Tetrahedron Letters No.28, pp. 2729-2732, 1967. Pergamon Press Ltd. Printed in Great Britain.

PREPARATION AND PHOTOLYSIS OF 2-DIAZO-6-OXIMINO- AND 2,6-BISDIAZO-4-TERT. BUTYLCYCLOHEXANONE

R. Tasovac, M. Stefanović, and A. Stojiljković
Department of Chemistry, Faculty of Sciences,[x] and
Institute of Chemistry, Technology and Metallurgy
Belgrade, Yugoslavia

(Received 3 April 1967)

Reaction mechanism of diazoketone photolysis is assumed to involve the formation of α-keto-carbene intermediates, final products being dependent on the molecular structure and reaction medium. Numerous examples of Wolff-rearrangement (1) 1,2-hydrogen shift (2) and intermolecular reactions (3) are available.

However, the photolysis of bisdiazo compounds has been investigated only in case of 1,2-bisdiazo cyclic compounds (4) and with reactants in which two diazo groups were placed apart (5). Therefore, it seemed to be of interest to study the photolytic reactions of 1,3-bisdiazoketones which might be expected to afford keto 1,3-dicarbene intermediates. So far no data on this problem have been reported except for a note on the possible reaction path of bisdiazocyclohexanone decomposition (6)[xx].

---

[x] Full address: Studentski Trg 16, P.O.Box 550, Belgrade, Yugoslavia

[xx] After this manuscript was ready for publication, M.C. Cava, E.Y. Glamkowski and Ph.M. Weintranp (J.Org.Chem. **31**, 2755/1966)

In this paper we report on the preparation of 2,6-bisdiazo-cyclohexanone, 2-diazo-6-oximino- and 2,6-bisdiazo-4-tert.butylcyclohexanone and on their photolytic reactions.

Diazoketones were prepared according to Forster procedure (7) by the action of chloramine on oximinoketones in ammoniacal solution. The starting 2,6-dioximinocyclohexanone (I) and 2,6-dioximino-4-tert.butylcyclohexanone (II) were obtained by the oximination of the corresponding ketones with methyl nitrite in the yield of 75-80%. On the basis of the coloured metal complexes (8) these compounds were assumed to possess *anti*, *anti* configuration. In order to get evidence of the stereochemical relationship of oximino groups we have measured their ultraviolet absorption spectra and observed a characteristic bathochromic shift from 270 mμ to 335 mμ in alkaline media, which is consistent with the known spectral behaviour of *anti*-oximino-ketones (9). Another effect, general in the system having *anti*-oximino groups (10), was found with acetates of I and II which showed a hypsochromic shift from 270 mμ to above 211 mμ. Moreover, we carried out the solvolysis of acetates of I and II in aqueous-alcoholic solution and obtained products which also pointed to *anti*, *anti* configuration (11)[xxx].

---

reported first examples of steroidal α, α'-bisdiazoketones; However, upon ultraviolet irradiation of these compounds they obtained amorphous acidic fractions which were not further investigated.

[xxx] Ultraviolet irradiation of acetates of I and II in dioxane solution for various time periods gave a complex mixture of liquid acidic products (gas chromatography revealed the presence of ten components) which failed to be resolved so far.

Chloramination of I gave an oily product in 20% of the yield which showed all the characteristics of bisdiazoketones (ν CO=1610 cm^{-1} ; ν N_2=2060 cm^{-1}, on treatment with HI cyclohexanone was regenerated). However, efforts to obtain it in pure state were unsuccessful since it proved to be unstable and decomposed on standing. Therefore, further investigations were carried out with the corresponding 4-tert.butyl derivative (II) in the hope that the reaction product might be crystalline and more easily isolated. By the action of chloramine on II at low temperature (0-1°C) we succeeded in isolating crystalline monodiazo-6-oximino-4-tert.butylcyclohexanone (III) in a rather poor yield of 10%. However, at slightly higher temperature (5-10°C) solid 2,6-bisdiazo-4-tert.butylcyclohexanone (IV) was obtained in the yield of 48%. Structures of these compounds were deduced from elemental analysis and spectral characteristics (Compound III, m. p. 162-164°C, ν OH=3230 cm^{-1}, ν N_2=2090 cm^{-1}, ν CO=1680 cm^{-1}; $\lambda^{CH_3OH}_{max}$ =262 mμ and 325 mμ. Compound IV, m.p. 106-108°C, ν N_2=2060 cm^{-1}, ν CO=1610 cm^{-1} and $\lambda^{CH_3OH}_{max}$=325 mμ).

Irradiation of diazooximinoketone III in absolute ethanol under nitrogen and constant stirring at the room temperature for a period of 20 hours gave as the main reaction product a crystalline substance which was identified as the ethyl ester of 3-tert.butyl-5-oximinocyclopentane-carboxylic acid (V) on the basis of elemental analysis, spectral characteristics and saponification number; m.p. 30°C; yield 48%. Therefore, it follows that the oximino group was left intact during irradiation and the keto-carbene, formed by the expulsion of nitrogen, underwent Wolff rearrangement involving ring contraction.

Irradiation of 2,6-bisdiazoketone IV gave a more complex mixture of reaction products, from which we succeeded in isolating through column chromatography an oily substance to which the structure of the ethylester of 3-tert.butyl-cyclo-pent-1-ene-carboxylic acid (VI), yield 18%, was assigned on the basis of elemental analysis, chemical behaviour and infrared spectral characteristics; this structure was further suggested by appreciable ultraviolet absorption at 222 mμ characteristic of α, β-unsaturated cyclopentenecarboxylic acids (12). Unsaturation was characterized by positive tetranitromethane test. From these data it seems probable that keto-1,3-dicarbene displayed a combination of Wolff rearrangement and 1,2-hydrogen shift. It is not known whether the reaction and products are due to simultaneous or consecutive loss of diazo groups. Simultaneous loss of nitrogen from diazo groups would lead to keto 1,3-dicarbene, but production of VI might be explained by consecutive reactions without involving intermediate keto-dicarbene formation.

REFERENCES

1..F. Weygand and H.J. Bestmann, Angew.Chem., **72**, 535 (1960)
W. Kirmse, Carbene Chemistry, 118, (1964) and references therein.

2. V. Fraunen, Ann., **602**, 199 (1957)

3. W. Treibs, M. Quarg, Ann., **598**, 38 (1955)
H. Grundmann, Ann., **536**, 29 (1938)
P. Yates, J.Am.Chem.Soc., **74**, 5376 (1952)

4. A.T. Blomguist and L.H. Lin, J.Am.Chem.Soc., **75**, 2153 (1953)

5. K.W. Murray and A.M. Trozzolo, J.Org.Chem., **26**, 3109 (1967)

6. W. Kirmse, L. Horner and K. Muth, unpublished, cf. Angew. Chem., **71**, 539 (1959)

7. M.O. Forster, J.Chem.Soc., **107**, 260 (1915)

8. T.W.J. Taylor, E.K. Ewhank, J.Chem.Soc., 2818 (1926)
T.W.J. Taylor, J.Chem.Soc., 2018 (1937)

9. D.H.R. Barton, J.M. Beaton, J.Am.Chem.Soc., **83**, 4083 (1961)

10. A. Hassner, J.H. Pomeranz, J.Org.Chem., **27**, 1760 (1962)

11. Unpublished paper