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Intramolecular 1,3-Dipolar Cycloadditions of Aryl Azides Bearing Alkenyl, Alkynyl, and Nitrile Groups

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Azido compounds **1** containing dipolarophile groups, such as C=C, C≡C, and C≡N bonds, were synthesized from the corresponding anilines and thermally decomposed in aromatic hydrocarbon solvents. Bridgehead nitrogen aziridines **3** were obtained from **1a–c,** probably through an intramolecular cycloaddition leading to unstable Δ^2-1,2,3-triazolines. From **1d–g,** the corresponding 1,3-cycloaddition products, namely the fused-ring triazoles **7** and tetrazoles **8,** were isolated in good yields.

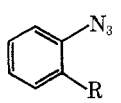
1,3-Dipoles bearing an additional function able to behave as a dipolarophile appear to be very interesting substrates. In fact, the intramolecular cycloaddition of a properly functionalized 1,3-dipole represents a general scheme for the synthesis of fused ring heterocycles. Nevertheless, in spite of the copious literature on 1,3-dipolar cycloadditions, intramolecular examples have as yet received little attention.

With azides, intramolecular cycloadditions have been occasionally reported,[1,2] but systematic data are available only for a series of azidoalkenes.[3] Also, a mechanism involving an intramolecular 1,3-dipolar cycloaddition to the carbonyl function is possibly operating in the formation of 3-arylanthranils from 2-azidobenzophenones, as proposed on the basis of a kinetic investigation.[4].

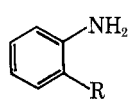
The present paper describes the results which we obtained from a series of structurally related aryl azides bearing different dipolarophile groups.

Results and Discussion

Azido compounds **1** were synthesized from the corresponding anilines **2** by diazotization and treatment of the intermediate diazonium salts with sodium azide.



1a, R = $OCH_2CH{=}CH_2$
b, R = $OCH_2C(Me){=}CH_2$
c, R = $OCH_2CH{=}CHPh$
d, R = $OCH_2C{\equiv}CH$



2e, R = $OCH_2C{\equiv}CPh$
f, R = OCH_2CN
g, R = CH_2CH_2CN

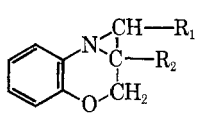
Reaction yields as well as physical and spectral data are collected in Table I.

All the compounds studied were decomposed by refluxing in aromatic hydrocarbon solvents. Temperatures were chosen on the basis of the different substrate reactivities. Each run was continued until all the starting material was consumed as indicated by thin layer chromatographic analyses of the reaction mixture.

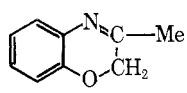
Experimental conditions and reaction products, which are summarized in Table II, will now be considered and discussed for the different kinds of substrates.

Aryl Azides Bearing an Alkenyl Substituent. The decomposition of azides **1a, 1b,** and **1c** was performed in boiling benzene, the reaction time being respectively 6, 11, and 16 hr. In the case of **1a,** the crude product was a mixture of two components, which were isolated by column chromatography and identified as 1,1a-dihydro-2*H*-azirino[2,1-*c*][1,4]benzoxazine (**3a**) and 3-methyl-2*H*-1,4-benzoxazine (**4**).[5] However, the reactions of **1b** and **1c** gave essentially only the aziridines **3b** and **3c,** respectively.

Structures **3a–c** were assigned on the basis of elemental analyses, NMR spectra, and chemical behavior. The chemical shifts found for the protons of the aziridine ring in these



3a, $R_1 = R_2 = H$
b, $R_1 = H$; $R_2 = Me$
c, $R_1 = Ph$; $R_2 = H$



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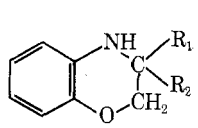


5a, $R_1 = H$; $R_2 = Me$
b, $R_1 = R_2 = Me$
c, $R_1 = H$; $R_2 = CH_2Ph$

Table I
Preparation of Azido Compounds 1[a]

