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Sulfonyl Derivatives of Benzotriazole: Part 1. A Novel Approach to the Activation of Carboxylic Acids

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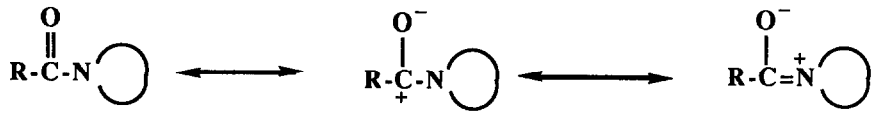
Abstract: *1-Acylbenzotriazoles (8, R = Me, Et, n-Bu and Ph) are prepared in good yields by fusion of benzotriazole and acid chlorides at 80 - 100°C. In cases when the corresponding acid chlorides are not available, 1-acylbenzotriazoles are conveniently available from 1-(1-methanesulfonyl)benzotriazole and the respective carboxylic acids as illustrated by the preparation of 2-, 3-, and 4-pyridoyl-, 2-pyrrolylcarbonyl- and 2-furoyl-benzotriazole in yields of 80 - 95%. Preparations of two sulfonyl derivatives of benzotriazole are also described.*

Acylazoles are versatile activated derivatives of carboxylic acids, particularly useful for acylations when the acid chloride could produce undesired complications. Acylazoles are unlike other tertiary amides in that there is less contribution from resonance forms of type (3) to the structure than the corresponding tertiary amides, hence the positive nature of the carbonyl carbon is retained.[1] Thus N-acylimidazoles and N-acylbenzimidazoles are powerful acylation agents and have been widely involved in reactions which result in the acylation of diverse nucleophiles[2] to produce aldehydes, ketones, carboxylic esters, amides, hydrazides and anhydrides.[3-4] An example of a very useful acylimidazole is 1,1′-carbonyldiimidazole, which is extremely reactive toward nucleophiles, crystalline, and much more easily handled than phosgene.[2,5]



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While N-acylimidazoles and N-acylbenzimidazoles have been well developed and reviewed,[4] the corresponding N-acylbenzotriazoles are far less exploited. Acylbenzotriazoles have been used in the anionic polymerization of lactams to obtain polymers with high molecular weight in short reaction times.[6] N-Acetylbenzotriazole is particularly important in the acetylation of proteins because of its unique reactivity towards amino and phenolic residues and its stability in acidic media.[7] N-Acylbenzotriazoles give ketones with trialkylaluminums.[8] The acetone-sensitized photolysis of 1-benzoylbenzotriazole forms a cyclopentadiene derivative via a Wolff rearrangement[9] and the thermolysis of 1-benzoylbenzotriazole gave a benzoxazole derivative.[10] N-Acylbenzotriazoles undergo thermal intermolecular acyl exchange reactions.[11] The hydrolysis and aminolysis of N-acylbenzotriazoles have also been investigated.[12-13]

In honor of the 65th anniversary of Charles Rees and in commemoration of 4 decades of friendship.

Several synthetic methods for N-acylbenzotriazoles are available. Most previous preparations of acylbenzotriazoles have utilized acid chlorides by reaction with (i) 1-(trimethylsilyl)benzotriazole;[14] with (ii) 1-(tributylstannyl)benzotriazole[15] or with (iii) 1-(hydroxymethyl)benzotriazole which loses formaldehyde.[16] Benzotriazole in dry pyridine treated dropwise with cooling with aroyl chlorides yielded 1-aroylbenzotriazoles.[17] 1-Acetylbenzotriazole was also prepared from benzotriazole and acetyl chloride in 61% yield in dry benzene.[18] Most of the published work on acylbenzotriazoles has been limited to 1-benzoyl- and 1-acetyl-benzotriazole.

