BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (1), 365—366 (1975)

Synthesis and Rearrangement of Ethyl Aryloxyglyoxalate Arylhydrazones

A. Sami SHAWALI[1] and N. F. EWEISS
Department of Chemistry, Faculty of Science, University of Kuwait, Kuwait
H. M. HASSANEEN and M. SAMI
Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

(Received July 18, 1974)

Synopsis. Ethyl chloroglyoxalate arylhydrazones (III) react with sodium phenolates in ethanol and give ethyl aryloxyglyoxalate arylhydrazones (IV). The latter ester hydrazones rearrange at high temperatures to the hydrazides (V). Structural assignments have been made on the basis of elemental and spectral analyses and independent chemical evidence whenever possible.

Arylhydrazones of aryl carboxylates (I)[2–5] have been recently found to undergo a Chapman-like rearrangement[6] on heating and give the hydrazides (II). In previous communications, the synthesis and thermal rearrangement of two types of these esters were discussed.[2–5] In view of our continuing interest in this reaction, we have extended it to arylhydrazones of dicarboxylic acid esters. In this communication we wish to report on the synthesis and thermolysis of a series of ethyl aryloxyglyoxalate arylhydrazones (IV).

RC(OAr′):NNHAr
I


$$\mathrm{RCONHN}\begin{matrix}\mathrm{Ar'}\\ \mathrm{Ar}\end{matrix}$$
II

EtOOCC(Cl):NNHAr
III

EtOOCC(OAr′)=NNHAr
IV

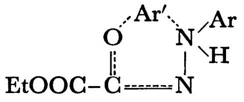

$$\mathrm{EtOOCCONHN}\begin{matrix}\mathrm{Ar'}\\ \mathrm{Ar}\end{matrix}$$
V

EtOOCCON(Ar′)NHAr
VI

Treatment of ethyl chloroglyoxalate arylhydrazones (III)[7] with ethanolic sodium phenolate at room temperature gave the corresponding esters (IV) in 60—80% yields. The structure assignments of the latter esters were derived from their elemental analyses and the following spectral data. Thus, the IR spectra of all products (IV) obtained exhibit two characteristic strong absorption bands near 1245 and 1720 cm^{-1}. The former band was assigned to the asymmetric stretch of the aryl ether linkage[3,8] whereas the latter to the α,β-unsaturated ester carbonyl group.[9] The absorption in the UV region was in each case characterized by the presence of three bands in the 340—320; 290—270; and 240—225 nm regions. Such spectral characteristics are similar to those of typical hydrazones.[3,9,10] The physical constants of the esters (IV) prepared are shown in Table 1.

Next we have found that heating IVa (Ar=Ar′=C_6H_5) in xylene for 4 hr under reflux afforded a colorless product that was analyzed correctly to be $C_{16}H_{16}N_2O_3$. It was distinguished from the starting material (IVa) by the lack of the C–OAr band and the presence of two CO bands at 1740 and 1710 cm^{-1} in its IR spectrum. On the basis of these data, the product thus obtained was assigned the structure of the hydrazide (Va, Ar=Ar′=C_6H_5). That the product obtained was the hydrazide Va and not the isomeric hydrazide (VIa, Ar=Ar′=C_6H_5) was supported by the fact that it gives upon hydrolysis an asymmetric diphenylhydrazine identified as its benzoyl derivative.[11]

The foregoing results indicate that the thermolysis of IV results in a 1,4-shift of an aryl group from oxygen to nitrogen probably *via* a five-membered cyclic transition state of type VII.[3]


VII

Chemical evidence for the structure V was further provided by the thermal rearrangement of the two isomeric esters IVb (Ar=C_6H_5; Ar′=4-$CH_3C_6H_4$) and

