

## Photochemical and Thermal Reactions of Heterocycles. Part I. Photolysis, Thermolysis, and Mass Spectral Fragmentation of Mesoionic 1,2,4-Triazol-3-ones

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Photolysis of the mesoionic 1,2,4-triazol-3-ones (7a—d) gave the corresponding benzimidazoles, azobenzenes, and aryl isocyanates. A mechanism is postulated which involves consecutive valence isomerisations of the triazolone (7) to give the bicyclic intermediate (14) and then the isomeric triazolone (15), followed by fragmentation. An oxidative cyclisation involving the phenyl substituents occurred on irradiation of the triphenyl-triazolone (7e). Pyrolysis of the triaryltriazolones (7e and f) gave the corresponding *N*-(diarylmethylene)anilines (18) by N → C migration of the *N* (1)-substituent. These results are compared with the high resolution mass spectra of the triazolones (7a—e).

ALTHOUGH the preparation and properties of mesoionic compounds have been extensively investigated,<sup>1</sup> their photochemical behaviour was practically unknown when our study was initiated.<sup>2,3</sup> Krauch *et al.*<sup>4</sup> have isolated the oxadiazolone (5a) from the complex mixture produced by photolysis of 3-phenylsydnone (1a), and rationalised

its formation in terms of a route involving the bicyclic intermediate (2), its fragmentation to the diazirine (3), and the recombination of carbon dioxide with (3) or its open-chain isomer (4).

We thought that other mesoionic systems might photoisomerise to a bicyclic system such as (2), since a disrotatory cyclisation at the ring positions which are active

<sup>1</sup> M. Ohta and H. Kato, 'Nonbenzenoid Aromatics,' ed. J. P. Snyder, Academic Press, New York, 1969, vol. 1, p. 117.

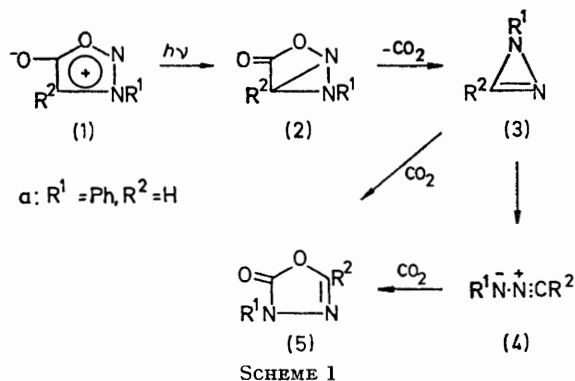
<sup>2</sup> (a) H. Kato, K. Kawamura, T. Shiba, and M. Ohta, *Chem. Comm.*, 1970, 959; (b) H. Kato, T. Shiba, H. Yoshida, and S. Fujimori, *ibid.*, p. 1591.

<sup>3</sup> Preliminary report, H. Kato, T. Shiba, and Y. Miki, *J.C.S. Chem. Comm.*, 1972, 498.

<sup>4</sup> C. H. Krauch, J. Kuhls, and H.-J. Piek, *Tetrahedron Letters*, 1966, 4043.

for 1,3-dipolar cycloaddition should be photochemically allowed. Fragmentation of the bicyclic intermediates derived from five-membered mesoionic compounds should give fully conjugated antiaromatic systems such as (3).<sup>5</sup> Related open-chain 1,3-dipolar species are often considered as intermediates in the photofragmentation of many heterocyclic systems, and the possibilities of interconversion amongst two or more 1,3-dipolar species *via* such 4 $\pi$ -antiaromatic intermediates or transition states should be borne in mind.<sup>6</sup> Hence, we thought it worthwhile to investigate systematically the photochemical behaviour of five-membered mesoionic systems. We report here the photochemical reactions of the mesoionic 1,2,4-triazol-3-ones (7) as well as their fragmentation by thermolysis and by electron impact.