Scheme 1

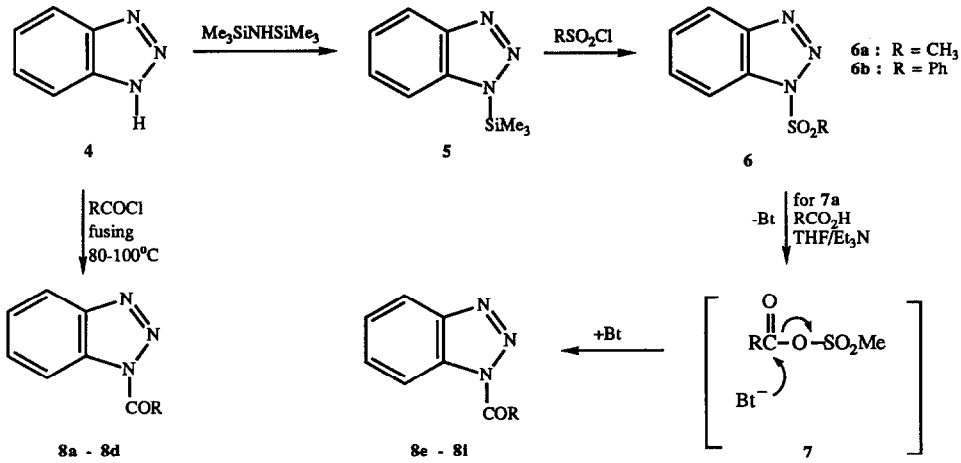

Table 1. Preparation of Sulfonylbenzotriazoles and Acylbenzotriazoles

compd	R	yield(%)	mp(°C)	Lit. mp(°C)	recryst. solvent	molecular formula	calcd			found		
							C	H	N	C	H	N
6a	Me	60	104-106	110-112[23]	benzene	$C_7H_7N_3O_2S$	42.63	3.58	21.31	42.45	3.43	21.18
6b	Ph	59	124-126	124[21]	benzene	$C_{12}H_9N_3O_2S$	65.27	3.79	17.56	65.12	3.66	17.27
8a	Me	70	51-52	51[18]	aq.MeOH	$C_8H_7N_3O$		—			—	
8b	Et	90	80-82	—	EtOH	$C_{13}H_9N_3O$	61.71	5.14	24.00	61.60	5.17	24.12
8c	n-Bu	79	42-44	—	MeOH	$C_9H_9N_3O$	65.02	6.40	20.68	64.94	6.52	20.82
8d	Ph	90	112-113	112-113[16]	MeOH	$C_{11}H_{13}N_3O$		—			—	
8e	2-Py	90	97-100	—	$CHCl_3$/hexane	$C_{12}H_8N_4O$	64.28	3.60	24.99	64.07	3.57	25.25
8f	3-Py	92	86-89	—	$CHCl_3$/hexane	$C_{12}H_8N_4O$	64.28	3.60	24.99	64.26	3.57	25.28
8g	4-Py	80	148-150	—	$CHCl_3$/hexane	$C_{12}H_8N_4O$	64.28	3.60	24.99	64.60	3.61	25.44
8h	2-pyrrolyl	80	161-162	—	MeOH	$C_{11}H_8N_4O$	62.26	3.80	26.40	62.63	3.76	26.29
8i	2-furanyl	95	172-174	—	MeOH	$C_{11}H_7N_3O_2$	61.97	3.31	19.71	61.94	3.38	19.69

We now describe two general and convenient methods for the synthesis of N-acylbenzotriazoles. The first of our methods yields these compounds in good yield directly from benzotriazole and acid chloride without using any solvent. Thus, 1-benzoyl- (**8a**), 1-acetyl- (**8b**), 1-propanoyl- (**8c**) and 1-pentanonyl-benzotriazole (**8d**) were prepared in 70 - 90% yields by simply fusing an equimolar mixture of benzotriazole and the respective acid chloride at 80 - 100°C, see Scheme 1 and Table 1.

However, neither this new approach nor any of the others using an acid chloride is convenient for the many carboxylic acids of which the corresponding acid chlorides are unstable or difficult to obtain such as the pyridinecarboxylic acids. Another route involves treatment of o-nitroacetanilide with Al-Hg to obtain acetyl-o-phenylenediamine which is then cyclized on treatment with sodium nitrite,[19] but this is not generally useful because of the lack of the monoacylated o-phenylenediamines.

The second method that we wish to report represents a new convenient, high yielding approach which gives the N-acylbenzotriazoles directly from carboxylic acids, by their reaction with 1-(methanesulfonyl)benzotriazole.