Compd	Yield, %	Mp, °C	NMR spectrum ($CDCl_3$), τ (J, Hz)
1a	80	Oil[b]	2.8–3.4 (4 H, m, aromatics), 3.6–4.2 (1 H, m, CH=), 4.3–4.9 (2 H, m, CH_2=), 5.48 (2 H, m, CH_2O)
1b	88	Oil[b]	2.8–3.3 (4 H, m, aromatics), 4.8–5.1 (2 H, m, CH_2=), 5.54 (2 H, s, CH_2O), 8.15 (3 H, s, CH_3)
1c	63	49	2.5–3.2 (9 H, m, aromatics), 3.29 (1 H, d, $J = 16$, CH=), 3.61 (1 H, dt, $J = 5$ and 16, CH=), 5.28 (2 H, d, $J = 5$, CH_2O)
1d	29	Oil[c]	2.7–3.1 (4 H, m, aromatics), 5.30 (2 H, d, $J = 2.5$, CH_2O), 7.44 (1 H, t, $J = 2.5$, CH≡)
1e	68	Oil[b]	2.5–3.1 (9 H, m, aromatics), 5.12 (2 H, s, CH_2O)
1f	63	67	2.9 (4 H, m, aromatics), 5.19 (2 H, s, CH_2O)
1g	76	Oil[b]	2.5–3.0 (4 H, m, aromatics), 6.9–7.6 (4 H, m, CH_2CH_2)

[a] All compounds listed gave, in the ir spectrum, a strong band in the region 2120–2130 cm^{-1}. [b] Purity better than 95% (NMR). [c] The NMR analysis showed, together with **1d**, 15% of triazole **7a** (see later in the text).

compounds (Table III) agree with those reported for several aziridines.[6] Also, the absence of a geminal coupling in the case of **3a** and **3b** is not unprecedented for bridgehead nitrogen aziridines.[7] For compound **3c**, the vicinal coupling constant observed for the aziridine protons (3.5 Hz) compares well to trans coupling given in the literature.[6]

Catalytic hydrogenation of **3a–c** afforded the corresponding benzomorpholines **5a–c**. Compound **5a**[5] was also obtained from **4** by reduction with $LiAlH_4$.

It is noteworthy that aziridines **3a–c** are thermally stable (distillation in vacuo was possible without change), while they are readily transformed in the presence of acidic species, which cause extensive resinification, particularly in the case of **3a**.

The following points help to explain the above reactions. The known behavior of several Δ^2-1,2,3-triazolines, which thermally decompose to give aziridines[8–11] and imine derivatives,[10] suggests that the formation of **3a–c** and **4** could in-

Table II
Decomposition of Azido Compounds 1[a]

Compd	Solvent	Time, hr	Product(s) (yield, %)	Isolation procedure[b]
1a	Benzene	6	**3a** (58) + **4** (28)	A [diethyl ether–triethylamine (9:1)]
1b	Benzene	11	**3b** (69)	A [diethyl ether–triethylamine (9:1)]
1c	Benzene	16	**3c** (70)	B (*n*-pentane)
1d	Benzene	0.5	**7a** (75)	A (diethyl ether)
1e	Toluene	3	**7b** (78)	B (benzene)
1f	Xylene	4	**8a** (45)	A [benzene–ethanol (9:1)]
1g	Xylene	17	**8b** (25)	A [benzene–ethanol (9:1)]

[a] By refluxing 0.1 *M* solutions. [b] A = silica gel chromatography (eluent in parentheses), B = crystallization (solvent in parentheses).

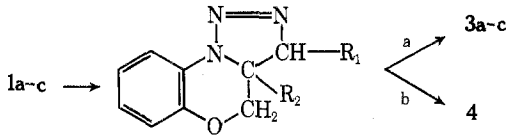
Table III
Physical, Spectral, and Analytical Data of Fused Ring Heterocycles 3, 7, and 8