**Preparation of the Triazolones.**—The 5-unsubstituted triazolones (7a–c) were prepared by thermal ring closure of 1,4-diaryl-1-formylsemicarbazides (6a–c).<sup>7</sup> The *p*-tolyl derivatives (7b and c) have been prepared independently by Smith *et al.*<sup>8</sup> The cycloaddition–extrusion reaction of 3-phenylsydnone (1a) with an excess of phenyl isocyanate at 120–140 °C also gave the triazolone (7a).<sup>9</sup>



but when the two compounds were boiled together, 3,5,7-triphenyl-1,3,5,7-tetra-azabicyclo[2.2.1]heptane-2,5-dione (8) was formed. The adduct (8) was also formed by the reaction of the triazolone (7a) with phenyl isocyanate. The identification of the adduct (8) is based on its i.r. spectrum (no NH; one carbonyl band at 1745 cm<sup>-1</sup>) and its dissociation into the triazolone (7a) by pyrolysis. Such adducts of a heterocumulene with a mesoionic compound have been isolated occasionally.<sup>10</sup>

The corresponding 5-methyltriazolone (7d) was prepared by heating the acetylsemicarbazide (6d) in *t*-pentyl alcohol in the presence of sodium *t*-pentyl oxide with azeotropic removal of the water formed. Attempts to cyclise compound (6d) by pyrolysis or by conventional treatment with an alkoxide<sup>11</sup> were not successful. The 1,5-diphenyl-4-*p*-tolyl derivative (7f) was prepared by base-catalysed cyclisation of the semicarbazide (6f).

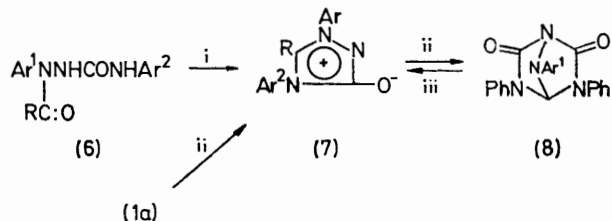
<sup>5</sup> Review, H. Kato, *Yuki Gosei Kagaku Kyokai-Shi (J. Synthetic Org. Chem., Japan)*, 1971, **29**, 146.

<sup>6</sup> J. H. Boyer, 'Mechanism of Molecular Migrations,' ed. B. S. Thyagarajan, Interscience, New York, 1969, vol. 2, p. 267.

<sup>7</sup> M. Busch, *J. prakt. Chem.*, 1903, **67**, 201.

<sup>8</sup> R. H. Smith, J. L. Deutsch, P. A. Almeter, D. S. Johnson, and S. M. Roblyer, *J. Heterocyclic Chem.*, 1970, **7**, 671.

**Photolysis.**—Irradiation of the 1,4-diphenyltriazolone (7a) in dichloromethane containing methanol with a high-pressure mercury lamp through a Pyrex filter gave benzimidazole (9a) (18%), azobenzene (10a) (4%), and methyl



a; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R = H

b; Ar<sup>1</sup> = Ph, Ar<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>, R = H

c; Ar<sup>1</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>, Ar<sup>2</sup> = Ph, R = H

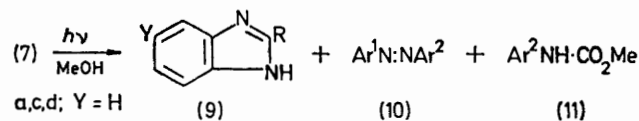
d; Ar<sup>1</sup> = Ar<sup>2</sup> = Ph, R = Me

