# Studies on the azidolysis of 4-arylidene and 4-alkylidene 5(4)-oxazolones. Part II

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4-Alkylidene-5(4)-oxazolones (1) react with sodium azide in acetic acid in 5 min, or with hydrazoic acid in benzene to give the diazide 2. The latter gives by thermolysis the oxadiazine (4), which forms on hydrolysis the diamide (5). The corresponding monoazides (3) react with sodium azide – acetic acid mixture to give the corresponding diazides.

4-Arylidene-5(4)-oxazolones (8) react under the same conditions to give  $\alpha$ -[tetrazolyl-(1)]-acrylic acid derivatives (9).

The work of Deorha and Gupta (6) is reinvestigated. The constitution of the products is discussed chemically and spectroscopically.

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In a previous publication (1) it was stated that 4-arylidene-5(4)-oxazolones react with sodium azide in acetic acid to give  $\alpha$ -[tetrazolyl-(1)]acrylic acid derivatives, while in the case of 4alkylidene-5(4)-oxazolone, a neutral compound was obtained, benzamide (5*a*). A mechanism was proposed for the formation of the latter compound.

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In this study we attempted to discern the possible intermediates involved in both reactions.

When 4-isopropylidene-2-phenyl-5(4)-oxazolone (1a) is allowed to react with sodium azide and acetic acid for 3h, 5a is obtained (1) together with a small quantity of 6a; while permitting short reaction time (5 min) an azido compound (2*a*) ( $vN_3 = 2125 \text{ cm}^{-1}$ ), m.p. 146 °C is obtained. Analytical data prove that the above azido compound is a diazide. Isopropylidene hippuric azide (3a) is known (2) (m.p. 92 °C) to be obtained via the hydrazide - sodium nitrite route. In addition to the azidolysis of the oxazolone ring, the azido group adds to the double bond of  $\alpha,\beta$ -unsaturated carbon atoms. This is also known to be true of acrylates (3). It is also known that the exo-double bond of 4-isopropylidene-2-phenyl-5(4)-oxazolone adds ammonia or mercaptans (4). Thermolysis of both azides 2aand 3a gives the same product, 3,4-dihydro-4isopropylidene-6-phenyl-2-oxo-1,3,5-oxadiazine (4a), m.p. 186 °C via the Curtius rearrangement and cyclization. Hydrolysis of the latter by water or dilute acetic acid gives N-isobutyroyl benzamide (5a). The monoazide (3a) gives the diazide (2a) when treated with sodium azide and acetic acid mixture.

The diazide (2a), when treated with aqueous sodium azide in acetic acid at (100 °C), gives mainly 5a and some 6a. Similarly the oxadiazine (4a) gives mainly 5a and a little 6a.

The only difference between the monoazide and the diazide is their behavior on pyrolysis. The monoazide gives the oxadiazine (4a) whereas the diazide gives 5-phenyltetrazole (6a).

A mixture of hydrazoic acid and 4-isopropylidene-2-phenyl-5(4)-oxazolone (1a) in benzene solution at room temperature precipitated the diazide (2a) after one week, and the solution proved to contain 5-phenyltetrazole (6a). When (4a) is refluxed with glacial acetic acid the oxazolone (1a) is formed.

Similarly, when 2-*p*-chlorophenyl-4-isopropylidene-5(4)-oxazolone (1*b*) and 2-anisyl-4-isopropylidene-5(4)-oxazolone (1*c*) were treated with sodium azide and acetic acid and were allowed to stand for a long time, a mixture of *N*-isobutyroyl-*p*-chlorobenzamide (5*b*) and 5-*p*chlorophenyltetrazole (6*b*); *N*-isobutyroylanisamide (5*c*) and 5-anisyltetrazole (6*c*), respectively were obtained together. 4-Cyclohexylidene-2-phenyl-5(4)-oxazolone (1*d*) behaves similarly (see Scheme 1).

2-Aryl-4-fluorenylidene (7a and b) failed to react with hydrazoic acid. This may be attributed to their insolubility in the reaction medium.

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2-Aryl-4-arylidene-5(4)-oxazolones (8a-d), when treated with sodium azide in acetic acid or hydrazoic acid in benzene, gave only the corre-

7*a*; Ar =  $C_6H_5$ *b*; Ar =  $C_6H_4OCH_3(p-)$ 

Ar



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#### AWAD AND FAHMY: STUDIES ON AZIDOLYSIS. PART II

We have prepared the corresponding hydrazides (10) from which the corresponding azides (11) were obtained by treatment with sodium nitrite and hydrochloric acid. These azides do not react with sodium azide and acetic acid mixture and no diazide could be isolated. When these azides (11) are heated in benzene, oxadiazines of type 12 are obtained.



The analytical data of these compounds do not assist in distinguishing between the tetrazolyl acid and the azide structure; however, the region of the  $vN_3$  in the infrared (i.r.) spectra of these compounds is devoid of any absorption. This excludes the azide structure for these compounds.

