pump and was maintained at 0.1 ml/min. The nitrogen flow rate was 45 ml/min. The reaction products were collected in a receiver (cooled with ice) and analyzed.

2. Isomerization in the Presence of Potassium tert-Butoxide. This was accomplished at 180-210°C in an autoclave by the method in [1]. Mass spectrum (m/z, relative intensity, %): VII: 41 (20),* 43 (34.8), 55 (9.9), 67 (11.0), 95 (34.9), 109 (11.6), 123 (100.0), 166 (12.0); VIII: 41 (51.3), 43 (13.0), 53 (20.0), 54 (19.0), 55 (36.7), 67 (46.0), 68 (26.5), 71 (100.0), 79 (15.3), 81 (90.4), 84 (14.1), 95 (26.1), 96 (86.6), 97 (8.9), 166 (17.6).

3. Isomerization on Na/Al_2O_3. The catalyst was prepared by the method in [3], a solution of I or III in dry heptane was added, the mixture was thermostatted, and the reaction was carried out with stirring. After cooling, the reaction mixture was analyzed (Table 1).

4. Isomerization under the Influence of Iron Pentacarbonyl. A mixture of 9.8 g (0.1 mole) of I or III, 0.2 g of powdered NaOH, and 0.2 g of $Fe(CO)_5$ was placed in an autoclave and the mixture was heated at 180°C as argon was blown through it. The precipitate that formed after the reaction mass was cooled was removed by filtration, and the solution was washed with water, dried with $MgSO_4$, and analyzed (Table 2).

LITERATURE CITED

1. E. L. Eliel, B. E. Nowak, and R. A. Daignault, J. Org. Chem., 30, 2441 (1965).
2. I. Delaunau, A. Lebouc, and O. Riobe, Bull. Soc. Chim. France, Nos. 9-10, 547 (1979).
3. J. Shabtai, J. Org. Chem., 28, 2893 (1963).
4. M. Davidson, D. Lambroso, and M. Nellin, Belgian Patent No. 610941; Chem. Abstr., 57, 14934 (1962).
5. W. Rebatka, West German Patent No. 2,803,987; Chem. Abstr., 91, 175179 (1979).

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*The fragments with intensities ⩾10% with respect to the maximum peak are presented.

PHOTOLYSIS OF 5-DIAZO-2,2-DIMETHYL-4,6-DIOXO-1,3-DIOXANE (DIAZOISOPROPYLIDENEMALONIC ACID)†

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UDC 541.141'467.2'483.3

The principal pathway in the photochemical (λ > 210 nm) transformation of 5-diazo-2,2-dimethyl-4,6-dioxo-1,3-dioxane in an aqueous medium (or in methanol) is splitting out of nitrogen and the Wolff rearrangement to give the stable 2,2-dimethyl-5-oxo-1,3-dioxolane-4-carboxylic acid (or its methyl ester), which undergoes decarboxylation only at temperatures above 150°C, whereas it undergoes hydrolysis to a hydroxymalonic acid in the presence of trifluoroacetic acid.

One of the most characteristic reactions of 2-diazo ketones is the Wolff rearrangement [2]. For a long time it was supposed that a similar intramolecular process, viz., [1, 2] migration of an alkoxy group to an electrophilic center, is not realized in the diazo ester series [3]. However, it was subsequently established, both in the photolysis and in the thermolysis of various acyclic esters of diazoacetic and diazomalonic esters (see, e.g. [4, 5]), that products of the Wolff rearrangement are formed (in low yields). The question of the Wolff rearrangement of a cyclic ester of diazomalonic acid, viz., 5-diazo-2,2-dimethyl-4,6-dioxo-1,3-dioxane (I), remained a subject of dispute.

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†Communication 6 from the series "Chemistry of diazo dicarbonyl compounds." See [1] for Communication 5.