e; Ar<sup>1</sup> = Ar<sup>2</sup> = R = Ph

f; Ar<sup>1</sup> = R = Ph, Ar<sup>2</sup> = *p*-MeC<sub>6</sub>H<sub>4</sub>

Reagents: i, heat or RONa; ii, PhNCO; iii, heat

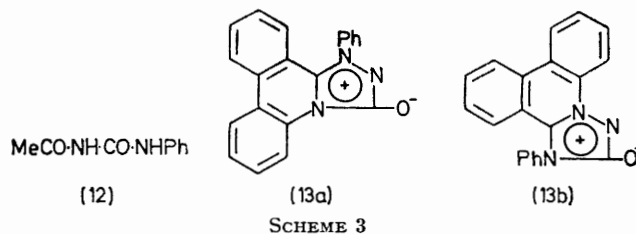
phenylcarbamate (11a) (25%). A similar photolysis of the 1-phenyl-4-*p*-tolyltriazolone (7b) gave benzimidazole (9a) (32%), 4-methylazobenzene (10b) (23%), and methyl *p*-tolylcarbamate (11b) (44%); and 4-phenyl-1-*p*-tolyltriazolone (7c) likewise gave 5(6)-methylbenzimidazole (9b) (44%), 4-methylazobenzene (10b) (10%), and methyl phenylcarbamate (11a) (32%). Irradiation in methanol of the 5-methyl-1,4-diphenyltriazolone (7d) through a Pyrex filter gave 2-methylbenzimidazole (9d) (22%), methyl phenylcarbamate (11a) (40%), and 1-acetyl-3-phenylurea (12) (0.8%). The formation of a small amount of azobenzene was suggested by g.l.c., but it could not be characterised further. Similar irradiation of the triphenyltriazolone (7e)<sup>11</sup> in methanol gave one main product (83%) to which a triazolophenanthridine structure (13a or b) is assigned. The appearance of the i.r. carbonyl band at the same position as that of (7e)



a, c, d; Y = H

b; Y = Me

R, Ar<sup>1</sup>, and Ar<sup>2</sup> as Scheme 2



(1680 cm<sup>-1</sup>) supports the view that the mesoionic structure is retained in the photoproduct, but the spectral

<sup>9</sup> H. Kato, S. Sato, and M. Ohta, *Tetrahedron Letters*, 1967, 4261.

<sup>10</sup> T. Shiba and H. Kato, *Bull. Chem. Soc. Japan*, 1970, **43**, 3491; W. D. Ollis and C. A. Ramsden, *Chem. Comm.*, 1971, 1222; *J.C.S. Perkin I*, 1974, 633; K. T. Potts and S. Husain, *J. Org. Chem.*, 1971, **36**, 3368; K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *ibid.*, 1974, **39**, 3619.

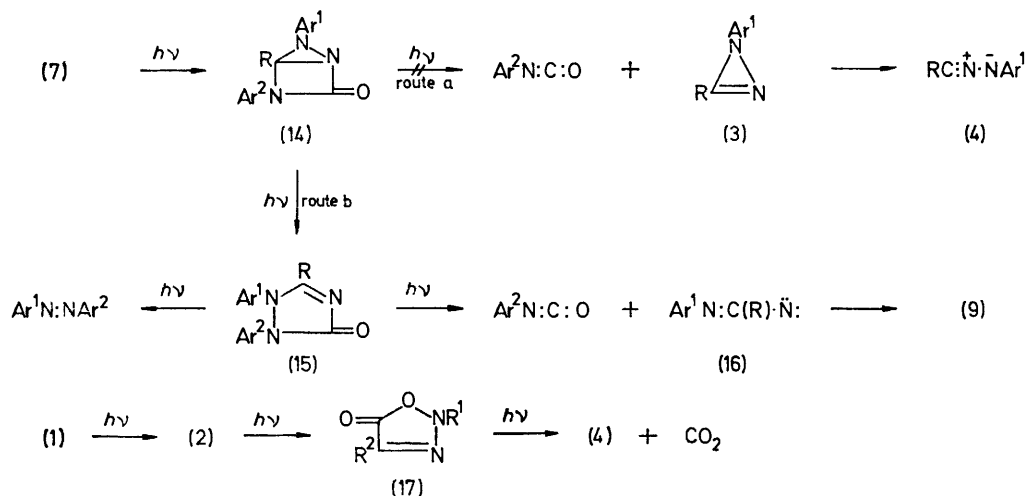
<sup>11</sup> K. T. Potts, S. K. Roy, and D. P. Jones, *J. Org. Chem.*, 1967, **32**, 2245.

data did not differentiate between structures (13a and b.) Also found was a trace of a component having the same g.l.c. retention time as methyl phenylcarbamate, but azobenzene was not detected.

