Thermally Induced Fragmentation and Cyclisation of *C*-Azidohydrazones

Luca Bruché, Luisa Garanti* and Gaetano Zecchi

Dipartimento di Chimica Organica e Industriale dell'Università, Centro C.N.R. sulla Sintesi e Stereochimica di Speciali Sistemi Organici, Via Golgi, 19, 20133 Milano, Italy

Received September 16, 1988

C-Azidohydrazones **2** were synthesized from the corresponding *C*-chlorohydrazones **1** and submitted to thermal decomposition in boiling benzene. Various kinds of products were obtained due to competitive modes of evolution of first-formed nitrenes **13**, namely hydrogen abstraction to form aminohydrazones **3** and benzotriazepine **8**, and radical fragmentation to give ultimatively diaryls **4** and arylglyoxylate arylhydrazones **5**. Ring-closed products, namely 1,2,4-triazoles **6** and imidazolones **7** were also formed.

J. Heterocyclic Chem., **26**, 619 (1989).

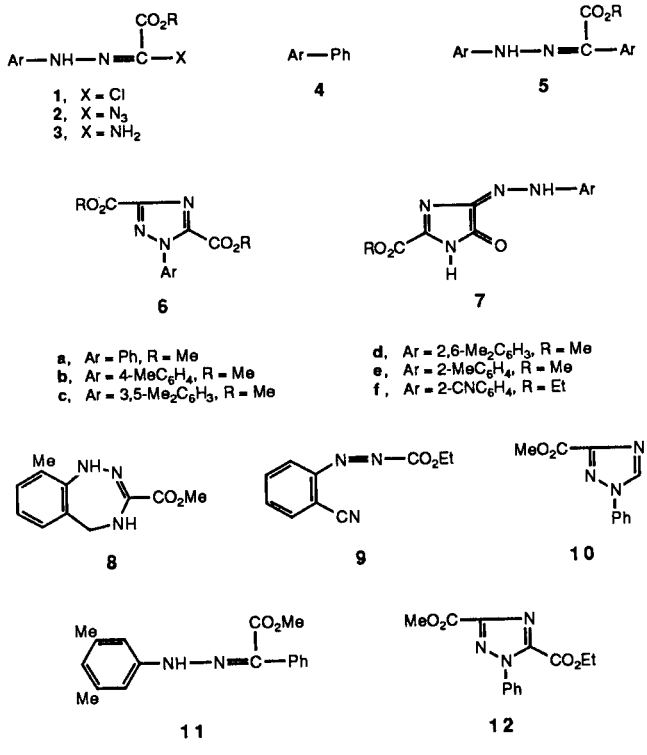
Organic azides are useful intermediates in view of their ability to undergo 1,3-dipolar cycloadditions as well as to behave as a source of nitrenes [1,2]. However, little is known about *C*-azidohydrazones, in which the additional presence of the hydrazone moiety can be thought to open new mechanistic and synthetic possibilities [3]. Thus, we turned our attention to the thermally induced behaviour of this class of azido compounds.

Results.

The azidohydrazones under study **2a-f** were readily accessible by nucleophilic substitution of the corresponding chlorohydrazones **1a-f** with sodium azide under phase-transfer conditions (see Table 1). Their decomposition was carried out in boiling benzene and led to complex mixtures whose chromatographic separation provided the products indicated in Table 2. While the known compounds were identified by comparison with authentic samples, the new structures were assigned on the basis of analytical and spectral data (see Table 3). Furthermore, the aminohydrazones **3c-f** were synthesized independently by treatment of the corresponding chlorohydrazones **1c-f** with ammonia. For imidazolones **7d,e**, the observed ir frequency of the endocyclic carbonyl group is lower than the reported values for similar compounds [4-6]; this can be ascribed to an intramolecular hydrogen bond involving the hydrazone moiety, as really evidenced on submitting **7d** to X-ray diffraction study [7].