The tetrazolyl acid structure of 14 and 15 is further confirmed by the ultraviolet (u.v.) spectra which shows for 14  $\lambda_{max}$  235 mµ;  $\varepsilon_{max}$ 11 760,  $\lambda_{max}$  229 mµ;  $\varepsilon_{max}$  16 120 and for 15  $\lambda_{max}$ 237 mµ;  $\varepsilon_{max}$  17 280,  $\lambda_{max}$  237 mµ;  $\varepsilon_{max}$  37 800. Similar absorption was recorded in our previous work (1).



The corresponding hydrazides (16 and 17) and azides (18 and 19) were prepared, which, by heating gave the corresponding oxadiazine (20 and 21). These oxadiazines do not show vNH.

It seems that the reaction of alkylidene oxazolones with hydrazoic acid or sodium azide – acetic acid mixture starts by 1,4-addition of hydrazoic acid to the  $\alpha$ , $\beta$ -unsaturated system.



For arylidene oxazolones, the fractional positive charge on C-4 is dissipated on the aromatic ring.



This may be the reason for the fact that alkylidene oxazolones behave differently from arylidene oxazolones towards hydrazoic acid.

The u.v. spectra of 4-alkylidene hippuric hydrazides show one band (225–258 m $\mu$ ) depending upon the nature of the benzamido group;

It may be noted that, in contrast to acrylates, cinnamic acid and cinnamate do not react with hydrazoic acid (3). It is also known that oxadiazines give by alkaline hydrolysis the corresponding phenylacetic acid (5).

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From our investigation it is clear that 4arylidene oxazolones differ from the 4-alkylidene derivatives towards hydrazoic acid. However, Deorha and Gupta (6) reportedly obtained from sodium azide – acetic acid mixture using 2phenyl-4-(3'-methylbenzfurfurylidene)-5(4)-oxazolone (13), the corresponding azide which they failed to identify. They heated these products and obtained the corresponding oxadiazine (21).



In contrary, it was found in the present investigation that 4-furfurylidene-2-phenyl-5(4)-oxazolone and 2-phenyl-4-(3'-methylbenzfur-furylidene)-5(4)-oxazolone (13) gave, with sodium azide – acetic acid mixture, only the tetrazolyl acids (14) and (15), regardless of whether the reaction was carried out in the cold for a prolonged time (6), or as described here.

| TABLE I                                      |  |
|--|--|
| Alkylidene and arylidene hippuric hydrazides |  |

|              |        | Malaka - |                          |            |       |                   |       |            | 10/   | ¥ Theorem                   |                              | Infrared     |                  |
|--------------|--------|----------|--------------------------|------------|-------|-------------------|-------|------------|-------|-----------------------------|------------------------------|--------------|------------------|
| Compound     | Yield* | point    |                          |            | - 76  | <sup>7</sup> 6 H% |       | N %        |       |                             |                              | VNH          | vC==0            |
|              | %      | °C       | Formula                  | Calculated | Found | Calculated        | Found | Calculated | Found | $\lambda_{max}$ mµ          | Emax                         | cm-1         | cm <sup>-1</sup> |
| 1'a(2)       |        |          |                          |            |       |                   |       |            |       | 225-235                     | 23664                        |              |                  |
| 1 <i>'b</i>  | 68     | 163      | C12H14N3O2CI             | 53.83      | 54.11 | 5.23              | 5.01  | 15.70      | 15.24 | 237.5                       | 22344                        | 3250         | 1640             |
| 1'c          | 67     | 162      | C13H17N3O3               | 59.30      | 59.20 | 6.51              | 5.98  | 15.96      | 15.63 | 254258                      | 21868                        | 3200         | 1625             |
| 1'd          | 79     | 174-176  | $C_{15}H_{19}N_3O_2$     | 65.91      | 65.02 | 7.01              | 7.33  | 15.37      | 14.56 | 227.5                       | 14508                        | 3300         | 1650             |
| 10 <i>a</i>  | 71     | 174      | $C_{17}H_{17}N_3O_3$     | 65.58      | 65.09 | 5.50              | 5.69  | 13.50      | 12.60 | 226.5,<br>302.5             | 23690, 27600                 | 3250         | 1640             |
| 106          | 77     | 166–170  | $C_{17}H_{15}N_{3}O_{4}$ | 62.71      | 62.54 | 4.65              | 5.01  | 12.92      | 11.30 | 227–237,<br>320             | 13386, 10476                 | 3300         | 1640             |
| 10 <i>c</i>  | 80     | 170–172  | $C_{18}H_{17}N_3O_2$     | 70.34      | 69.47 | 5.58              | 6.02  | 13.67      | 13.15 | 228–234;<br>320–335         | 24640, 26880                 | 3300         | 1670             |
| 16<br>17(12) | 61     | 171–172  | $C_{14}H_{13}N_3O_3$     | 61.98      | 62.89 | 4.83              | 4.88  | 15.49      | 14.71 | 230, 310<br>223;<br>330–338 | 17920, 29680<br>22320, 33480 | 3300<br>3300 | 1650<br>1670     |

\*The time of reaction was in all cases 1 h.