The above results show that irradiation of the mesoionic triazolones (7a—d) causes fragmentation to a benzimidazole, an azobenzene, and an aryl isocyanate. The formation of azobenzene is probably due to an intramolecular fragmentation rather than an intermolecular attack or dimerisation of a nitrene because neither azobenzene nor 4,4'-dimethylazobenzene was isolated from photolysis of the triazolones (7b and c). These results rule out a reaction path analogous to that proposed for the photoreactions of sydnone (Scheme 4; route a) because such a path does not account for the formation of

latter gives a benzimidazole. Intermediate formation of an azomethine nitrene and its cyclisation to a benzimidazole have been proposed for the photochemical and thermal fragmentation of many heterocyclic systems, and in many cases the intermediate could not be trapped.<sup>5,6,14,15</sup> The reason for this indirect fragmentation may be that the formation of an antiaromatic intermediate (3) can be by-passed by this mechanism.

The results presented here not only cast doubt on the possible interconversion of an azomethine nitrene and a nitrilimine through a diazirine intermediate,<sup>6</sup> but also suggest that the photochemical transformations of many mesoionic ring systems may be analogous to that proposed here.<sup>2,4,12,16</sup> Sydnone, for example, may isomerise *via* the bicyclic intermediate (2) to the oxadiazolone



SCHEME 4

azobenzene, and it should give the same diazirine (3) or nitrilimine (4) intermediate as derived from sydnone.<sup>4,12</sup> In our hands photolysis of 3-phenylsydnone (1a) gave no benzimidazole, and attempts at trapping the intermediate of the triazolone photolysis with dimethyl acetylenedicarboxylate were unsuccessful, though intermediates in the photolysis of sydnone and related systems are readily trapped by a variety of dipolarophiles.<sup>5,6,12-14</sup>

A mechanism which affords all the compounds isolated is shown in Scheme 4 (route b). Instead of direct fragmentation, the bicyclic intermediate (14) undergoes valence isomerisation to give the triazolone (15). This may decompose either to an azobenzene or to an isocyanate and an azomethine nitrene (16), and cyclisation of the

(17), which could decompose directly to the nitrilimine (4), avoiding in this way the high-energy diazirine intermediate (3). Many such photochemical transposition reactions of heterocycles are known,<sup>17</sup> including those of a mesoionic 1,3-dithiol-4-imine<sup>2b</sup> and a mesoionic thiazol-4-one.<sup>16b</sup>

The oxidative photocyclisation of the triphenyltriazolone (7e) is of the type encountered in many *o*-diphenyl-substituted compounds,<sup>18</sup> including a mesoionic compound,<sup>19</sup> and does not require further discussion.

**Pyrolysis.**—Pyrolysis of the triphenyltriazolone (7e) at 350–360 °C gave *N*-(diphenylmethylene)aniline (18a).

<sup>15</sup> F. L. Bach, J. Karliner, and G. E. von Lear, *Chem. Comm.*, 1969, 1110; J. H. Boyer and P. J. A. Frints, *J. Heterocyclic Chem.*, 1971, **7**, 59; 71.

<sup>16</sup> (a) H. Gotthardt, *Tetrahedron Letters*, 1971, 1277; *Chem. Ber.*, 1972, **105**, 188; A. Holm, N. Harrit, K. Bechgaard, O. Buchardt, and S. E. Harnung, *J.C.S. Chem. Comm.*, 1972, 1125; (b) O. Buchardt, J. Domanus, N. Harrit, and A. Holm, *ibid.*, 1974, 376.

<sup>17</sup> A. LaBlache-Comber and M.-A. Remy, *Bull. Soc. chim. France*, 1971, 679; S. T. Reid, *Adv. Heterocyclic Chem.*, 1970, **11**, 1.

<sup>18</sup> F. R. Stermitz, 'Organic Photochemistry,' ed. O. L. Chapman, Marcel Dekker, New York, 1967, vol. 1, p. 247.