Compd	Mp, °C (bp, °C)	Recrystn solvent	NMR spectrum ($CDCl_3$), τ (J, Hz)	Empirical formula	Anal., % Calcd C, H, N Found C, H, N
3a	(78–80, 0.001 mm)		2.6–3.3 (4 H, m, aromatics), 5.55–6.10 (2 H, m, CH_2O), 7.05–7.35 (1 H, m, CH), 7.60, 7.94 (each 1 H, two d, $J = 5$ and 4, CH_2N)	C_9H_9NO	73.45, 6.16, 9.52 73.68, 6.08, 9.23
3b	(83–85, 0.1 mm)		2.6–3.3 (4 H, m, aromatics), 5.83, 6.08 (each 1 H, AB type, $J = 11$, CH_2O) 7.76 (2 H, s, CH_2N),[a] 8.65 (3 H, s, CH_3)	$C_{10}H_{11}NO$	74.51, 6.88, 8.69 74.12, 6.50, 8.89
3c	74	*n*-Pentane	2.5–3.2 (9 H, m, aromatics), 5.6–5.8 (2 H, m, CH_2O), 6.75 (1 H, d, $J = 3.5$, CH), 7.0–7.2 (1 H, m, CH)	$C_{15}H_{13}NO$	80.69, 5.87, 6.27 80.55, 5.77, 6.30
7a	52	*n*-Pentane	1.8–2.0, 2.6–2.9 (1 H and 3 H, m, aromatics), 2.40 (1 H, s, CH), 4.62 (2 H, s, CH_2O)	$C_9H_7N_3O$	62.42, 4.07, 24.27 61.92, 3.70, 24.27
7b	195	Benzene	1.8–2.0, 2.2–2.9 (1 H and 8 H, m, aromatics), 4.43 (2 H, s, CH_2O)	$C_{15}H_{11}N_3O$	72.27, 4.45, 16.86 72.24. 4.43, 16.94
8a	152	Diethyl ether	1.9–2.2, 2.5–3.0 (1 H and 3 H, m, aromatics), 4.37 (2 H, s, CH_2O)	$C_8H_6N_4O$	55.17, 3.47, 32.17 55.40, 3.56, 32.07
8b	113	Diethyl ether	1.9–2.2, 2.4–2.7 (1 H and 3 H, m, aromatics), 6.5–6.9 (4 H, m, CH_2CH_2)	$C_9H_8N_4$	62.77, 4.68, 32.54 62.89, 4.90, 32.07

[a] Splitting of this signal was observed in benzene-d_6 at 100 MHz, where two singlets appeared each counting for one proton (τ 8.05, 8.14).

volve, as the first stage, an intramolecular cycloaddition leading to the unstable triazolines **6** (see Scheme I). The in-

Scheme I



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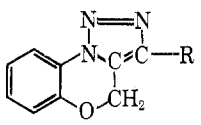
tervention of such an intermediate was deduced in the case of **1b** by carrying out the decomposition at room temperature in hexadeuteriobenzene and monitoring the reaction progress by NMR analyses; in addition to the signals of the starting azide and the final product, the spectrum showed a set of signals, which disappeared when the reaction went to completion. These signals are reasonably attributed to the triazoline **6**, R_1 = H; R_2 = Me [τ 6.43 (2 H, s, CH_2O), 6.79, 7.35 (each 1 H, AB type, J = 10.5 Hz, CH_2N), 9.20 (3 H, s, CH_3)].

The subsequent decomposition of the intermediate triazolines involves nitrogen extrusion according to one or both of the pathways shown in Scheme I. The lack of the products formed through pathway b when starting from azide **1b** is well accounted for by the lower migratory aptitude of the methyl group with respect to the hydrogen atom.[12] Instead, in the case of **1c**, the stabilizing effect of the phenyl group on the adjacent electron-deficient carbon atom may be invoked to justify the observed behavior.

Aryl Azides Bearing an Alkynyl Substituent. While the transformation of azide **1e** was complete after 3 hr refluxing in toluene, under the same conditions compound **1d** entirely disappeared after ca. 15 min. In fact the slow reaction of the latter azide even at room temperature made it impossible to purify. However, in spite of their different reactivities, both azides **1d** and **1e** gave the triazole derivative of formula **7** as the only decomposition product (see Table III for physical, analytical, and NMR data).