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|      | TABLE II      |       |
|------|---------------|-------|
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| Alkylidene a | nd arylidene | oxadiazine |
|--------------|--------------|------------|
|              | ·            |            |

|                   |          |       |             |                      |            |       |            |       |            |       |                          |                       |      | Infrared <sup>†</sup>  |
|-------------------|----------|-------|-------------|----------------------|------------|-------|------------|-------|------------|-------|--------------------------|-----------------------|------|------------------------|
|                   | Reaction | Vield | Melting     |                      | C%         |       | H%         | o     | N°         | é     | Ultravi                  | olet                  |      |                        |
| Compound          | time*    | %     | point (°C)  | Formula              | Calculated | Found | Calculated | Found | Calculated | Found | λ <sub>max</sub> mμ      | Emax                  | VNH  | $\delta$ -lactone (14) |
| 4a(13)‡           |          |       |             |                      |            |       |            |       |            |       | 237                      | 17762                 | 3325 | 1750                   |
| <b>4</b> <i>b</i> | 15 min   | 55    | 165         | C12H11N2O2C1         | 57.48      | 57.08 | 4.43       | 4.03  | 11.17      | 10.04 | 237                      | 15368                 | 3225 | 1775                   |
| <b>4</b> c‡       | 15 min   | 66    | 180         | $C_{13}H_{14}N_2O_3$ | 63.40      | 63.17 | 5.73       | 6.05  | 11.38      | 11.64 | 256                      | 18816                 | 3300 | 1750                   |
| 4d‡               | 15 min   | 55    | 162-164     | $C_{15}H_{16}N_2O_2$ | 70.29      | 70.69 | 6.29       | 6.66  | 10.93      | 10.63 | 223-230                  | 16400                 | 3300 | 1750                   |
| 12a               | 30 min   | 54    | 171         | $C_{17}H_{14}N_2O_3$ | 69.37      | 65.15 | 4.80       | 5.67  | 9.52       | 8.72  | 224–230, 276–286,<br>289 | 31600, 25520<br>2640  | 3300 | 1760                   |
| 126               | 1 h      | 64    | over<br>360 | $C_{17}H_{12}N_2O_4$ | 66.23      | 66.06 | 3.92       | 4.62  | 9.09       | 8.68  | 227.5,268,<br>274–282    | 13440, 11760<br>12432 | 3300 | 1750                   |
| 12 <i>c</i>       | 1 h      | 65    | 235-237     | $C_{18}H_{14}N_2O_2$ | 74.47      | 75.02 | 4.86       | 5.14  | 9.65       | 9.26  | 227.5,284-298            | 19760, 18620          | 3325 | 1760                   |
| 20                | 30 min   | 66    | 165166      | C14H10N 2O3          | 66.13      | 66.86 | 3.96       | 4.46  | 11.02      | 10.86 | 239.5,278                | 15960, 21000          |      | 1800                   |
| 21(12)            |          |       |             |                      |            |       |            |       |            |       | 224-231, 317.5           | 13200, 18040          |      | 1790                   |

\*The reported time and yields are for the experiments using the corresponding monoazide.

 $\frac{1}{10}$  cm<sup>-1</sup>,  $\frac{1}{10}$  c

|  |  |  |  |  | (a) A start of the second start of the seco |  |  |
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|             |        | Mali        | . 1.4   |   | 2N avail   | obla  | TI  | travialat  |                         | Infrared            |              |
|-------------|--------|-------------|---------|---|------------|-------|---|--|-------------------------|---------------------|--------------|
| Compound    | Yield* | point<br>°C |         | Formula                                   | Calculated | Found | λ μμ  |  | vNH<br>cm <sup>-1</sup> | $vN_3$<br>$cm^{-1}$ | vC=C         |
| 3a(2)       |        |             |         |   |            |       | 236, 243, 297, 310                          | 19440, 19880, 23976, 24300                         | 3125                    | 2125                | 1675,        |
| 36          | 48     | 86-87 (de   | ecomp.) | $C_{12}H_{14}N_4O_2Cl$                    | 10.05      | 9.86  | 225, 236, 242, 248, 302. 5, 310             | 11524, 13400, 16080, 16616,<br>23852, 24254        | 3250                    | 2125                | 1690<br>1630 |
| 3 <i>c</i>  | 47     | 84-85 (de   | ecomp.) | $C_{13}H_{14}N_4O_3\\$                    | 10.21      | 9.99  | 256, 320                                    | 28880, 29260                                       | 3300                    | 2125                | 1690<br>1630 |
| 3 <i>d</i>  | 48     | 72 (de      | ecomp.) | $C_{15}H_{16}N_{4}O_{2}$                  | 9.86       | 9.82  | 226, 241, 296, 310                          | 12480, 11440, 3120, 2600                           | 3300                    | 2125                | 1690<br>1650 |
| 11 <i>a</i> | 62     | 107-110 (de | ecomp.) | $C_{17} {\rm H}_{14} {\rm N}_4 {\rm O}_3$ | 8.69       | 8.65  | 226–232, 246, 260, 300–310, 384<br>393, 397 | 13080, 13360, 12426, 13516,<br>19184, 17876, 17440 | 3450                    | 2150                | 1650         |
| 11b         | 67     | 74 (de      | ecomp.) | $C_{17}H_{12}N_4O_4$                      | 8.28       | 8.37  | 264, 392                                    | 12792, 20336                                       | 3250                    | 2150                | 1680<br>1650 |
| <b>11</b> c | 57     | 116-117 (de | ecomp.) | $C_{18}H_{14}N_4O_2$                      | 8.80       | 8.76  | 240.5, 274, 383                             | 5400, 5130, 15930                                  | 3300                    | 2150                | 1700<br>1650 |
| 18          | 62     | 110 (de     | ecomp.) | $C_{14}H_{10}N_4O_3$                      | 9.92       | 9.80  | 262, 385, 399                               | 9996, 18156, 16932                                 | 3250                    | 2150                | 1700<br>1650 |
| 19          | 57     | 94 (de      | ecomp.) | $C_{19}H_{14}N_4O_3$                      | 8.20       | 7.90  | 355, 405, 425                               | 20680, 23760, 24200                                | 3325                    | 2175                | 1700<br>1640 |