The solvent effect on the product distribution was explored for one substrate. When azidohydrazone **2a** was decomposed in boiling dioxane, biphenyl **4a** was not found among the products while small amounts of methyl phenylglyoxylate and of triazole **10** [8] were isolated. In boiling ethanol, the decomposition of **2a** gave the aminohydrazone **3a** in substantial yield.

Aminohydrazones **3** were shown to be thermally stable; however, they tended to disappear in the presence of azidohydrazones **2**. This fact suggested the idea of a cross experiment to gain mechanistic informations. Thus, heating



equimolar amounts of azidohydrazone **2c** and aminohydrazone **3a** in boiling benzene gave, in addition to the products already obtained from the thermolysis of **2c**, compounds **4a**, **6a**, and **11**, the formation of which demonstrates that a reaction involving the aminohydrazone **3a** has occurred. The new structure **11** was proven by way of an independent synthesis from methyl phenylglyoxylate and 3,5-dimethylphenylhydrazine. At this stage of our investigation, we devised the opportunity of submitting aminohydrazone **3c** to oxidation with manganese dioxide, a reagent known to convert hydrazines into azo derivatives [9] and *N*-aryl-*C*-arylaminohydrazones into 1,4-diaryl-1,2,4-triaza-1,3-dienes [10]. Actually, the treatment of **3c** with manganese dioxide in benzene at room temperature resulted in a mixture containing diaryl **4c** and triazole **6c**,