Sulfonyl derivatives of benzotriazole, such as 1,1′-sulfonyl dibenzotriazole and N-(alkylsulfonyl)benzotriazoles, have been prepared as herbicides, mutagens, insecticides, acaricides, fungicides and antibacterials.[20,21-22] They have also been used as activators for sodium perborate bleaching agents.[24] However, their applications in organic synthesis have not yet been exploited. Literature methods for the synthesis of compounds of types **6** and **7** include treatment of sulfonyl azides with benzene diazonium-o-carboxylate via a benzyne intermediate,[25] reaction of 1-(trimethylsilyl)benzotriazole with sulfuryl chloride,[20] treatment of the corresponding sulfonyl chloride with benzotriazole in dioxane in the presence of sodium hydroxide[26] or in alkaline aqueous acetone solution.[27] Reaction of o-phenylenediamine with sulfonyl chlorides followed by ring closure with sodium nitrite in hydrochloric acid also gave (alkylsulfonyl)benzotriazoles.[23] Other methods involve the activation of the heterocyclic nitrogen by organostannylation and its subsequent destannylation by the corresponding sulfonyl chloride[21] and the treatment of 1,2-di(benzotriazol-1-yl)ethane-1,2-diol with p-toluenesulfonyl chloride.[28]

1-(Trimethylsilyl)benzotriazole, in which the nitrogen is activated, reacts similarly with methanesulfonyl chloride and benzenesulfonyl chloride to give the corresponding 1-(methanesulfonyl)- and 1-(benzenesulfonyl)-benzotriazoles (**6a** and **6b**) in 60% and 59% yields, respectively. None of the 2-substituted benzotriazoles are obtained. The procedure, comprising treatment of equimolar amounts of the sulfonyl chloride with 1-(trimethylsilyl)benzotriazole at 80°C - 100°C for 3 h, is simple and convenient.

1-(Methanesulfonyl)benzotriazole **6a** is a useful reagent for the convension of carboxylic acids into their corresponding 1-acylbenzotriazoles **8e** to **i**. The procedure involves heating under reflux an equimolar mixture of the carboxylic acid and 1-(methanesulfonyl)benzotriazole in the presence of an equimolar amount of triethylamine. The yields are good to excellent and the workup is easy (Scheme 1 and Table 1). The carboxylic acids converted into the acylbenzotriazoles include 2-, 3- and 4-pyridinecarboxylic acid (**8e, 8f** and **8g**), 2-pyrrolecarboxylic acid (**8h**) and 2-furoic acid (**8i**). All give 1-acylbenzotriazoles based on their spectral data, 2-acylbenzotriazoles are not observed. The similar reaction of 1-(benzenesulfonyl)benzotriazole **6b** with carboxylic acids is less smooth under these conditions.

The mechanism for the formation of acylbenzotriazoles **8e -8i** from 1-methanesulfonylbenzotriazoles and carboxlic acid is shown in Scheme 1: the carboxylate (formed in the presence of triethylamine) attacks the sulfur atom of 1-(methanesulfonyl)benzotriazole followed by the departure of benzotriazole to give the intermediate **7**. Then the addition of benzotriazole anion to the carbonyl carbon and elimination of alkanesulfonate gives the final product **8**.

This preparation of 1-acylbenzotriazoles from carboxylic acids provides a potentially useful method for the activation of carboxylic acids. The well known activation of carboxylic acids involves conversion of the acids into their chlorides, however, the disadvantages of using acid chlorides are obvious. They are highly reactive and often result in undesired complications; many acid chlorides are unstable, difficult to prepare, and/or liquids with unpleasant odors.

The acid chlorides of some carboxylic acids such as pyridine and other heterocyclic carboxylic acids are either unstable or can not be prepared due to the attack by acid chloride on the nitrogen atom of heterocyclic carboxylic acids whereas their corresponding acylbenzotriazoles are easy to obtain in high yields as shown. Acylbenzotriazoles are solid and stable on storage.

The 1-acylbenzotriazoles, **8a - 8d** prepared from benzotriazole and acid chlorides and **8e - 8i** from 1-(methanesulfonyl)benzotriazole and carboxylic acids, are new compounds except for **8a** and **8d**. They are characterized by their elemental analyses (Table 1) and by their ^1H and ^{13}C NMR and mass spectra. NMR studies of the 1-acetylbenzotriazole have previously been reported.[29-30] Two doublets and two triplets representing the typical 1-substituted benzotriazole protons were seen in the ^1H NMR spectra. The detailed assignments of the ^1H NMR spectra for compounds **7** and **8** are listed in the experimental section. In the ^{13}C NMR spectra, the carbonyl carbons of aliphatic acylbenzotriazoles (**8a, 8b and 8c**) appear at about 170 ppm which is in agreement with the previous report,[29] while those of 1-(arylcarbonyl)benzotriazoles (**8d, 8e, 8f** and **8g**) are at ca. 165 ppm. However, the carbonyl carbon signal is at 156.4 ppm for 1-(2-pyrrolylcarbonyl)benzotriazole **8h** and at 154.9 ppm for 1-(2-furanylcarbonyl)benzotriazole **8i**. The mass spectra of compounds **8e - 8i** were recorded. Their molecular ion peaks are observed and other major ions include those from loss of CO, RCO and benzotriazolyl groups.