 TABLE III

 Alkylidene and arylidene hippuric monoazides

\*The time of reaction in all cases was 30 min.

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however, the 4-arylidene analogues show two bands at  $(225-258 \text{ m}\mu)$  and  $(300-335 \text{ m}\mu)$  (see Table I). The oxadiazines behave similarly (see Table II). The known value of the azido (7) (285 m $\mu$ ) is shifted to longer wavelength in the case of compounds under investigation (see Table III). Similar observations have been reported (7).

The electronic spectra of the alkylidene azides are similar with the expected bathochromic shift according to the substituent. The diazides show identical spectra.

All the azides and diazides show in the i.r. spectra the characteristic stretching frequency of the azido group (8) (see Table III).

#### Addendum

The azides and diazides are difficult to analyze by the normal procedure since they are easily decomposed. We have devised a micro method by which they can be analyzed by heating in dilute acetic acid and collecting the nitrogen evolved on a micro scale. For monoazides,  $N_2$ /mole is obtained while for diazides, in addition to the evolved nitrogen, hydrazoic acid was obtained. This required us to use a potassium permanganate or ceric sulfate trap to oxidize the liberated hydrazoic acid and 5N/mole were obtained, in this case. This work has been published elsewhere (9).

#### Experimental

Melting points are not corrected. Analyses were carried out by National Research Center, Microanalytical Unit, Doki, Cairo and by Alfred Bernhard, Max Planck Institute, Mulheim, Germany. Infrared spectra were measured on a Perkin–Elmer Infracord model 137 spectrophotometer using KBr wafer technique. Ultraviolet spectra were measured on a Perkin–Elmer Spectracord model 4000A spectrophotometer using ethyl alcohol solutions.

## Preparation of Some New 5(4)-Oxazolones

2-Anisyl-4-fluorenylidene-5(4)-oxazolone (7b)

A mixture (10 g) anisuric acid, fluorenone (9 g), fused sodium acetate (8 g), and acetic anhydride (30 ml) was heated on a hot plate until all the solid liquefied, then heating was continued on a boiling water-bath for 1 h after which the mixture was cooled and filtered. The yellow crystalline precipitate (yield 47%) was crystallized from glacial acetic acid, m.p. 226-227°C.

Anal. Calcd. for  $C_{23}H_{15}NO_3$ : C, 78.18; H, 4.25; N, 3.97. Found: C, 77.60; H, 4.44; N, 4.01.

2-Anisyl-4-(p-chlorobenzylidene)-5(4)-oxazolone (8a)

A mixture of anisuric acid (10 g), p-chlorobenzaldehyde (7.3 g), sodium acetate (8 g), and acetic anhydride (30 ml) was heated on a hot plate until all the solid liquefied, then heating was continued on a boiling water-bath for 1 h after which the mixture was cooled and filtered. The yellow crystalline precipitate (yield 53 %) was crystallized from ethyl acetate, m.p. 211 °C.

Anal. Calcd. for C<sub>17</sub>H<sub>12</sub>NO<sub>3</sub>Cl: C, 64.96; H, 3.82; N, 4.45. Found: C, 64.85; H, 3.87; N, 4.76.

2-Anisyl-4-isopropylidene-5(4)-oxazolone (1c)

A mixture of anisuric acid (10 g), acetone (170 ml), acetic anhydride (16 ml), and sodium bicarbonate (4.6 g) was refluxed for 6 h after which the mixture was allowed

to cool. The mixture was filtered and poured on crushed ice (500 g) and diluted with ice-cold water to 1.51. The precipitated solid (yield, 54%) was removed by filtration and recrystallized from light petroleum ether, m.p. 108 °C.

Anal. Calcd. for  $C_{13}H_{13}NO_3$ : C, 67.52; H, 5.67; N, 6.06. Found: C, 67.33; H, 5.56; N, 5.45.

#### Action of Aqueous Sodium Azide Solution and Acetic Acid on

(a) 4-Isopropylidene-2-phenyl-5(4)-oxazolone (1a)

A mixture of sodium azide (1 g in the least amount of water) and 1*a* (1 g in the least amount of glacial acetic acid) was heated on a water-bath for 5 min. The mixture was then poured on crushed ice, to give 2a, m.p. 145-146 °C (decomp.); (yield, 69%). It decomposed upon crystallization from most common solvents (e.g. ethyl acetate, alcohol, benzene).

Anal. Calcd. for  $C_{12}H_{13}N_7O_2(5N)$ : N, 24.46. Found: N, 24.70.