TABLE 1. ETHYL ARYLOXYGLYOXALATE ARYLHYDRAZONES $C_2H_5OOCC(OC_6H_4X)$=$NNHC_6H_4Y$

Compound No.	Substituents X	Substituents Y	Mp °C	Yield %	Molecular Formula	C % Calcd	C % Found	H % Calcd	H % Found	N % Calcd	N % Found
IVa	H	H	82—83	68	$C_{16}H_{16}N_2O_3$	67.59	67.50	5.67	5.70	9.85	10.00
IVb	H	4-CH_3	89—90	65	$C_{17}H_{18}N_2O_3$	68.43	67.93	6.08	6.10	9.39	9.37
IVc	4-CH_3	H	115—117	81	$C_{17}H_{18}N_2O_3$	68.43	68.26	6.08	6.04	9.39	9.33
IVd	4-Br	H	109	65	$C_{16}H_{15}BrN_2O_3$	52.90	52.84	4.16	4.18	7.71	7.67
IVe	4-Cl	H	107	72	$C_{16}H_{15}ClN_2O_3$	60.09	59.89	5.04	4.80	8.76	8.58
IVf	4-NO_2	H	129—130	78	$C_{16}H_{15}N_3O_5$	58.35	58.41	4.60	4.64	12.76	12.90
IVg	4-Br	4-CH_3	92—93	83	$C_{17}H_{17}BrN_2O_3$	54.12	54.08	4.54	4.47	7.42	7.60
IVh	4-NO_2	4-CH_3	167—168	80	$C_{17}H_{17}N_3O_5$	59.46	59.62	4.99	5.02	12.23	12.04
IVi	4-Br	3-CH_3	107—108	64	$C_{17}H_{17}BrN_2O_3$[a]	54.12	53.93	4.54	4.47	7.42	7.38
IVj	4-NO_2	3-CH_3	120—121	70	$C_{17}H_{17}N_3O_5$	59.46	59.01	4.99	4.85	12.23	12.15
IVk	3-CH_3	H	119	65	$C_{17}H_{18}N_2O_3$	68.43	68.50	6.08	5.98	9.39	9.30

a) Br, %: Calcd, 21.18; Found, 21.19%.

TABLE 2. HYDRAZIDES (V), $\mathrm{C_2H_5OOCCONHN}\Big\langle\begin{matrix}\mathrm{C_6H_4X}\\ \mathrm{C_6H_4Y}\end{matrix}$

Compound No.	Substituents X	Substituents Y	Mp °C	Yield %	Molecular Formula	Nitrogen % Calcd	Nitrogen % Found
Va	H	H	128—129	80	$C_{16}H_{16}N_2O_3$[a]	9.85	9.80
Vb	H	4-CH_3	104—105	85	$C_{17}H_{18}N_2O_3$[b]	9.39	9.50
Vd	4-Br	H	126	81	$C_{16}H_{15}BrN_2O_3$[c]	7.71	7.66
Ve	4-Cl	H	136—137	79	$C_{16}H_{15}ClN_2O_3$[d]	8.76	8.59
Vf	4-NO_2	H	184—185	82	$C_{16}H_{15}N_3O_5$	12.76	12.69
Vg	4-Br	4-CH_3	95—96	80	$C_{17}H_{17}BrN_2O_3$	7.42	7.39
Vk	3-CH_3	H	86—87	80	$C_{17}H_{18}N_2O_3$	9.39	9.18

a) Anal. Found: C, 67.43; H, 5.50%. Calcd: C, 67.59; H, 5.67%. b) Anal. Found: C, 68.27; H, 6.01%. Calcd: C, 68.43; H, 6.08%. c) Anal. Found: Br, 21.65%. Calcd: Br, 22.00%. d) Anal. Found: Cl, 11.04%. Calcd: Cl, 11.08%.

IVc (Ar=4-$CH_3C_6H_4$; Ar′=C_6H_5). The products obtained from the thermolysis of these two esters were identical in all respects. Other ester hydrazones in series IV, when subjected to the same treatment gave the corresponding hydrazides (V) in 80—88% yields. Table 2 lists the rearrangement products obtained together with their properties.

Experimental

Mp's were determined on a Meltemp apparatus and are uncorrected. IR spectra were obtained on a Beckman IR 12 spectrophotometer in KBr. UV spectra were measured on a Unicam SP1000 spectrophotometer in 95% EtOH. Microanalyses were performed by Alfred Bernhardt, Microanalytisches Laboratorium, West Germany.