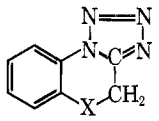
7a, R = H
b, R = Ph

Although the isolation of **7a,b** from **1d,e** is not surprising, it is noteworthy as the first example of intramolecular cycloaddition of the azido group to the acetylenic function. The greater reactivity of **1d** in comparison to **1e** is somewhat unexpected considering that the conjugated alkynes are usually better dipolarophiles than the unconjugated.[13] On the other hand, the bulky phenyl substituent may hinder the approach of the reactant groups; in this regard, phenyl azide cycloadds to methyl propiolate 50 times faster than to ethyl phenylpropiolate.[14]

Aryl Azides Bearing a Nitrile Function. Azidonitriles **1f,g** were found to be more stable compounds than the related azides **1a–e**. In fact, as shown in Table II, a higher temperature was required for their decomposition.

Starting from both **1f** and **1g**, the reaction led, apart from some untractable tar, to the tetrazole derivative **8** in satisfactory yields. Physical, analytical, and spectral data are given in Table III.

The ring closure leading to **8a,b** can reasonably be interpreted in terms of an intramolecular 1,3-dipolar cycloaddition. Actually, in intermolecular reactions, only nitrile groups activated by electron-withdrawing substituents



8a, X = O
b, X = CH_2

have been shown to behave as dipolarophiles toward azides.[15] Unactivated 4-azidobutyronitrile and 5-azidovaleronitrile gave 1,5-polymethylenetetrazoles only in the presence of an acidic catalyst.[15,16]

Clearly, in the case of **1f,g**, the mutual ortho disposition of the two interreacting groups provides a favorable stereochemical constraint to the intramolecular approach. Some activating effect by the oxygen atom could be responsible for the greater reactivity of **1f** with respect to **1g**.

Experimental Section

All melting points and boiling points are uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 377 spectrophotometer. NMR spectra were taken on a Varian A-60A instrument with Me_4Si as internal standard.

Anilines **2a**,[17] **2d**,[18] **2e**,[19] and **2f**[20] were prepared as reported.

Aniline 2b. A solution of $SnCl_2$ (17.9 g) in concentrated HCl (98 ml) was slowly added to a solution of 2-methyl-3-(2-nitrophenoxy)propene[21] (15.0 g) in acetic acid (90 ml) at 15°. Zinc powder (50.3 g) was then added portionwise under stirring and cooling. After 45 min at room temperature, the mixture was filtered and the solvent was partly removed under reduced pressure. The residue was treated with chloroform and water, then the aqueous layer was separated, made alkaline by ammonia, and extracted with chloroform. The organic solution was dried over $MgSO_4$ and evaporated and the oily residue was distilled in vacuo to give aniline **2b** in 44% yield: bp 105–110° (0.5 mm); ir (film) 3500, 3430 cm^{-1} (NH_2); NMR ($CDCl_3$) τ 3.0–3.6 (4 H, m, aromatics), 4.8–5.2 (2 H, m, CH_2=), 5.58 (2 H, s, CH_2O), 6.31 (2 H, broad s, NH_2), 8.17 (3 H, s, CH_3).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 74.02; H, 7.98; N, 8.45.

3-(2-Nitrophenoxy)-1-phenylpropene. A mixture of 2-nitrophenol (20.8 g), potassium carbonate (20.7 g), cinnamyl bromide (30.5 g), and dry acetone (200 ml) was refluxed for 6 hr. The solvent was partly removed, ether and water were then added, and the organic layer was dried on $MgSO_4$ and evaporated. The residue was taken up with a small amount of benzene and filtered to afford 3-(2-nitrophenoxy)-1-phenylpropene in 73% yield: mp 72–73° (*n*-hexane–benzene); NMR (CCl_4) τ 2.2–3.5 (10 H, m, aromatics and CH=), 3.77 (1 H, dt, J = 15 and 5 Hz, CH=), 5.30 (2 H, d, J = 5 Hz, CH_2O).

Anal. Calcd for $C_{15}H_{13}NO_3$: C, 70.58; H, 5.13; N, 5.49. Found: C, 71.00; H, 5.04; N, 5.49.

