  
**10**: m.p.  $148 - 151^\circ\text{C}$ . -  $^1\text{H}$  NMR:  $\delta = 2.91$  (t,  $J_{4,5} = 1.7$ ; 4-H), 4.03 (t; 5-H), 7.23 (tt; *p*-H), 7.36 (m; *m*-H), 7.53 (m; *o*-H). -  $^{13}\text{C}$  NMR:  $\delta = 34.1$  (ddt,  $J_{C,H} = 173$ , 11, 3; C-4), 35.4 (dd,  $J_{C,H} = 217$ , 5; C-5), 128.2 (s; C-1), 150.4 (s; C-3a), 126.2 (dt; *o*-C), 126.8 (dt; *p*-C), 128.8 (dd; *m*-C), 134.4 (s; *ipso*-C)  
**11**: m.p.  $120 - 122^\circ\text{C}$ . - IR:  $\tilde{\nu} = 1640$ , 1625 (C=O)  
**12**: m.p.  $140 - 143^\circ\text{C}$ .  
**13**: m.p.  $131 - 132^\circ\text{C}$ . - IR:  $\tilde{\nu} = 1735$  (C=O, C=N). -  $^1\text{H}$  NMR:  $\delta = 2.03$ , 2.61 (each dt;  $J_{2,5} = 4.9$ ,  $J_{1,2} = J_{1,5} = J_{2,6} = J_{5,6} = 1.9$ ; 2-, 5-H), 3.27, 3.42 (each dt,  $J_{1,6} = 7.2$ ; 1-, 6-H), 2.34 (s; *p*- $\text{CH}_3$ ), 2.53 (s; 2 *o*- $\text{CH}_3$ ), 6.97 (br.s; 2 *m*-H). -  $^{13}\text{C}$  NMR:  $\delta = 9.4$ , 11.9 (each d; C-1, -6), 33.2, 42.8 (each d; C-2, -5), 43.1 (s; C-3), 159.4 (s; C=N), 212.9 (s; C-4), 20.3 (q; 2 *o*- $\text{CH}_3$ ), 21.6 (q; *p*- $\text{CH}_3$ ), 117.8 (s; *ipso*-C), 129.5 (d; 2 *m*-C), 141.9 (s; 2 *o*-C), 144.1 (s; *p*-C)

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## Nitrogen Triiodide\*\*

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In addition to the stable  $\text{NF}_3$ ,<sup>[11]</sup> only the binary nitrogen trihalides  $\text{NCl}_3$ , which is explosive, and  $\text{NBr}_3$ ,<sup>[12]</sup> which was

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