Ethyl chloroglyoxalate arylhydrazones (IIIa—c) used in the synthesis of IV were prepared from the corresponding substituted anilines by diazotization and coupling with ethyl α-chloroacetoacetate in NaOAc-buffered solution of EtOH as previously described.[7] The compounds prepared gave the following values on analysis: (Compound No., Ar, mp, N% found, N% calcd): IIIa, C_6H_5, 79—80 °C (lit,[7b] mp 77—79 °C); IIIb, 4-$CH_3C_6H_4$, 96—97 °C, 11.62, 11.65; and IIIc, 3-$CH_3C_6H_4$, 74—75 °C, 11.59, 11.65.

Ethyl Aryloxyglyoxalate Arylhydrazones (IVa—k). To an ethanolic solution of sodium ethoxide [prepared from sodium metal (0.11 g, 0.005 g·atom) and 20 ml of absolute ethanol] was added 0.005 mol of the appropriate phenol. After being stirred for 10 min, III (0.005 mol) was added and the mixture was stirred for further 60 min, then left overnight at room temperature. The crude product precipitated was collected, washed with water and finally recrystallized from ethanol. The compounds prepared and their physical constants are given in Table 1.

Thermolysis of IV. Ethyl phenoxylglyoxalate *p*-tolylhydrazone (IVb) (0.8 g) in xylene (25 ml) was refluxed for 4 hr, then cooled. The white solid precipitated was collected and recrystallized from ethanol. A yield of 0.65 g (80%) of the hydrazide (Vb) melting at 104—105 °C was obtained. When the isomeric ester (IVc) was similarly treated, the same hydrazide (Vb) was obtained in 85% yield, mp 104 °C, not depressed when mixed with the product formed above by thermolysis of IVb.

The thermolysis of other ester hydrazones in series IV was performed by the same method described above and afforded the hydrazides listed in Table 2.

Hydrolysis of Va. Va (1 g) was refluxed in 95% ethanol (20 ml) and concd hydrochloric acid (20 ml) for 6 hr. The reaction mixture was concentrated to 1/4 volume, cooled, made alkaline and finally was extracted with ether. Treatment of the ether extract, after being dried, with benzoyl chloride while cooling and work up yielded white solid (0.5 g), which, on recrystallization from ethanol, gave *N*′-benzoyl-*N*,*N*-diphenylhydrazine, mp 189—190 °C. The mixture mp of the latter with an authentic sample[11] showed no depression.

References

1) To whom all inquiries should be addressed.

2) A. S. Shawali and H. M. Hassaneen, *Tetrahedron Lett.*, **1972**, 1299.

3) A. S. Shawali and H. M. Hassaneen, *Tetrahedron*, **28**, 5903 (1972).

4) A. S. Shawali and M. K. Ibrahim, This Bulletin, **46**, 1798 (1973).

5) A. F. Hegarty, J. A. Kearney, and F. L. Scott, *Tetrahedron Lett.*, **1972**, 3211.

6) J. W. Schulenberg and S. Archer, "Organic Reactions," Chap. 1, John Wiley & Sons, Inc., New York (1965).

7) a) D. A. Bowack and A. Lapworth, *J. Chem. Soc.*, **87**, 1859 (1905); b) R. Huisgen and H. J. Koch, *Ann. Chem.*, **591**, 200 (1955).

8) R. M. Silverstein and G. C. Bassler, "Spectroscopic Identification of Organic Compounds," John Wiley & Sons, Inc., New York (1967), pp. 91—93.

9) A. S. Shawali and A. Osman, *Tetrahedron*, **27**, 2517 (1971).

10) A. S. Shawali, M. I. Ali, M. M. Naoum, and A. L. Elansari, *ibid.*, **28**, 3805 (1972).

11) D. B. Sharp and C. S. Hamilton, *J. Amer. Chem. Soc.*, **68**, 588 (1946).