Aniline 2c. A solution of $SnCl_2$ (10.0 g) in concentrated HCl (75 ml) was slowly added to a solution of 3-(2-nitrophenoxy)-1-phenylpropene (13.5 g) in acetic acid (370 ml) at 15°. Zinc powder (37 g) was added portionwise under stirring and cooling. After 1 hr at room temperature, the mixture was filtered and the solution was adjusted to pH 5 by ammonia; then the solvent was removed in vacuo. The residue was made alkaline by ammonia and extracted several times with chloroform. The organic solution was washed with 10% NaOH, dried over $MgSO_4$, and evaporated. The residue was taken up with diisopropyl ether. Addition of *n*-hexane caused separation of aniline **2c** in 20% yield: mp 75–76°; ir (Nujol) 3550, 3430 (NH_2), 1630 cm^{-1} (C=C); NMR (CCl_4) τ 2.5–3.0 (4 H, m, C_6H_4), 3.1–3.8 (6 H, m, C_6H_5 and CH=CH), 5.38 (2 H, d, J = 5 Hz, CH_2O), 6.40 (2 H, broad s, NH_2).

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 80.15; H, 6.50; N, 6.38.

Aniline 2g. A mixture of 2-nitrocinnamonitrile[22] (11.0 g), 10% Pd/C (1.0 g), and ethanol (150 ml) was stirred under hydrogen atmosphere while cooling at 15°. When the absorption became slow (4.5 l.), the mixture was filtered and fresh catalyst was added (1.0 g). The hydrogen absorption continued until an overall amount of 6.2 l. was taken up. The catalyst was filtered off, the filtrate was concentrated, and the residue gave aniline **2g** in 69% yield: bp 128–132° (0.1 mm); ir (film) 3220 (NH_2), 2180 cm^{-1} (C≡N); NMR ($CDCl_3$) τ 2.8–3.5 (4 H, m, aromatics), 6.45 (2 H, broad s, NH_2), 7.0–7.7 (4 H, m, CH_2CH_2).

Anal. Calcd for $C_9H_{10}N_2$: C, 73.94; H, 6.90; N, 19.16. Found: C, 74.20; H, 6.99; N, 19.01.

Preparation of Azides 1. General Procedure. A solution of sodium nitrite (0.052 mol) in water (10 ml) was added dropwise to a solution of aniline **2** (0.050 mol) in 4 *N* HCl (60 ml) under vigorous stirring and ice cooling. The mixture was then neutralized by $NaHCO_3$ and a solution of sodium azide (0.050 mol) in water (35 ml) was slowly added at ca. 5°. After 30 min, the mixture was extracted with ether and the organic solution was dried over $MgSO_4$. The solvent was removed under reduced pressure and afforded practically pure azide **1**, with the exception of **1c** and **1d**, which were purified by silica gel chromatography using as eluent respectively benzene and a solution of diethyl ether–*n*-hexane (4:1). See Table I.

Decomposition of Azides 1. General Procedure. A 0.1 *M* solution of azide **1** was refluxed until all the starting material was consumed (see Table II for solvents and reaction times). The solvent was then evaporated under reduced pressure and the residue was worked up according to the procedure indicated in Table II. Physical, spectral, and analytical data of compounds **3, 7,** and **8** are collected in Table III. Compound **4**[5] gave the following NMR spectrum ($CDCl_3$): τ 2.6–3.3 (4 H, m, aromatics), 5.53 (2 H, s, CH_2), 7.90 (3 H, s, CH_3).

Catalytic Hydrogenation of Aziridine 3a. A solution of **3a** in ethanol (40 ml) was stirred under hydrogen atmosphere in the presence of Pd/C. When the theoretical amount of hydrogen was absorbed, the catalyst was filtered off and the solvent was evaporated. Distillation in vacuo of the oily residue furnished compound **5a** in 65% yield: bp 80–83° (0.4 mm) [lit.[5] bp 150–152° (24 mm)]; NMR, see ref 23.

Catalytic Hydrogenation of Aziridine 3b. Compound **5b** was obtained from **3b** according to the above procedure in 72% yield: bp 85–88° (0.4 mm); NMR ($CDCl_3$) τ 3.1–3.6 (4 H, m, aromatics), 6.20 (2 H, s, CH_2), 6.70 (1 H, broad s, NH), 8.81 (6 H, s, two CH_3).