When this reaction was carried out for 3 h and the reaction mixture poured on crushed ice, the product was removed by filtration digested in sodium bicarbonate solution, and again removed by filtration. The insoluble part proved to be 5a (yield 83 %)(1), m.p. 154 °C. The above filtrates were mixed together and concentrated to a small volume (~2 ml), acidified with HCl, filtered while hot, and allowed to cool. After scratching, the crystalline product was removed by filtration and proved to be 6a by melting point and mixture melting point (10), yield 5%.

(b) 2-p-Chlorophenyl-4-isopropylidene-5(4)-oxazolone (1b)

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The reaction was carried out as above and after 15 min the starting material was recovered unchanged (m.p. and mixture m.p.). When the reaction was carried out for 3 h and the reaction mixture poured on crushed ice, the product was removed by filtration, digested in sodium bicarbonate solution, and again removed by filtration. The insoluble part proved to be 5b (1), m.p. 134 °C, yield 83 %. The filtrate was acidified with cold dilute HCl and the precipitated product was removed by filtration and recrystallized from light petroleum (b.p. 100–120 °C) as colorless needles, m.p. 253 °C, yield 16%. The latter proved to be 5-p-chlorophenyltetrazole (6b) identified by melting point and mixture melting point experiment with an authentic sample (10).

(c) 2-Anisyl-4-isopropylidene-5(4)-oxazolone (1c)

The reaction was carried out as in (a). After 10 min 2c was obtained and removed by filtration, m.p. 134 °C (decomp.); yield 58%. It decomposes upon crystallization from most common solvents (e.g. ethyl acetate, alcohol).

Anal. Calcd. for  $C_{13}H_{15}N_7O_3(5N)$ : N, 22.09. Found: N, 22.00.

When the reaction was carried out for 1 h and the reaction mixture poured on crushed ice, the product was removed by filtration, digested in sodium bicarbonate solution, and again removed by filtration. The insoluble part (5c) was crystallized from light petroleum (b.p. 60-80 °C) as colorless needles. m.p. 121 °C, vield 31 %.

80 °C) as colorless needles, m.p. 121 °C, yield 31%.
 Anal. Calcd. for C<sub>12</sub>H<sub>15</sub>NO<sub>3</sub>: C, 65.15; H, 7.78; N, 6.33. Found: C, 65.79; H, 7.35; N, 6.51.

The filtrate was acidified with cold dilute HCl and the precipitated product (6c) was removed by filtration and

recrystallized from ethyl acetate as colorless needles, m.p. 233 °C, yield 52%.

Anal. Calcd. for  $C_8H_8N_4O$ : C, 54.54; H, 4.54; N, 31.75. Found: C, 54.71; H, 4.87; N, 31.75.

(d) 4-Cyclohexylidene-2-phenyl-5(4)-oxazolone (1d)

The reaction was carried out as in (a). After  $10 \min (2d)$  yield, 73% was obtained, m.p. 126–127 °C (decomp.). It decomposes upon crystallization from most common solvents.

Anal. Calcd. for  $C_{15}H_{17}N_7O_2(5N)$ : N, 21.43. Found: N, 21.25.

The reaction was carried out for 1 h and the reaction mixture poured on crushed ice. The product was removed by filtration, digested in sodium bicarbonate solution, and again removed by filtration. The insoluble part, yield, 73% m.p. 157 °C, was previously identified as (5d) (1). The filtrate was acidified with cold dilute HCl and the precipitated product was removed by filtration and recrystallized from ethyl acetate as colorless needles, m.p. 212-213 °C, yield, 24%. The latter proved to be 5-phenyl-tetrazole (6a) identified by melting point and mixture melting point experiment with authentic sample (10).

Anal. Calcd. for  $C_7H_6N_4$ : C, 57.60; H, 4.11; N, 37.75. Found: C, 58.1; H, 4.64; N, 37.32.

(e) 4-Fluorenylidene-2-phenyl-5(4)-oxazolone (7a)

The reaction was carried out as in (a). After 15 min or 3 h the starting material was recovered unchanged (m.p. and mixture m.p.). Similarly 2-anisyl-4-fluorenylidene-5(4)-oxazolone (7b) was recovered unchanged.

(f) 2-Anisyl-4(p-chlorobenzylidene)-5(4)-oxazolone

(**8**a)

The reaction was carried out as in (a). After 15 min the starting material was recovered unchanged (m.p. and mixture m.p.). The reaction was carried out for 1 h and the reaction mixture poured on crushed ice. The product was removed by filtration and digested in sodium bicarbonate. The unchanged oxazolone was extracted with ether and aqueous layer was acidified with cold dilute HCl. The precipitated product (9a) was removed by filtration and recrystallized from ethyl acetate as colorless crystals, m.p. 185 °C, yield 90%.

Anal. Calcd. for C<sub>17</sub>H<sub>13</sub>N<sub>4</sub>O<sub>3</sub>Cl: C, 57.17; H, 3.64; N, 15.86. Found: C, 57.08; H, 3.89; N, 15.91.

Similarly 4-anisylidene-2-phenyl-5(4)-oxazolone (8b), 2-phenyl-4-piperonylidene-5(4)-oxazolone (8c), and 4-cinnamylidene-2-phenyl-5(4)-oxazolone (8d) were recovered unchanged, after 15 min.