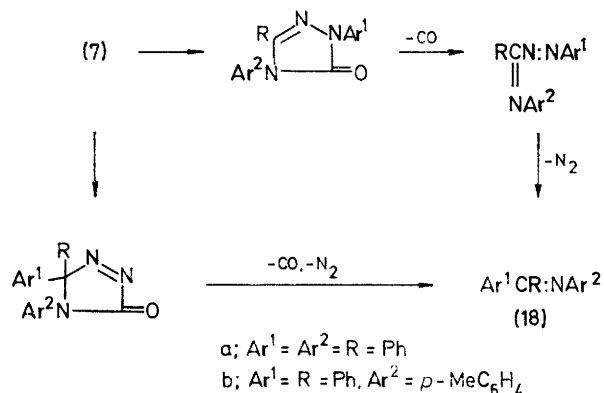
<sup>19</sup> R. M. Moriarty, J. M. Kleigman, and R. B. Desai, *Chem. Comm.*, 1967, 1255; R. M. Moriarty and R. Mukerjee, *Tetrahedron Letters*, 1969, 4627.

<sup>12</sup> Y. Huseya, A. Chinone, and M. Ohta, *Bull. Chem. Soc. Japan*, 1971, **44**, 1667; 1972, **45**, 3202; C. S. Angedivar and M. V. George, *J. Org. Chem.*, 1971, **36**, 1589; M. Märkyl, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1971, **54**, 1275; H. Gotthardt and F. Reiter, *Tetrahedron Letters*, 1971, 2749.

<sup>13</sup> S. Y. Hong and J. E. Baldwin, *Tetrahedron*, 1968, **24**, 3787; J. S. Clovis, A. Eckell, R. Huisgen, and R. Sustmann, *Chem. Ber.*, 1969, **100**, 60; P. Scheiner, *J. Org. Chem.*, 1969, **34**, 199; T. Sasaki and K. Kanematsu, *J. Chem. Soc. (C)*, 1971, 2147.

<sup>14</sup> (a) P. Beak and W. R. Messer, 'Organic Photochemistry,' ed. O. L. Chapman, Dekker, New York, 1969, vol. 2, p. 117; (b) P. A. S. Smith, 'Nitrenes,' ed. W. Lwowski, Interscience, New York, 1970, p. 99.

Pyrolysis of the 4-*p*-tolyl derivative (7f) gave the corresponding *p*-toluidine derivative (18b), showing that the *N*(1)-aryl group migrated to the carbon atom. Mechanisms which account for the thermal decomposition are given in Scheme 5. Pyrolyses of the 1,4-diphenyl (7a) and the 5-methyl-1,4-diphenyl derivative (7d) gave mixtures of products (see Experimental section). G.l.c. analyses of the pyrolysates from the triazolones (7a, d, and e) all showed the formation of benzonitrile, but in no case was fragmentation into phenyl isocyanate detected.



SCHEME 5

**Mass Spectra.**—In agreement with the general fragmentation pattern reported<sup>20</sup> independently of our work,<sup>21</sup> the mass spectra of the mesoionic triazolones (7a—e) show an intense peak corresponding to  $RC:\overset{+}{N}Ar^2$ . In the case of the 5-unsubstituted derivatives (7a—c), this is accompanied by another intense peak corresponding to  $[Ar^1NHNCO]^+$  and a medium-intensity fragment corresponding to loss of HNCO from the molecular ion. In contrast to the photofragmentation, fragmentation into  $Ar^2NCO$  is not observed in the mass spectra. Principal ions observed in the mass spectra of the triazolones (7a—e) are listed in the Table.

Relative intensities (%) of principal ions in the mass spectra of the mesoionic 1,2,4-triazol-3-ones (7a—e)<sup>a</sup>

<i>M</i> <sup>+</sup>	(7a)	(7b)	(7c)	(7d)	(7e)
$RC:\overset{+}{N}Ar^1$	52	77	59	24	15
$RC:\overset{+}{N}Ar^2$	86	8	5	100	100
$[Ar^1NHNCO]^+$	71	82	100		
$[Ar^1N=NH]^+$	23	19	23		
$Ar^1N_2^+$	(14) <sup>b</sup>	8	15		
$[Ar^1N:C:NAr^2]^+$	14	17	11		
$[Ar^1]^+$		27	36		
$[Ar^2]^+$	100	74	88	51	(89) <sup>c</sup>

<sup>a</sup> The assignment is based on accurate mass determination which agreed within 0.005 m.u. with the assigned compositions.