In summary, 1-acylbenzotriazoles have been prepared by two different methods. The workup procedures of both methods are simple and the products are easily purified. The reactivity of 1-acylbenzotriazoles and their synthetic applications are now under investigation.

Experimental

Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. The ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were taken on a VXR-300 spectrometer in $CDCl_3$ or DMSO-d_6. Mass spectra were obtained on an AEI MS 30 mass spectrometer. Elemental analyses were performed at the University of Florida. 1-(Trimethylsilyl)benzotriazole was prepared as described in the literature.[14]

1-(Substitutedsulfonyl)benzotriazoles **6**, General Procedure

The mixture of an alkane- or arenesulfonyl chloride (0.1 mol) and 1-(trimethylsilyl)benzotriazole (19.1 g, 0.1 mol) was stirred for 3 h at 80°C. The resulting precipitate was filtered off and washed with dry methylene chloride. The crude product was recrystallized from benzene to give the sulfonyl benzotriazole.

1-(Methanesulfonyl)benzotriazole **6a**

^1H NMR (DMSO-d_6): δ 8.30 (d, J = 8.3 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.83 (t, J = 8.2 Hz, 1H), 7.65 (t, J = 8.3 Hz, 1H), 3.87 (s, 3H, CH_3); ^{13}C NMR: δ 144.6, 131.2, 130.6, 126.1, 120.2, 112.0, 42.5.

1-(Benzenesulfonyl)benzotriazole **6b**

^1H NMR ($CDCl_3$): δ 8.20-8.06 (m, 4H), 7.71-7.60 (m, 2H), 7.55-7.44 (m, 3H); ^{13}C NMR: δ 144.8, 135.2, 131.8, 130.3, 129.6, 127.8, 125.8, 120.6, 120.5, 112.0.

1-Acylbenzotriazoles, Method A,

A mixture of benzotriazole (1.19 g, 10 mmol) and an acid chloride (20 mmol) was fused at 80 - 100°C for about 15 min under a condenser. After cooling, the solid was washed with methanol and water and recrystallized from benzene or ethanol to give the 1-acylbenzotriazole (Table 1).

1-Acetylbenzotriazole **8a**

^1H NMR ($CDCl_3$): δ 8.20 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 8.2 Hz, 1H), 7.59 (t, J = 8.1 Hz, 1H), 7.46 (t, J = 8.1 Hz, 1H), 3.00 (s, 3H, CH_3); ^{13}C NMR: δ 169.5, 146.1, 130.9, 130.3, 126.1, 120.0, 114.3, 23.2.

1-Propanoylbenzotriazole **8b**

^1H NMR ($CDCl_3$): δ 8.27 (d, J = 8.2 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 7.62 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.2 Hz,

1H), 3.46 (q, J = 7.4 Hz, 2H), 1.42 (t, J = 7.4 Hz, 3H); ^{13}C NMR: δ 173.3, 146.1, 131.1, 130.3, 126.0, 120.1, 114.4, 29.1, 8.4.

1-Pentanoylbenzotriazole **8c**

^{1}H NMR ($CDCl_3$): δ 8.25 (d, J = 8.3 Hz, 1H), 8.05 (d, J = 8.3 Hz, 1H), 7.63 (t, J = 8.2 Hz, 1H), 7.47 (t, J = 8.2 Hz, 1H), 3.42 (t, J = 7.3 Hz, 2H), 1.98 (m, 2H), 1.55 (m, 2H), 1.01 (t, J = 7.3 Hz, 3H); ^{13}C NMR: δ 172.5, 146.0, 130.9, 130.1, 125.9, 119.9, 114.3, 35.1, 26.3, 22.1, 13.6.

1-Benzoylbenzotriazole **8d**

^{1}H NMR ($CDCl_3$): δ 8.37 (d, J = 8.3 Hz, 1H), 8.21 (d, J = 7.1 Hz, 2H), 8.15 (d, J = 8.4 Hz, 1H), 7.68 (t, J = 7.2 Hz, 2H), 7.60-7.50 (m, 3H); ^{13}C NMR: δ 166.6, 145.6, 133.6, 132.3, 131.7, 131.4, 130.3, 128.4, 126.3, 120.1, 114.7.