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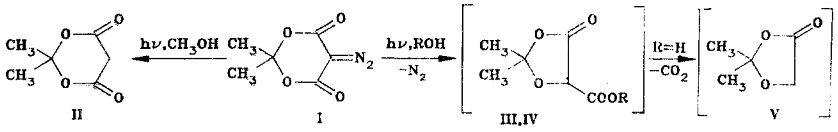
TABLE 1. Irradiation Conditions and Yields of the Reaction Products[a]

Irradiation conditions	Yields of reaction products, %				
	III	IV	II	VI	other reaction products
THF/H_2O; 3.5 h	56[b]	—	5	14	20
CH_3OH; 1 h 6 min	—	63	4	5	14

[a]These are the yields of the chromatographically pure substances. [b]According to the results of PMR spectroscopy, the amount of oxo acid III in the reaction mixture ranges from 60% to 63%, whereas the overall amount of acids (from the results of potentiometric titration) ranges from 72% to 73%.

On the other hand, it has been shown that the Wolff rearrangement is not observed in the photolysis of diazo compound I in methanol, and only isopropenylidenemalonic acid [Meldrum acid (II)] is formed as a result of the reductive elimination of nitrogen [6].



III R=H; IV R=CH_3

In another paper, on the other hand, it was reported that the photolysis of diazo compound I in a mixture of benzene with water or in methanol leads to the formation of only products of the Wolff rearrangement, viz., an "unstable β-keto acid" (III) or its methyl ester (IV) [7]. However, Kammula and co-workers [7] do not present any characteristics whatsoever of the reaction products formed, and, thus, their structures were not proved.*

The literature data on the transformations of diazo compound I in an aprotic medium (in the presence of olefins) are also extremely contradictory [8-10].

We made a comparative study of the photochemical transformations of O-, N-, and other heterocyclic analogs of diazodimedone [11]. In the course of these investigations we established that two principal photochemical processes are observed in the irradiation of diazo compound I with UV light ($\lambda > 210$ nm) in a protic medium, viz., aqueous tetrahydrofuran (THF) or methanol: splitting out of nitrogen and photochemical isomerization of diazo compound I to diazirine VI (Table 1).

The chief pathway in the photochemical decomposition of diazo compound I in both protic solvents, as in the case of the corresponding carbocyclic analogs [11], is the Wolff rearrangement. The result of this reaction is ring contraction with the formation of 2,2-dimethyl-5-oxo-1,3-dioxolane-4-carboxylic acid (III) (in an aqueous medium) or its methyl ester — in the case of photolysis in methanol. We found that 5-oxo acid III, under normal conditions, is absolutely stable, melts without decomposition at 105°C, and undergoes decomposition only upon heating above 150°C to give 4-oxo-2,2-dimethyldioxolane (V).

We also isolated, in a small amount from the reaction mixture, another photolysis product, viz., Meldrum acid (II); however, the yield of the latter in both solvents is an order of magnitude lower than the percentage of the products of the Wolff rearrangement.

The photochemical isomerization of diazo compound I to give diazirine VI under the indicated conditions of irradiation proceeds in low yield, and was evidently observed for the first time [9] in a protic medium for diazo compounds. In solution at 20°C diazirine VI undergoes rather rapid thermal isomerization to give diazo compound I; however, in solid form it remains unchanged for several months.

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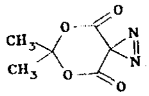
*Compounds III-V have not been described in the literature. With the exception of the assertion by Kammula [7], the literature cited in the indicated paper does not contain information regarding dioxolane V.



VI

In addition to the indicated compounds, from the reaction mixture, after irradiation in an aqueous medium, we also isolated diazo compound I (2% yield), malonic acid (6% yield), and tartramic acid (12% yield). These compounds are evidently formed as a result of subsequent dark and/or catalytic transformations of I-III, respectively, during the workup or separation of the reaction mixture on silica gel. Similar hydrolysis has already been observed in the case of the application of analytically pure Meldrum acid (II) and oxo acid III onto a plate for TLC. After elution with ether, in addition to starting II and III, the characteristic "spots" of, respectively, malonic and tartramic acids are detected on the plate. These qualitative observations are in agreement with the literature data, according to which 2,2-disubstituted 1,3-dioxanes and 1,3-dioxolanes are readily hydrolyzed in the presence of dilute acids [12] and on plates for TLC [13].