<sup>b</sup> Due in part to isotope peak of  $Ph\overset{+}{N}:CH$ . <sup>c</sup>  $Ar^1 + Ar^2 + R$ .

## EXPERIMENTAL

M.p.s were determined with a Yanagimoto hot-stage apparatus. U.v. and i.r. (KBr disc) spectra were recorded

<sup>20</sup> K. T. Potts, R. Armbruster, E. Houghton, and J. Kane, *Org. Mass Spectrometry*, 1973, 7, 203; W. D. Ollis and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 645.

with Hitachi EPS-2U and EPI-S2 spectrophotometers. N.m.r. spectra were obtained with a JEOL JNM-4H-100 (100 MHz) spectrometer for solutions in deuteriochloroform (tetramethylsilane internal standard). Low and high-resolution mass spectra were recorded with a Hitachi RMU-6 and a JEOL O1 SG Mattauch-Herzog double focusing spectrometer, respectively (75 eV; direct inlet technique). G.l.c. analyses were performed with a JEOL-750 instrument (columns of 10% Silicone DC 550, Ucon Oil 50HB, and Carbowax 20M on Chromosorb W-AW). Compounds stated to be identical were so on the basis of m.p., mixed m.p., and i.r. and n.m.r. determinations.

**Mesoionic 1,4-Diaryl-1,2,4-triazol-3-ones (7a—c).**—The procedures for the thermal cyclisation of the acylsemicarbazides (6a—c) were essentially identical with those reported.<sup>8</sup>

**The Mesoionic 1,4-Diphenyl-1,2,4-triazol-3-one (7a).**—A mixture of 3-phenylsydnone (1a) (1g) and phenyl isocyanate (2 ml) was heated at 120—130 °C for 3 h. After cooling, ether was added and the precipitate was recrystallised (ethanol-ether) to give compound (7a) (68%), identical with an authentic specimen.

**3,5,7-Triphenyl-1,3,5,7-tetra-azabicyclo[2.2.1]heptane-2,6-dione (8).**—(a) A mixture of 3-phenylsydnone (1a) (0.5 g) and phenyl isocyanate (1 ml) was heated under gentle reflux for 3 h. The excess of isocyanate was distilled off *in vacuo* and methanol was added to the residue. The precipitate was recrystallised (benzene-*n*-hexane) to give needles (31%), m.p. 177—178 °C (decomp.) (sealed capillary) (Found: C, 70.5; H, 4.35; N, 15.45.  $C_{21}H_{16}N_4O_2$  requires C, 70.75; H, 4.55; N, 15.7%),  $\nu$  (C:O) 1 745  $cm^{-1}$ ;  $\delta$  9.55 (1H, s) and 7.90—6.75 (15H, m).

(b) A mixture of the diphenyltriazolone (7a) (0.5 g) and phenyl isocyanate (1 ml) was treated as described above to give the adduct (8) (79%), identical with an authentic specimen.

**Pyrolysis of the Adduct (8).**—The adduct (8) (0.25 g) was heated in diphenyl ether (80 ml) at 190—200 °C for 40 min. The solvent was removed *in vacuo* and the residue was recrystallised (1,1,2-tetrachloroethane) to give the diphenyltriazolone (7a) (80%), identical with an authentic specimen.