Scheme

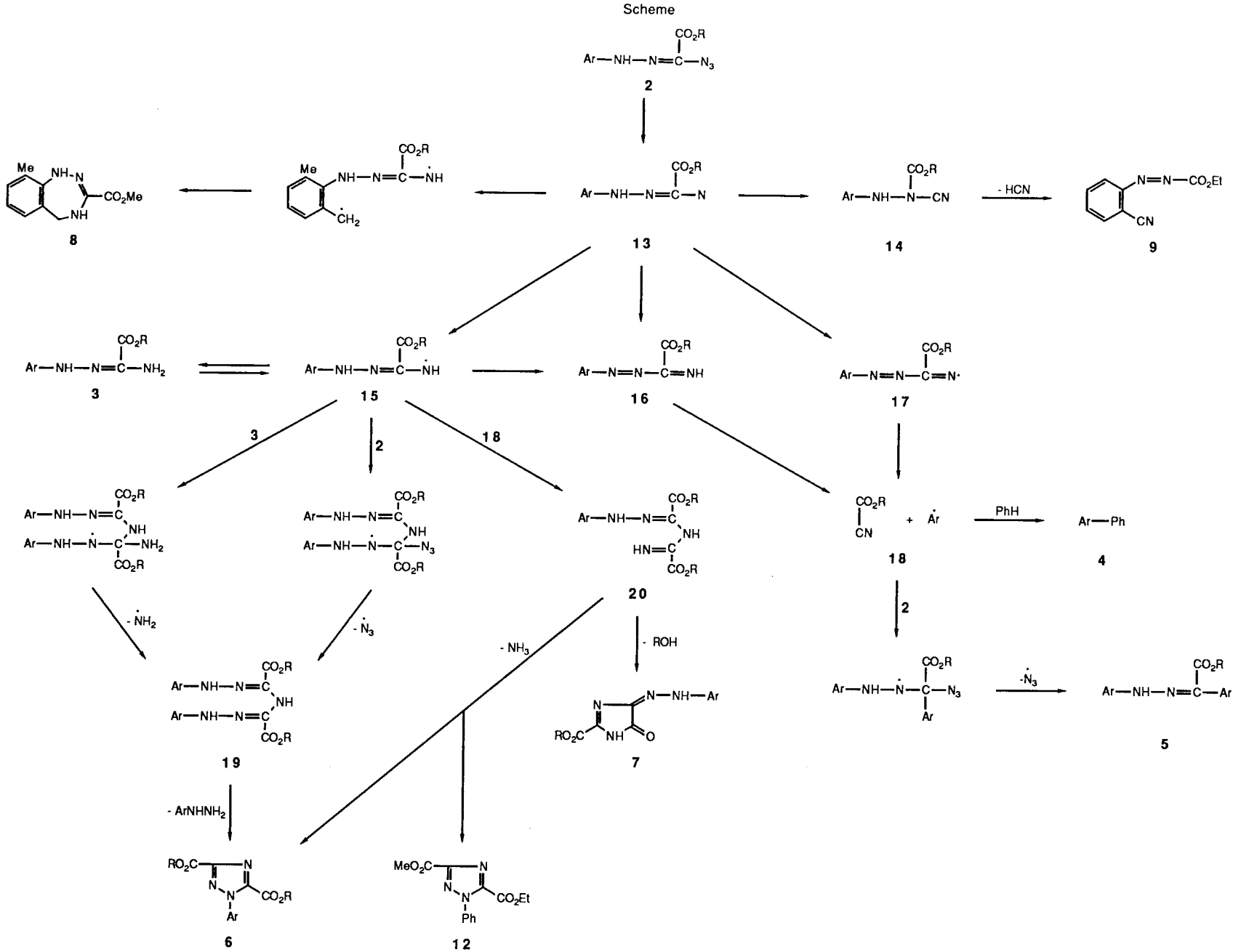

2
8
13
14
9
3
15
16
17
18
20
19
7
6
12
4
5
- HCN
PhH
- NH2
- N3
- NH3
- ROH
- ArNHNH2

Table 1

Preparation and Characterization of Azidohydrazones **2** [a] [b]

Compound	Time (hours)	Yield %	Mp °C	IR (Nujol), cm^{-1}	NMR, δ
2b	4	54	87-88	3270 2125 1690	2.32 (s, 3H), 3.95 (s, 3H), 7.10 (s, 4H), 8.2 (br s, 1H)
2c	4	52	73-74	3320 2135 1700	2.27 (s, 6H), 3.88 (s, 3H), 6.4-6.8 (m, 3H), 8.0 (br s, 1H)
2d	4	51	83-84	3330 2130 1695	2.36 (s, 6H), 3.90 (s, 3H), 6.95 (s, 3H), 7.9 (br s, 1H)
2e	4	45	77-78	3330 2125 1695	2.30 (s, 3H), 3.98 (s, 3H), 6.7-7.5 (m, 4H), 8.1 (br s, 1H)
2f	0.5	82	103-104	3320 2210 2150 1700	1.43 (t, 3H), 4.40 (q, 2H), 6.8-7.1 (m, 1H), 7.35-7.75 (m, 3H), 8.6 (br s, 1H)

[a] For **2a** see reference [3]. [b] Thermal lability precluded the obtainment of analytically pure samples.

but not arylglyoxylate arylhydrazone **5c**.

As an effort to shed light on the route leading to the triazole products, further experiments were carried out, thus ascertaining the following points: (i) the thermolysis of azidohydrazone **2a** in the presence of ethyl cyanoformate gave the mixed ester **12** as an additional product, without suppressing however the formation of the dimethyl ester **6a**; (ii) when treating aminohydrazone **3a** with an excess of ethyl cyanoformate in boiling benzene, no reaction was practically observed within 8 hours; (iii) the treatment of **3a** with ethyl cyanoformate in the presence of azobis-isobutyronitrile resulted after 5 hours in a mixture containing diphenyl **4a**, the dimethyl ester **6a**, and the mixed ester **12**; in spite of the excess of ethyl cyanoformate, compound **6a** was still predominant with respect to **12**.

Table 2

Thermal Decomposition of Azidohydrazones **2** [a]

Compound	Products (% yield)						
	3	**4**	**5**	**6**	**7**	**8**	**9**
2a	15 [b]	22 [c]	13 [d]	6	—	—	—
2b	13	21 [e]	17	7	—	—	—
2c	9	24 [f]	11	6	—	—	—
2d	8	—	—	16	10	4	—
2e	5	18 [g]	2	20	6	—	—
2f	8	22 [h]	—	17	—	—	6

[a] In boiling benzene (4 hours). [b] Reference [5]. [c] Reference [22]. [d] Reference [25]. [e] Reference [26]. [f] Reference [23]. [g] Reference [27]. [h] Reference [28].