1-Acylbenzotriazoles, Method B,

A mixture of a heterocyclic carboxylic acid and 1-(methanesulfonyl)benzotriazole was refluxed in THF overnight. The solvent was evaporated and the residue dissolved in chloroform, washed with water, dried over anhydrous $MgSO_4$ and evaporated to give a crude product which was recrystallized from the appropriate solvent.

1-(2-Pyridylcarbonyl)benzotriazole **8e**

^{1}H NMR ($CDCl_3$): δ 8.87 (d, J = 4.8 Hz, 1H, 6-PyH), 8.37 (d, J = 8.2 Hz, 1H, BtH), 8.15 (m, 2H), 7.96 (t, J = 7.8 Hz, 1H, PyH), 7.71 (t, J = 8.2 Hz, 1H, BtH), 7.52-7.50 (m, 2H); ^{13}C NMR: δ 165.1, 149.8, 149.7, 145.6, 136.7, 131.9, 130.4, 126.8, 126.4, 126.2, 120.1, 114.4; MS: (m/e) 225 (M^+ + 1, 18%), 196 (M^+ - CO, 100%).

1-(3-Pyridylcarbonyl)benzotriazole **8f**

^{1}H NMR ($CDCl_3$): δ 9.43 (d, J = 2.2 Hz, 1H, 2-PyH), 8.91 (dd, J = 1.7 and 4.9 Hz, 6-PyH), 8.57 (dt, J = 8.0, 2.0 Hz, 1H, 4-PyH); 8.38 (d, J = 8.3 Hz, 1H, BtH); 8.17 (d, J = 8.2 Hz, 1H, BtH), 7.73 (t, J = 8.2 Hz, 1H, BtH), 7.60-7.52 (m, 2H); ^{13}C NMR: δ 165.0, 153.7, 152.1, 145.8, 139.1, 131.9, 130.8, 127.8, 126.8, 125.7, 123.2, 120.3; MS: (m/e) 224 (M^+, 6%), 196 (M^+ - CO, 100%), 119 (M^+ - PyCO, 26%), 106 (M^+ - Bt, 59), 78 (Py^+, 71%).

1-(4-Pyridylcarbonyl)benzotriazole **8g**

^{1}H NMR ($CDCl_3$): δ 8.90 (d, J = 6.1 Hz, 2H, 2,6-PyH), 8.36 (d, J = 8.3 Hz, 1H, BtH), 8.16 (d, J = 8.3 Hz, 1H, BtH), 8.03 (d, J = 6.1 Hz, 2H, 3,5-PyH), 7.75 (t, J = 8.3 Hz, 1H, BtH), 7.59 (t, J = 8.2 Hz, 1H, BtH); ^{13}C NMR: δ 165.2, 150.3, 145.7, 138.6, 131.7, 131.0, 126.9, 124.3, 120.3, 114.6; MS: (m/e) 224 (M^+, 13%), 196 (M^+ - CO, 33%), 119 (M^+ - PyCO, 100%), 106 (M^+ - Bt, 50%).

1-(2-Pyrroylcarbonyl)benzotriazole **8h**

^{1}H NMR (DMSO-d_6): δ 12.4 (br, 1H, NH), 8.33 (d, J = 8.3 Hz, 1H, BtH), 8.26 (d, J = 8.3 Hz, 1H, BtH), 7.81 (t, J = 8.2 Hz, 1H, BtH), 7.78 (m, 2H), 7.41 (m, 1H), 6.42 (dd, J = 2.4 and 4.0 Hz, 1H); ^{13}C NMR: δ 156.4, 144.8, 131.8, 130.1, 128.1, 126.0, 123.6, 121.7, 119.7, 114.2, 111.1; MS: (m/e) 212 (M^+, 100%), 184 (M^+ - CO, 7%), 119 (Bt^+, 3%).

1-(2-Furoyl)benzotriazole **8i**

^{1}H NMR ($CDCl_3$): δ 8.38 (d, J = 8.3 Hz, 1H, BtH), 8.15 (m, 2H), 7.88 (d, J = 0.9 Hz, 1H, FuH), 7.69 (t, J = 8.0 Hz, 1H, BtH), 7.55 (t, J = 8.1 Hz, 1H, BtH), 6.73 (dd, J = 1.6 and 3.7 Hz, 1H); ^{13}C NMR: 154.9, 148.9, 145.4, 144.4, 132.0, 130.4, 126.2, 124.7, 120.1, 114.6, 112.9; MS: (M/e): 213 (M^+, 2%), 185 (M^+ - CO, 100%), 146 ($BtCO^+$, 73%), 95 (M^+ - Bt, 81%).