**The Mesoionic 5-Methyl-1,4-diphenyl-1,2,4-triazol-3-one (7d).**—A solution of sodium (0.33 g) in *t*-pentyl alcohol (250 ml) was boiled in an apparatus set up for distillation, and 1-acetyl-1,4-diphenylsemicarbazide (6d) (10 g) was added. After boiling for 30 min, the precipitate was collected and recrystallised (dimethylformamide) to give needles (48%), m.p. 289—291 °C (Found: C, 71.2; H, 5.2; N, 17.05.  $C_{15}H_{13}N_3O$  requires C, 71.7; H, 5.2; N, 16.7%),  $\lambda_{max}$  (EtOH) 216 (log  $\epsilon$  4.11) and 272 nm (3.79);  $\nu$  (C:O) 1 678  $cm^{-1}$ ;  $\delta$  7.65—7.30 (10H, m, aromatic), and 2.43 (3H, s, Me).

**1-Benzoyl-1-phenyl-4-*p*-tolylsemicarbazide (6f).**—This was prepared from 1-phenyl-4-*p*-tolylsemicarbazide and benzoyl chloride in pyridine, as needles (from butan-1-ol) (68%), m.p. 211—212 °C (Found: C, 72.85; H, 5.4; N, 12.2.  $C_{21}H_{19}N_3O_2$  requires C, 73.05; H, 5.55; N, 12.15%),  $\nu_{max}$  3 375, 3 240, 1 678, and 1 640  $cm^{-1}$ .

**The Mesoionic 1,5-Diphenyl-4-*p*-tolyl-1,2,4-triazol-3-one (7f).**—This was prepared by sodium ethoxide-catalysed cyclisation of the semicarbazide (6f), by the general procedure of Potts *et al.*<sup>11</sup> Repeated recrystallisation from dimethylformamide and then from ethanol gave the pure triazolone (7f), m.p. 302—303 °C (Found: C, 76.85; H, 5.15; N, 12.75.  $C_{21}H_{17}N_3O$  requires C, 77.05; H, 5.25; N,

<sup>21</sup> H. Kato and T. Shiba, Abstracts, Third International Congress of Heterocyclic Chemistry, Sendai, Japan, 1971, p. 502.

12.85%),  $\nu$  (C=O) 1 680  $\text{cm}^{-1}$ ;  $\delta$  7.45—6.95 (14H, m, aromatic) and 2.32 (3H, s, Me).

**Photolysis of the Triazolones (7).**—(a) 1,4-Diphenyl-1,2,4-triazol-3-one (7a) [ $\lambda_{\text{max}}$  (EtOH) 226 (log  $\epsilon$  4.21) and 300 nm (4.01)] (1.003 g) in dichloromethane (190 ml) and methanol (10 ml) was deaerated with nitrogen and irradiated through a Pyrex filter with a 100 W immersion-type high-pressure mercury lamp at 10—20 °C for 51 h. The mixture was extracted with aqueous 5% hydrochloric acid and the extract was concentrated, dissolved in methanol, and precipitated with dichloromethane. Recrystallisation (nitromethane) gave needles of benzimidazole hydrochloride monohydrate (18%), which was converted into benzimidazole (both identical with authentic specimens). The organic layer of the acid extraction was chromatographed (silica; benzene) to give azobenzene (4%) and methyl phenylcarbamate (25%), both identical with authentic specimens.

(b) 1-Phenyl-4-*p*-tolyl-1,2,4-triazol-3-one (7b) (0.46 g) in dichloromethane containing methanol (5% v/v) was irradiated and worked up similarly to give benzimidazole hydrochloride monohydrate (32%), 4-methylazobenzene (23%), and methyl *p*-tolylcarbamate (44%), all identical with authentic specimens.

(c) 4-Phenyl-1-*p*-tolyl-1,2,4-triazol-3-one (7c) (0.476 g) was treated similarly to give 4-methylazobenzene (10%) and methyl phenylcarbamate (32%), both identical with authentic specimens, and 5(6)-methylbenzimidazole (44%), m.p. 113—114 °C (lit.,<sup>22</sup> 113—114 °C) (Found: N, 21.35.  $\text{C}_8\text{H}_8\text{N}_2$  requires N, 21.2%),  $\delta$  11.99br (1H, s, NH), 8.26 (1H, s, 2-H), 7.68 (1H, d, *J* 8 Hz, 7-H), 7.58 (1H, s, 4-H), 7.22 (1H, d, *J* 8 Hz, 6-H), and 2.52 (3H, s, Me).