Discussion.

The above findings indicate the occurrence of a complex set of parallel-consecutive reactions, which are illustrated in the Scheme. The starting azides **2** undergo thermally induced loss of nitrogen to generate the peculiar nitrenes **13**, for which a biradical resonance form can be conceived possibly determining a low-energy triplet state. These nitrenes evolve to the corresponding primary amines **3** upon hydrogen abstraction from the environment. In the case of azidohydrazone **2d**, intramolecular hydrogen abstraction from the neighbouring methyl group and subsequent radical recombination lead to the benzotriazepine **8**. Both inter- and intra-molecular examples of hydrogen abstraction by nitrenes are amply documented [11-13]. However, the nitrene species **13** can also follow a fragmentation pathway, presumably *via* the tautomeric azo-form **16** and/or the corresponding iminyl radical **17**, to originate an aryl radical along with alkyl cyanoformate **18**. Fragmentation of azoarenes to aryl radicals [14] as well as of iminyl radicals to nitriles [15] has precedent in the literature. Capture of Ar· by the solvent (benzene) constitutes an obvious route to diaryls **4**, while its reaction with the carbon-nitrogen double bond of **2** represents a possible pathway to arylglyoxylate arylhydrazones **5**.

Both triazoles **6** and imidazolones **7** can be thought to derive from the same open-chain precursors **20** through two competitive cyclisation processes, the relative extent of which is plausibly the consequence of steric factors. The species **20** may in turn be formed by reaction of the aminohydrazones **3** with alkyl cyanoformate *via* the nitrogen ra-

Table 3

Physical, Spectral and Analytical Data of New Compounds [a]