References

(1) M. R. Grimmett, in "Comprehensive Heterocyclic Chemistry," ed by A. R. Katritzky, C. W. Rees and K. T. Potts, Pergamon Press, Oxford, 1984, Vol. 5, P. 451

(2) a. Keumi, T.; Saga, H.; Kitajima, H. Bull. Chem. Soc. Jpn. **1980**, 53, 1638.

b. Walter, W.; Radke, M. Liebigs Ann. Chem. **1979**, 1756.

(3). Keumi, T.; Yamamoto, T.; Saga, H.; Kitajima, H. Bull. Chem. Soc. Jpn. **1981**, 54, 1579.

(4). Staab, H. A.; Rohr, W. "Newer Methods of Preparative Organic Chemistry", ed. by Foerst, W. Academic Press, New York, Vol. 5, p.61, **1962**.

(5). Ogata, M.; Matsumoto, H.; Kida, S.; Shimizu, S. Heterocycles, **1980**, 14, 97.

(6). Reimschuessel, H. K.; Boardman, F. US Pat. 3,350,364 (1967). Chem. Abstr. **1968**, 68, 3357m.

(7). Reboud-Ravaux, M.; Ghelis, C. Eur. J. Biochem. **1976**, 65, 25.

(8). Tolstikov, G. A.; Valitov, F. Kh.; Kuchin, A. V. Dokl. Akad. Nauk SSSR **1982**, 265, 1406. Chem. Abstr. **1983**, 98, 52710z.

(9). Tsujimoto, K.; Ohashi, M.; Yonezawa, T. Bull. Chem. Soc. Jpn. **1972**, 45, 515.

(10). Hubert, A. J.; Reimlinger, H. Chem. Ber. **1970**, 103, 2828.

(11). Druliner, J. D. J. Am. Chem. Soc. **1968**, 90, 6879.

(12). Reboud-Ravaux, M. J. Am. Chem. Soc. **1980**, 102, 1039.

(13). Gopalakrishnan, G.; Hogg, J. L. J. Org. Chem. **1981**, 46, 4959.

(14). Gasparani, J. P.; Gassend, R.; Maire, J. C.; Elguero, J. J. Organometallic Chem. **1980**, 188, 141.

(15). Gassend, R.; Maire, J. C.; Pommier, C. J. Organometallic Chem. **1977**, 137, 185.

(16). Gaylord, N. G. J. Am. Chem. Soc. **1954**, 76, 285.

(17). Kreutzberger, A.; Dietz, E. Arzneim. Forsch. **1970**, 20, 1723. Chem. Abstr. **1971**, 74, 53663c.

(18). Stabb, H. A. Chem. Ber. **1957**, 90, 1320.

(19). Bell, F.; Kenyon, J. J. Chem. Soc. **1926**, 954.

(20). Purygin, P. P.; Ivanov, I. P.; Laletina, Z. P.; Selezneva, E. S. Khim. Farm. Zh. **1983**, 17, 1319. Chem. Abstr. **1984**, 100, 120976c.

(21). Soundararajan, R.; Balasubramanian, T. R. Chem. and Ind. (London) **1985**, 3, 92.

(22). Sasse, K.; Wegler, R.; Grewe, F. Brit. Pat. **1961**, 885,843. Chem. Abstr. **1962**, 57, 4676.

(23). Beveridge, S.; Huppatz, J. L. Aust. J. Chem. **1972**, 25, 1341.

(24). Finley, J. H.; Brubaker, G. R.; Baum, B. M. Eur. Pat. Appl. 9,998 (1980), Chem. Abstr. **1980**, 93, 116350p.

(25). Ried, W.; Schoen, M. Chem. Ber. **1965**, 98, 3142.

(26). Mozolis, V.; Jokubaityte, S.; Rastenyte, L. Liet. TSR Mokslu Akad. Darb. Ser. B, **1969**, 77. Chem. Abstr. **1970**, 72, 12651n.

(27). Sasse, K.; Wegler, R.; Grewe, F. US Pat. 2,943,017 (1960). Chem. Abstr. **1960**, 54, 24806.

(28). Katritzky, A. R.; Fan, W. Q. J. Heterocyclic Chem. **1990**, 27, 1543.

(29). Fruchier, A.; Elguero, J.; Hegarty, A. F.; McCarthy, D. G. Org. Magn. Resonance **1980**, 13, 339.

(30). Begtrup, M.; Claramunt, R. M.; Elguero, J. J. Chem. Soc. Perkin Trans. 2 **1978**, 99.