(g) 4-Furfurylidene-2-phenyl-5(4)-oxazolone

The reaction was carried out as in (a). After 15 min the starting material was recovered unchanged (as shown by m.p. and mixture m.p.). When the reaction was carried out as in (a) for 1 h, the precipitated product (14) was removed by filtration and recrystallized from ethyl acetate as greenish-yellow crystals, m.p. 184–185 °C (decomp.), yield 85%.

Anal. Calcd. for C<sub>14</sub> H<sub>10</sub>N<sub>4</sub>O<sub>3</sub>: C, 59.57; H, 3.57; N, 19.85. Found: C, 59.64; H, 3.64; N, 19.74.

(h) 2-Phenyl-4-(3'-methylbenzfurfurylidene)-5(4)oxazolone (13)

The reaction was carried out as in (a), after 15 min the starting material was recovered unchanged (as shown by

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## TABLE IV

Action of hydrazoic acid solution in benzene on 4-alkylidene and arylidene oxazolones

| Oxazolone  | Product  | Reaction<br>time | Solvent<br>of<br>crystallization | Melting<br>point<br>°C | Yield           | Reference |
|--|--|------------------|----------------------------------|------------------------|-----------------|-----------|
| <b>1</b> <i>a</i>                                    | Isopropylidene hippuric diazide (2a)                                   | 1 week           | _                                | 145–147                | 34              | _         |
|  | 5-Phenvltetrazol* (6a)   | 3 weeks          | <b></b> †                        | 212-213                | 26              | 10        |
| <b>1</b> b   | 5-p-Chlorophenyltetrazol (6b)  | 3 weeks          | +                                | 253                    | $\overline{78}$ | 10        |
| <b>1</b> <i>c</i>                                    | Isopropylidene anisuric diazide  | 1 week           | `                                | 134                    | 37              |           |
|  | 5- $Anisyltetrazol* (6c)$  | 3 weeks          | <u></u> †                        | 233                    | 39              | 10        |
| <b>1</b> d   | Cyclohexylidene hippuric diazide                                       | 1 week           |                                  | 127-128                | 29              |           |
|  | 5-Phenyltetrazol* (6a)   | 3 weeks          |                                  | 212-213                | 48              | 10        |
| <b>8</b> a   | α-[Tetrazolyl(1)]-5-anisyl-p-<br>chlorocinnamic acid (9a)              | 3 days           | —‡                               | 185                    | 90              | _         |
| <b>8</b> b   | $\alpha$ -[Tetrazolyl(1)]-5-phenyl-p-<br>methoxycinnamic acid (9b)     | 3 days           | —§                               | 185                    | 69              | 1         |
| <b>8</b> c   | α-[Tetrazolyl(1)]-5-phenyl-3,4-<br>methylenedioxycinnamic acid<br>(9c) | 3 days           | —§                               | 183                    | 70              | 1         |
| <b>8</b> d   | α-[Tetrazolyl(1)]-5-phenylbenzy-<br>lidenecrotonic acid (9d)           | 3 days           | —‡                               | 225                    | 65              | 1         |
| 4-Furfury-<br>lidene-5-<br>phenyl-5(4)-<br>oxazolone | α-[Tetrazolyl(1)]-5-phenyl-<br>furfurylacrylic acid (14)               | 3 days           | ‡                                | 184185                 | 93              |           |

\*The reaction was completed using the mother liquors. †Light petroleum ether (b.p. 100-120 °C), ‡Ethyl acetate.

§Ethyl acetate – light petroleum ether (b.p. 40-60 °C).

m.p. and mixture m.p.). When the reaction was carried out as in (g) for 1 h, the precipitated product was removed by filtration and recrystallized from ethyl acetate - light petroleum (b.p. 40-60 °C) as colorless crystals of 15, m.p. 194 °C (decomp.), yield 71 %.
 Anal. Calcd. for C<sub>19</sub>H<sub>14</sub>N<sub>4</sub>O<sub>3</sub>: C, 65.89; H, 4.07; N,

16.10. Found: C, 65.14; H, 4.34; N, 15.27.

#### Action of Aqueous Sodium Azide Solution and Acetic Acid on

(a) 4-Furfurylidene-2-phenyl-5(4)-oxazolone

To a suspension of 4-furfurylidene-2-phenyl-5(4)oxazolone (0.15 mole) in distilled acetic acid (75 ml) was added sodium azide (0.15 mole in least amount of water). The mixture was vigorously stirred at room temperature till the color of the oxazolone became very faint. The solid product was removed by filtration, digested in sodium bicarbonate solution, and removed by filtration. The insoluble part proved to be unchanged (as shown by m.p. and mixture m.p.). The filtrate was acidified with cold dilute HCl and the precipitated product was removed by filtration and recrystallized from ethyl acetate to give greenish-yellow crystals, m.p. 184-185 °C (decomp.), yield 50%.

It proved to be identical (as shown by m.p. and mixture m.p.). with 14 obtained via action of sodium azide and acetic acid for 1 h on the title compound.