Compound	Mp [b] °C	IR (Nujol), cm^{-1}	NMR, δ	Analyses % Calcd./Found		
				C	H	N
3b	131	3470 3340 1720	2.31 (s, 3H), 3.92 (s, 3H), 4.4 (br s, 2H), 6.5 (br s, 1H), 6.8-7.2 (m, 4H)	57.96 58.08	6.32 6.21	20.28 20.16
3c	129-130	3475 3310 1725	2.30 (s, 6H), 3.93 (s, 3H), 4.5 (br s, 2H), 6.55 (s, 1H), 6.65 (br s, 1H), 6.75 (s, 2H)	59.71 59.82	6.83 6.77	18.99 19.05
3d	127	3460 3370 1735	2.31 (s, 6H), 3.88 (s, 3H), 4.8 (br s, 2H), 6.9-7.1 (overlapping, 4H)	59.71 59.64	6.83 6.89	18.99 18.87
3e	115	3440 3310 1720	2.25 (s, 3H), 3.92 (s, 3H), 4.4 (br s, 2H), 6.4 (br s, 1H), 6.7-7.6 (m, 4H)	57.96 57.79	6.32 6.35	20.28 20.40
3f	138	3415 3330 2220 1710	1.42 (t, 3H), 4.38 (q, 2H), 5.1 (br s, 2H), 6.7-7.0 (m, 1H), 7.1-7.7 (overlapping, 4H)	55.04 54.95	4.62 4.71	25.68 25.81
5b	70-71 [c]	3230 1665	2.33 (s, 3H), 2.41 (s, 3H), 3.89 (s, 3H), 7.0-7.7 (m, 8H), 12.3 (br s, 1H)	72.32 72.38	6.43 6.36	9.92 10.01
5c	120	3230 1675	2.31 (s, 6H), 2.38 (s, 6H), 3.88 (s, 3H), 6.62 (s, 1H), 6.87 (s, 2H), 6.97 (s, 1H), 7.20 (s, 2H), 12.3 (br s, 1H)	73.52 73.41	7.14 7.06	9.03 9.15
5e	107	3230 1670	2.28 (s, 3H), 2.35 (s, 3H), 3.75 (s, 3H), 6.8-7.65 (m, 8H), 12.55 (br s, 1H)	72.32 72.50	6.43 6.41	9.92 9.83
6a	138	1745	3.97 (s, 3H), 4.08 (s, 3H), 7.54 (s, 5H)	55.17 55.10	4.24 4.41	16.09 15.97
6b	163-164	1730	2.47 (s, 3H), 3.97 (s, 3H), 4.06 (s, 3H), 7.33 (s, 4H)	56.72 56.78	4.76 4.72	15.27 15.41
6c	181	1735	2.40 (s, 6H), 3.97 (s, 3H), 4.07 (s, 3H), 7.07 (s, 2H), 7.15 (s, 1H)	58.12 58.21	5.23 5.14	14.53 14.38
6d	135	1750 1735	2.00 (s, 6H), 3.90 (s, 3H), 4.05 (s, 3H), 7.0-7.4 (m, 4H)	58.12 58.03	5.23 5.32	14.53 14.44
6e	110	1740	2.11 (s, 3H), 3.95 (s, 3H), 4.09 (s, 3H), 7.1-7.6 (m, 4H)	56.72 56.90	4.76 4.73	15.27 15.35
6f	123-124	2220 1735	1.51 (t, 3H), 1.40 (t, 3H), 4.54 (q, 2H), 4.44 (q, 2H), 7.4-7.9 (m, 4H)	57.32 57.41	4.49 4.38	17.83 17.80
7d	204 [d]	1730 1670	2.55 (s, 6H), 4.05 (s, 3H), 7.0-7.2 (m, 3H)	56.93 56.84	5.15 5.17	20.43 20.52
7e	216 [d]	1730 1670	2.40 (s, 3H), 4.00 (s, 3H), 7.1-7.9 (m, 4H)	55.38 55.31	4.65 4.76	21.53 21.39
8	120-121	3350 1710	2.20 (s, 3H), 3.80 (s, 3H), 4.32 (d, J = 3, s after deuteration, 2H), 5.7 (br s, 1H, exchangeable), 6.5-7.1 (overlapped, 4H)	60.82 60.69	5.10 5.14	19.35 19.43
9	62-65 [c]	2220 1745	1.53 (t, 3H), 4.57 (q, 2H), 7.5-8.0 (m, 4H)	59.10 59.21	4.46 4.43	20.68 20.72
11	93	3250 1680	2.35 (s, 6H), 3.90 (s, 3H), 6.66 (s, 1H), 6.92 (s, 2H), 7.2-7.7 (m, 5H), 12.3 (br s, 1H)	72.32 72.25	6.43 6.51	9.92 9.96
12	86	1740	1.26 (t, 3H), 3.97 (s, 3H), 4.30 (q, 2H), 7.42 (s, 5H)	56.72 56.68	4.76 4.84	15.27 15.41

[a] All compounds listed gave correct molecular peaks in the mass spectra. [b] From diisopropyl ether unless otherwise stated. [c] From pentane-diethyl ether. [d] From diisopropyl ether-chloroform.

dical **15**, the intervention of which is consistent with the fact that such a reaction requires a radical source such as azobis-isobutyronitrile. However, it is to be noted that, in the treatment of aminohydrazone **3a** with ethyl cyanoformate as well as in the thermolysis of azidohydrazone **2a** in the presence of ethyl cyanoformate, the formation of the mixed ester **12** did not exceed that of the dimethyl ester **6a**. This means that other species, namely **3** and perhaps **2**, are capable of intercepting the nitrogen-radical **15** to give the intermediate **19** evolving to the final triazole **6**.