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.65; H, 7.95; N, 8.37.

Catalytic Hydrogenation of Aziridine 3c. The above procedure, when starting from **3c** (0.2 g), led to **5c** in 67% yield: mp 63° (*n*-pentane); NMR ($CDCl_3$) τ 2.5–3.6 (9 H, m, aromatics), 5.6–6.5 (4 H, m, OCH_2CH and NH), 7.1–7.4 (2 H, m, CH_2).

Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.60; H, 6.58; N, 6.05.

Reduction of 4. A solution of ketimine **4** (0.155 g) in anhydrous THF (10 ml) was added under stirring to a suspension of $LiAlH_4$ (0.4 g) in THF (50 ml). After 5 hr refluxing, the excess of $LiAlH_4$ was decomposed by ethyl acetate, water was added, and the mixture was extracted several times with ether. The organic solution was dried over Na_2SO_4 and evaporated. The residue was distilled in vacuo to afford **5a** in 65% yield.

Registry No.—**1a,** 55000-07-2; **1b,** 55000-08-3; **1c,** 55000-09-4; **1d,** 55000-10-7; **1e,** 55000-11-8; **1f,** 55000-12-9; **1g,** 55000-13-0; **2a,** 27096-64-6; **2b,** 55000-14-1; **2c,** 55000-15-2; **2d,** 52536-39-7; **2e,** 52536-40-0; **2f,** 31507-29-6; **2g,** 55000-16-3; **3a,** 55000-17-4; **3b,** 55000-18-5; **3c,** 55000-19-6; **4,** 55000-20-9; **5a,** 32329-20-7; **5b,** 55000-21-0; **5c,** 55000-22-1; **6** (R_1 = H; R_2 = Me), 55012-68-5; **7a,** 235-23-4; **7b,** 55000-23-2; **8a,** 55000-24-3; **8b,** 35213-60-6; 2-methyl-3-(2-nitrophenoxy)propene, 13414-54-5; 2-nitrophenol, 88-75-5; cinnamyl bromide, 4392-24-9; 3-(2-nitrophenoxy)-1-phenylpropene, 55000-25-4; 2-nitrocinnamonitrile, 55000-26-5.

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Synthesis of 3,4-Dihydro-1*H*-1,3,4-benzotriazepine-2,5-diones

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Two new routes to the title compounds have been developed. 3,4-Dihydro-3-methyl-1*H*-1,3,4-benzotriazepine-2,5-dione (**3**) was prepared by treating 2-carboalkoxyphenyl isocyanate (**1**) with methylhydrazine and cyclizing the semicarbazide ester (**2**) with base. The 4-methyl isomer of **3** (**7a**) was prepared by treating 2-isocyanatobenzoyl chloride (**6a**) with methylhydrazine. Two reports which disclose syntheses of extensive numbers of 3,4-dihydro-1*H*-1,3,4-benzotriazepine-2,5-diones are shown to be in error. These routes lead, instead, to 3-amino-2,4(1*H*,3*H*)-quinazolinediones.

In the past several years much research effort has been expended on the preparation of benzodiazepines for evaluation as potential psychotherapeutic agents. All six classes are known, and their chemistry and pharmacology have been studied extensively.[1]

Pharmaceutical interest in the benzotriazepines has evolved from the benzodiazepines. Of the six possible classes[2] of benzotriazepines, only three have been studied to date. No representatives of the benzo-1,2,3-, 1,2,4-, or 2,3,4-triazepine classes are known. Benzo-1,3,4-triazepines[3] and benzo-1,2,5-triazepines[4] are well documented in the literature. Benzo-1,3,5-triazepines[5] are documented in a few instances.

This report deals specifically with 3,4-dihydro-1*H*-1,3,4-benzotriazepine-2,5-diones. We have developed new, unequivocal entries into this class of compound which allow us to critically examine the few reported entries, and the compounds which have been made by these routes and assigned as 3,4-dihydro-1*H*-1,3,4-benzotriazepine-2,5-diones.

Treatment of 2-carboalkoxyphenyl isocyanates **1a** and