(d) 5-Methyl-1,4-diphenyl-1,2,4-triazol-3-one (7d) (0.50 g) in methanol (200 ml) was similarly irradiated for 55 h to give 2-methylbenzimidazole (22%), methyl phenylcarbamate (40%), 1-acetyl-3-phenylurea (0.8%), and unchanged triazolone (2.5%), all identical with authentic specimens. A benzene fraction from silica gel chromatography had a component showing the same g.l.c. retention times as azobenzene on several columns.

(e) 1,4,5-Triphenyl-1,2,4-triazol-3-one (7e) [ $\lambda_{\text{max}}$  ( $\text{CH}_2\text{Cl}_2$ ) 298 (log  $\epsilon$  3.89) and 316 nm (3.91)] (0.20 g) in methanol (200 ml) was irradiated for 50 h; the mixture was concentrated, and the precipitate was recrystallised (dioxan) to give prisms of the triazolophenanthridine (13a or b) (83%), m.p. 325.5—326 °C (sealed capillary) (Found: C, 77.1; H, 4.2; N, 13.3. Calc. for  $\text{C}_{20}\text{H}_{13}\text{N}_3\text{O}$ : C, 77.15; H, 4.2; N, 13.5%),

<sup>22</sup> H. Tiefenthaler, W. Dörscheln, H. Göth, and H. Schmid, *Helv. Chim. Acta*, 1967, **50**, 2244.

$\nu$  (C=O) 1 680  $\text{cm}^{-1}$ ;  $\delta$  8.79—8.48 (m) and 7.91—7.37 (m); *m/e* 311 (100,  $M^+$ ), 310 (90), 269 (42,  $M - \text{NCO}$ ), 268 (21), 255 (10,  $M - \text{NNCO}$ ), 254 (45), and 129 (20%). G.l.c. of the crude photolysate showed the presence of a component having the same retention times as methyl phenylcarbamate (0.48% by peak area evaluation).

**Pyrolysis of the Triazolones (7).**—A small amount of the triazolone (7a, d, or e) was sealed *in vacuo* in an ampoule and heated for 1 h in an oven at 400 °C. Methanol was added to the pyrolysate and the methanolic extract was analysed by g.l.c. In every case, the presence of a component with the same retention times as benzonitrile was detected, but in no case was a peak corresponding to methyl phenylcarbamate observed. Experiments directed at isolating other products were as follows.

(a) 1,4-Diphenyl-1,2,4-triazol-3-one (7a) (0.5 g) was heated at 310—330 °C for 1 h. The needles which sublimed during the pyrolysis and those collected by sublimation *in vacuo* of the crude pyrolysis residue were 1,3-diphenylurea (29%), identical with an authentic sample.

(b) 5-Methyl-1,4-diphenyl-1,2,4-triazol-3-one (7d) (40 mg) was heated at 300—320 °C for 1 h to give an intractable tar. A trace of sublimate (m.p. 102—110 °C) was shown to be impure acetanilide by comparison of its i.r. and n.m.r. spectra and g.l.c. retention times with those of an authentic specimen.

(c) 1,4,5-Triphenyl-1,2,4-triazol-3-one (7e) (0.5 g) was heated at 345—365 °C for 1 h. The sublimate was recrystallised (ethanol) to give *N*-(diphenylmethylene)aniline (55%), identical with an authentic specimen.

(d) 1,5-Diphenyl-4-*p*-tolyl-1,2,4-triazol-3-one (7f) (0.5 g) was heated *in vacuo* in a micro-distillation apparatus at 320—350 °C for 1 h. The residue was washed with cyclohexane to remove unchanged triazolone (7f) (56% recovery), and the washings and the distillate were purified by distillation *in vacuo* to give *N*-(diphenylmethylene)-*p*-toluidine (36% based on consumed triazolone), identical with an authentic specimen. This was further identified by hydrolysis (HCl) and conversion into benzophenone 2,4-dinitrophenylhydrazone and *N*-acetyl-*p*-toluidine, both identical with authentic specimens.

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