The role of aminohydrazones **3** deserves further comment. In a poor hydrogen-donating solvent such as benzene, it seems plausible that nitrenes **13** may abstract hydrogen atoms from **3**, *i.e.* that the pathway going from **15** of **3** may be reversible. Two facts speak in favour of this view: (i) the decomposition of azidohydrazone **2a** in a good hydrogen-donating solvent such as ethanol enhances the yield of aminohydrazone **3a** at the expense of the fragmentation products; (ii) the reaction of aminohydrazone **3c** with manganese dioxide (where **15** and **16** are acceptable intermediates) [9,10,13] just produces **4c** and **6c**. The proposed oxidation-reduction process between nitrenes **13** and aminohydrazones **3** accounts well for the formation of the crossed products **4a**, **6a**, and **11** when doing the thermolysis of **2c** in the presence of **3a**. As a tentative explanation for the obtainment of **9**, we suggest the intermediacy of the species **14**, whose formation would parallel that of nitriles *via* 1,2-shift of the α-substituent in vinyl nitrenes [16].

Finally, it is to be noted that compounds **2** did not undergo 1,5-cyclisation to tetrazoles, which has been shown to constitute a thermally induced reaction of *N,N*-disubstituted *C*-aryl-*C*-azidohydrazones [17].

EXPERIMENTAL

Melting points were determined on a Büchi apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 298 spectrophotometer. The nmr spectra were recorded in deuteriochloroform on a Varian EM-390 instrument (90 MHz); chemical shifts are given in δ from tetramethylsilane as the internal standard (J in Hz). Silica gel used for chromatography was Merck Kieselgel 60 (70-230 mesh ASTM).

Chlorohydrazones **1a** [18], **1b** [19] and **1e** [20] are known in the literature.

Preparation of Chlorohydrazones **1c,d,f**.

A solution of sodium nitrite (72 mmoles) and 3,5-dimethylaniline (72 mmoles) in 50% aqueous methanol (70 ml) was added dropwise to 10% aqueous hydrochloric acid (75 ml) with vigorous stirring and ice cooling. The mixture was adjusted to *p*H 4 with sodium acetate, then a solution of methyl 2-chloroacetoacetate (72 mmoles) in methanol (60 ml) was added dropwise. The resulting mixture was stirred at room temperature for 30 minutes, then was left standing overnight. The solvent was partly removed under reduced pressure and the residue was extracted with diethyl ether. The organic layer was washed with water, dried (sodium sulfate) and evaporated under reduced pressure. The residue was chromatographed on a silica gel column (400 g) with chloroform as eluant to give the chlorohydrazone **1c** (87%), mp 135° (from diisopropyl ether); ir (Nujol): 3245, 1710 cm^{-1}; ^1H nmr: δ 2.35 (s, 6H), 3.97 (s, 3H), 6.68 (s, 1H), 6.83 (m, 2H), 8.3 (br s, 1H).

Anal. Calcd. for $C_{11}H_{13}ClN_2O_2$: C, 54.87; H, 5.45; N, 11.63. Found: C, 55.01; H, 5.48; N, 11.52.

Following the same procedure, 2,6-dimethylaniline was converted into the chlorohydrazone **1d** (33%), mp 59-60° (from diisopropyl ether); ir (Nujol): 3245, 1710 cm^{-1}; ^1H nmr: δ 2.40 (s, 6H), 3.93 (s, 3H), 7.03 (s, 3H), 8.0 (br s, 1H).

Anal. Calcd. for $C_{11}H_{13}ClN_2O_2$: C, 54.87; H, 5.45; N, 11.63. Found: C, 54.75; H, 5.53; N, 11.71.

The same reaction procedure, on using 2-aminobenzonitrile and ethyl 2-chloroacetoacetate, afforded the chlorohydrazone **1f** (69%), mp 94° (from light petroleum-diethyl ether); ir (Nujol): 3300, 2220, 1720 cm^{-1}; ^1H nmr: δ 1.45 (t, 3H), 4.38 (q, 2H), 6.9-7.7 (m, 4H), 8.85 (br s, 1H).

Anal. Calcd. for $C_{11}H_{10}ClN_3O_2$: C, 52.48; H, 4.01; N, 16.69. Found: C, 52.41; H, 4.13; N, 16.78.

Preparation of Alkyl 2-(Arylhydrazono)-2-azidoacetates **2**.