#### (b) 2-Phenyl-4(3'-methylbenzfurfurylidene)-5(4)oxazolone 13

The reaction was carried out as above, the precipitated product (15) was crystallized from ethyl acetate - light petroleum (b.p. 40-60 °C), m.p. 194 °C (decomp.), yield 40%. It was identical with the product obtained by heating a mixture of an aqueous sodium azide, acetic acid, and 13 for 1 h (m.p. and mixture m.p.).

# Action of Hydrazoic Acid Solution (11) in Benzene on 4-Alkylidene and 4-Arylidene Oxazolones:

General Procedure

A mixture of hydrazoic acid solution in benzene (20 ml) and oxazolone (1 g in 20 ml dry benzene) was left at room temperature for the times specified in Table 1 and the resulting products were crystallized from suitable solvents (see Table IV).

Action of Hydrazine Hydrate on Oxazolones:

#### General Procedure

Hydrazine hydrate (100%) (4 ml) was added dropwise with occasional shaking to a suspension of the oxazolone (3 g) in methanol. After the addition had been completed, the reaction mixture was left for 1 h, whereby a crystalline precipitate was formed. It was removed by filtration and crystallized from a suitable solvent (see Table I).

### Action of Aqueous Sodium Nitrite and Hydrochloric Acid on Alkylidene and Arylidene Hippuric Hydrazides: General Procedure

A solution of sodium nitrite (1 g in least amount of icecold water) was added dropwise with shaking to an icecold solution or the hydrazide (2 g in least amount N-hydrochloric acid) so that the temperature did not rise above 5 °C. After the addition was completed, the reaction mixture was left at room temperature for 30 min, the product was then removed by filtration, dried, and its

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#### AWAD AND FAHMY: STUDIES ON AZIDOLYSIS. PART II

## TABLE V Action of glacial acetic acid on 1,3,5-oxadiazines

Solvent Melting °C Yield of Oxadiazine Oxazolone crystallization % Reference 4-Isopropylidene-2-phenyl (1*a*) 2-*p*-Chlorophenyl-4-isopropylidene (1*b*) 96 43 13 4a53 71 31 170-172 **4**b 1 2-Anisyl-4-iso-propylidene (1c) 4-Cyclohexylidene-2-phenyl (1d) 4c108 Inter alia 4d136 15 4-Cyclonexyndene-2-phenyl (1a 4-Anisylidene-2-phenyl (8b) 2-Phenyl-4-piperonylidene (8c) 4-Cinnamylidene-2-phenyl (8d) 4-Furfurylidene-2-phenyl 42 39 12a 160 16 126 197 17 42 12c 150 18 20 179 31 19 2-Phenyl-4(3'-methylbenzfurfurylidene (13)) 21 159-161 52 12

\*Ethyl alcohol – water. †Light petroleum ether (100–120 °C). ‡Ethyl acetate. §Ethyl acetate – light petroleum ether (100–120 °C). ||Glacial acetic acid.

m.p. was recorded. It decomposed upon crystallization from most common solvents (e.g. ethyl alcohol, ethyl acetate, benzene). (See Table III.)

#### Thermolysis of Alkylidene and Arylidene Hippuric Azides in Benzene: General Procedure

A suspension of the azide (mono- or diazides) in dry benzene (25 ml) was refluxed for 15 min on a boiling water-bath and cooled. The oxadiazine was removed by filtration and recrystallized from benzene (see Table II).

#### Action of Boiling Water on

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(a) 4-Isopropylidene-6-phenyl-2-oxo-1,3,5-oxadiazine (4a)

A suspension of 4a (1 g in 25 ml water) was refluxed for 2 h and was cooled and filtered; 5a was obtained in colorless needles (yield, 34%) from absolute ethanol, m.p. 154 °C, undepressed on admixture with an authentic sample (1).

(b) 6-p-Chlorophenyl-4-isopropylidene-2-oxo-1,3,5oxadiazine (4b)

The reaction was carried out as above, 5b was obtained (yield, 55%), m.p. 132-134 °C, undepressed on admixture with an authentic sample (1).

(c) 6-Anisyl-4-isopropylidene-2-oxo-1,3,5-oxadiazine (4c)

The reaction was carried out as in (a). N-Isobutyroylanisamide was obtained, m.p. 121 °C, yield 66%. It proved to be identical with the product obtained by the action of sodium azide and acetic acid for 1 h on 2anisyl-4-isopropylidene-5(4)-oxazolone.

(d) 4-Cyclohexylidene-6-phenyl-2-oxo-1,3,5-oxadiazine (4d)

The reaction was carried out as in (a). N-Hexahydrobenzoylbenzamide was obtained, m.p. 157 °C, yield 44 %. It proved to be identical with the product obtained by the action of sodium azide and acetic acid for 1 h on 4cyclohexylidene-2-phenyl-5(4)-oxazolone (1).

# Action of Glacial Acetic Acid on 1,3,5-Oxadiazines

When a solution of the oxadiazine (1 g) in glacial acetic acid (25 ml) was refluxed for 30 min and the mixture cooled; the corresponding oxazolone was ob-

tained and was identified by m.p. and mixture m.p. (see Table V).