A solution of compound **1** (8 mmoles) in benzene (60 ml) was treated with a solution of sodium azide (80 mmoles) and hexadecyltributylphosphonium bromide (0.4 mmole) in water (60 ml). The mixture was heated at 35° and stirred vigorously in the dark for the time indicated in Table 1. The aqueous layer was removed and the organic solution was washed with water and dried (sodium sulfate). After evaporation of the solvent under reduced pressure, diisopropyl ether was added and the crystalline product was collected by filtration, see Table 1.

Thermal Decomposition of Azidohydrazones **2**.

A solution of compound **2** (10 mmoles) in benzene (130 ml) was refluxed for 4 hours. The solvent was removed under reduced pressure and the residue chromatographed on a silica gel column. Elution with chloroform, followed by diethyl ether, afforded the products indicated in Table 2.

Preparation of Alkyl 2-Amino-2-(arylhydrazono)acetates **3c-f**.

A solution of chlorohydrazones **1c-f** (30 mmoles) in ethanol (200 ml) was cooled at −78°, then gaseous ammonia was bubbled under stirring for 1 hour. After 2 hours the solvent was evaporated under reduced pressure, benzene was added and ammonium chloride was eliminated by filtration. After removal of the solvent under reduced pressure, recrystallization of the residue from diisopropyl ether afforded aminohydrazones **3c-f** in yields ranging from 35 to 40%.

Thermal Decomposition of Azidohydrazone **2a** in Dioxane.

A solution of compound **2a** (2.85 g) in dioxane (100 ml) was refluxed for 2 hours. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column with dichloromethane as eluant to afford, in order of elution, the following products: **5a** (2%), methyl phenylglyoxylate [21] (2%), **3a** [5] (23%), **6a** (11%) and **10** [8] (5%).

Thermal Decomposition of Azidohydrazone **2a** in Ethanol.

A solution of compound **2a** (0.50 g) in ethanol (100 ml) was re-

fluxed for 3 hours. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column with diethyl ether-light petroleum (2:1) as eluant to afford aminohydrazone **3a** (0.23 g).

Thermal Decomposition of Azidohydrazone **2c** in the Presence of Aminohydrazone **3a**.

A solution of compounds **2c** (7 mmoles) and **3a** (7 mmoles) in benzene (60 ml) was refluxed for 5 hours. After removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column. Elution with dichloromethane, followed by diethyl ether, afforded the following products, in order of elution: **4a** [22] (4%), **4c** [23] (8%), **5c** (4%), **11** (2%), **3a** (30%), **3c** (17%), **6c** (5%), and **6a** (12%).

Preparation of Methyl 2-(3,5-Dimethylphenylhydrazono)-2-phenylacetate **11**.

A solution of methyl phenylglyoxylate [21] (5.8 mmoles) in ethanol (10 ml) was added dropwise with vigorous stirring to a solution of 3,5-dimethylhydrazine hydrochloride [24] (5.8 mmoles) and sodium acetate (17 mmoles) in water (10 ml). The mixture was refluxed for 1 hour, then the precipitate was filtered off, affording the title compound **11**, in 92% yield.

Oxidation of Aminohydrazone **3c** with Manganese Dioxide.

To a solution of compound **3c** (5 mmoles) in benzene (50 ml) was added manganese dioxide (5 mmoles). The mixture was stirred at room temperature for 4 hours, then the undissolved material was eliminated by filtration over celite. After evaporation of the solvent under reduced pressure, the residue was chromatographed on a silica gel column. Elution with dichloromethane, followed by diethyl ether, afforded compounds **4c** (9%) and **6c** (21%).

Thermal Decomposition of Azidohydrazone **2a** in the Presence of Ethyl Cyanoformate.

A solution of compound **2a** (7 mmoles) and ethyl cyanoformate (7 mmoles) in benzene (60 ml) was refluxed for 1.5 hours. After evaporation of the solvent under reduced pressure, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (2:1) as eluant, affording the following products in order of elution: **4a** (36%), **12** (5%), and **6a** (11%).

Reaction of Aminohydrazone **3a** with Ethyl Cyanoformate.

A solution of compound **3a** (1 mmole), ethyl cyanoformate (5 mmoles), and 2,2'-azobis(2-methylpropionitrile) (1 mmole) in benzene (30 ml) was refluxed for 5 hours. After evaporation of the solvent under reduced pressure, the residue was chromatgraphed on a silica gel column. Elution with dichloromethane, followed by diethyl ether, afforded compounds **4a** (11%), **12** (12%), and **6a** (24%).

Acknowledgement.

The authors thank Professor A. Citterio for helpful discussions.

REFERENCES AND NOTES

[1] "The Chemistry of the Azido Group," S. Patai, ed, Interscience, London, 1971.

[2] "Azides and Nitrenes", E. F. V. Scriven, ed, Academic Press, London, 1984.

[3] L. Bruché, L. Garanti and G. Zecchi, *J. Chem. Soc., Perkin Trans. 1*, 1472 (1984); *ibid.*, 1903 (1985).

[4] S. K. Gupta, *J. Org. Chem.*, **43**, 4663 (1978).

[5] F. Anzani, P. Dalla Croce and R. Stradi, *J. Heterocyclic Chem.*, **17**, 311 (1980).

[6] A. Afifi, M. A. El-Hashash and S. S. El-Kady, *Rev. Roum. Chim.*, **28**, 849 (1983).

[7] T. Pilati, unpublished work.

[8] K. Matsumoto, M. Suzuki, M. Tomie, N. Yoneda and M. Miyoshi, *Synthesis*, 609 (1975).

[9] A. J. Fatiadi, *Syntheis*, 133 (1976).

[10] R. Fusco and F. Sannicolò, *Tetrahedron Letters*, **23**, 1829 (1982); R. Fusco, A. Marchesini and F. Sannicolò, *J. Heterocyclic Chem.*, **23**, 1795 (1986).

[11] Ref [1], pp 265, 284 and 339.

[12] Ref [2], pp 58 and 115.

[13] J. M. Lindley, I. M. McRobbie, O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 982 (1980).

[14] "Free Radical Reactions", W. A. Waters, ed, Butterworth, London, 1973, p 150.

[15] W. J. Middleton, *J. Am. Chem. Soc.*, **93**, 423 (1971).

[16] A. Hassner, N. H. Wiegand and H. E. Gottlieb, *J. Org. Chem.*, **51**, 3176 (1986), and reference cited therein.

[17] S. Ito, Y. Tanaka and A. Kakehi, *Bull. Chem. Soc. Japan*, **57**, 539 (1984).

[18] R. Fusco and R. Romani, *Gazz. Chim. Ital.*, **76**, 419 (1946).

[19] H. Ehrhardt, G. Heubach and H. Mildenberger, *Ann. Chem.*, 994 (1982).

[20] M. T. Cocco, A. Maccioni and A. Plumitallo, *Farmaco, Ed. Sci.*, **40**, 272 (1985).

[21] E. P. Kohler and B. B. Corson, *J. Am. Chem. Soc.*, **45**, 1975 (1923).

[22] W. C. Weaver, *et al.*, in Kirk-Othmer "Encyclopedia of Chemical Technology", Vol 7, 3rd Ed, Wiley-Interscience, New York, 1979, p 782.

[23] P. B. Baker and B. C. Saunders, *Tetrahedron*, **30**, 3303 (1974).

[24] K. H. Snyder, H. R. Beilfuss and J. K. Williams, *J. Am. Chem. Soc.*, **75**, 1873 (1953).

[25] H. Neunhoffer, *Ann. Chem.*, 38 (1969).

[26] I. R. Sherwood, W. F. Short and R. Stansfield, *J. Chem. Soc.*, 1832 (1932).

[27] P. Jacobson and A. W. Nanninga, *Chem. Ber.*, **28**, 2548 (1895).

[28] E. B. Pedersen and S.-O. Lawesson, *Tetrahedron*, **29**, 4205 (1973).