#### Action of Aqueous Sodium Azide and Acetic Acid on (a) Isopropylidene Hippuric Azide (3a)

A mixture of sodium azide (1 g in least amount of water) and 3a (1 g in 14 ml dilute acetic acid) was left at room temperature for 4 h. The precipitated product (2a) was removed by filtration and dried, m.p. 145-146 °C (decomp.), yield 85%. It proved to be identical with the product obtained by the action of hydrazoic acid in benzene on 1a. Comparison was made by m.p., mixture m.p., and infrared spectrum.

(b) Isopropylidene Anisuric Azide (3c)

The reaction was carried out as in (a), 2c was obtained, m.p. 134° C (decomp.), yield 60%. It proved to be identical with the product obtained by action of hydrazoic acid in benzene on 1c. Comparison was made by melting point, mixture melting point, and infrared spectrum.

(c) Cyclohexylidene Hippuric Azide (3d)

The reaction was carried out as in (a), 2d was obtained (yield 69%), m.p. 126-127 °C (decomp.). It proved to be identical (by melting point and mixture melting point) with the product obtained by action of hydrazoic acid in benzene on 4-cyclohexylidene-2-phenyl-5(4)-oxazolone (1d). Similarly the reaction was carried out on 11a and 3methylbenzfurfurylidene azide 19 and the reactants were recovered (identification was made by m.p. and mixture m.p.).

#### Action of Aqueous Sodium Azide and Acetic Acid on (a) Isopropylidene Hippuric Diazide (2a) or 3,4-Dihydro-6-phenyl-4-isopropylidene-2-oxo-1,3,5oxadiazine (4a)

A mixture of sodium azide (1 g in least amount of water) and 2a or 4a (1 g in 20 ml dilute acetic acid) was heated on a boiling water bath for 1 h. The reaction mixture was cooled and the product was removed by filtration. It was recrystallized from absolute ethanol as colorless needles, m.p. 154  $^{\circ}C$  (1); yield 90 % in the case of 2a and 75% in the case of 4a. The product proved to be N-iso-butyroylbenzamide (5a). Identification was made by m.p. and mixture m.p. The filtrate was concentrated to a

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small volume ( $\sim 2$  ml), acidified with HCl, filtered while hot, and allowed to cool. The crystalline product was removed by filtration, m.p. 213 °C; yields, 5% in the case of 2a and 10% in the case of 4a. It proved to be 5-phenyltetrazole (6a). Identification was made by m.p. and mixture m.p.

#### (b) Isopropylidene Anisuric Diazide (2c) or 3,4-Dihydro-6-anisyl-4-isopropylidene-2-oxo-1,3,5-

oxadiazine (4c)

The reaction was carried out as in (a), the insoluble part, m.p. 121 °C, yields 57% in the case of 2c and 70% in the case of 4c. It proved to be N-isobutyroylanisamide (5c). Identification was made by m.p. and mixture m.p.

The filtrate was concentrated, was cooled, and the precipitate was removed by filtration. It was crystallized from ethylacetate as colorless needles; m.p., 233 °C (decomp.) (10); yields, 41 % in the case of 2c and 20 % in the case of 4c. It proved to be 5-anisyltetrazole (6c). Identification was made by m.p. and mixture m.p.

(c) Cyclohexylidene Hippuric Diazide (2d) or 3,4-Dihydro-6-phenyl-4-cyclohexylidene-2-oxo-1,3,5oxadiazine

The reaction was carried out as in (a), the insoluble part, m.p. 157 °C, yields 42 % in the case of 2d and 70 % in the case of 4d. It proved to be N-hexahydrobenzoylbenzamide (5d). Identification was made by m.p. and mixture m.p.

The filtrate gave 6a; m.p., 212–213 °C (decomp.) (10); yields, 66% in the case of 2d and 20% in the case of 4d. It was identified as 5-phenyltetrazole by m.p. and mixture m.p.

#### Pyrolysis of Monoazides and Diazides

(a) Alkylidene and Arylidene Hippuric Azide

Isopropylidene hippuric azide 3a (1 g) was heated at its melting point under vacuum (10 mm) for a few minutes till it solidified, 4a was obtained, m.p. 174 °C (decomp.), yield 50%. It proved to be identical with 4-isopropylidene-6-phenyl-2-oxo-1,3,5-oxadiazine (4a) obtained by thermolysis of 3a (13) (m.p. and mixture m.p.). Similarly isopropylidene-p-chlorohippuric azide (3b) gave 4b, m.p. 165° (decomp.), yield 55% (decomposition time 30 min), isopropylidene anisuric azide (3c) gave 4c, m.p. 180°, yield 55%, cyclohexylidene hippuric azide; (3d) gave 4d, m.p. 162-164°, yield 55%, anisylidene hippuric azide 11a gave 12a, m.p. 171°, yield 43%, and furfurylidene hippuric

azide (18) gave 20, m.p. 166°, yield 44 %.

(b) Alkylidene Hippuric Diazides

The reaction was carried out as above using 2a to give 6a, m.p. 211-213° (decomp.), yield 48%. The latter proved to be 5-phenyltetrazole by melting point and mixture melting point with an authentic specimen (10). Similarly isopropylidene anisuric diazide 2c gave 5anisyltetrazole 6c, m.p. 233° (10), yield 54%, and cyclohexylidene hippuric diazide (2d) gave 5-phenyltetrazole, m.p. 211-213 °C, yield 67 %.

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