In the methanolic reaction mixture we also identified diazo compound I (1% yield) and, hypothetically, 2,2-dimethyl-4,6-dioxo-5-methoxy-1,3-dioxane (VII) (2.5% yield), which formally can be regarded as the product of incorporation of a cyclic dicarbalkoxy carbene into the O—H bond of methanol, as well as products of hydrolysis of II and IV.

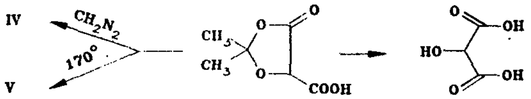
The structures of III-VI were established by means of spectral methods (IR and PMR spectroscopy) and were confirmed by chemical transformations.

The most distinctively structural features of 1,3-dioxolanes III-V show up in the PMR spectra. The signals of the geminal methyl groups, as in the case of other 2,2-disubstituted 1,3-dioxolanones [14], are observed at 1.55-1.70 ppm, whereas for I, II, and VI, which have 1,3-dioxane structures, they are found at 1,80-2.00 ppm. The signals of the methylidyne and methylene protons of III-V are shifted regularly to lower field (0.5-1.0 ppm, as compared, for example, with Meldrum acid).

The high frequencies of the valence vibrations of the carbonyl groups of III-V (above 1800 cm^{-1}) are also in agreement with the 1,3-dioxolane structure [14]. The position of the "doublet" band of the symmetrical deformation vibrations of the methyl groups, which is considered to be extremely convenient for diagnostic purposes [15], differs very little for 2,2-dimethyl-1,3-dioxolanones III-V and 2,2-dimethyl-1,3-dioxanes I, II, and VI (1390 ± 5 cm^{-1}).

The spectral characteristics provide evidence that 5-oxo acid III and its methyl ester V undergo virtually no enolization in solution.

We also studied some chemical transformations of 5-oxo acid III. Heating in an ampul at 170°C for 30 min leads to complete decarboxylation to give dioxolane V.



III

The hydrolysis of acid III in a mixture of chloroform with water with the addition of catalytic amounts of trifluoroacetic acid gives tartramic acid in high yield. Methyl ester IV is formed in quantitative yield from oxo acid III in an ether solution of diazomethane.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer, and the PMR spectra were recorded with a Varian CFT-20 spectrometer (80 MHz) at 25-30°C with tetramethylsilane (TMS) as the internal standard; the solvents and concentrations are indicated in each individual case. The potentiometric titration of a weighed sample of the substance in ethanol was accomplished with a 0.1 N solution of potassium hydroxide and a pH-673 pH meter with glass and calomel electrodes. Chromatography in a thin layer was carried out on Silufol UV-254 silica gel, while column chromatography was carried out on neutral Chemapol 40/100μ silica gel (activity II); the eluents were pentane—ether (3:1) (A), pentane—ether (2:1) (B), and pentane—ether (1:1) (C), as well as ether and methanol. Irradiation of diazo compound I was carried out with the UV light of a Hanau S-81 mercury lamp (110-130 W) in an apparatus with a quartz jacket (λ > 210 nm) [11].

5-Diazo-2,2-dimethyl-4,6-dioxo-1,3-dioxane (I). This compound, with mp 97°C [recrystallized from ethanol and sublimed *in vacuo* (0.03 mm) at 30-40°C] was obtained in 46% yield by a transfer reaction of the diazo function [16] in methylene chloride at 10-15°C. According to the data in [16], this compound had mp 94°C.

Irradiation of Diazo Compound I. A) In an Aqueous Medium. A solution of 1.70 g (0.01 mole) of diazo compound 1 in 80 ml of $THF-H_2O$ (40:1) was irradiated with vigorous stirring until nitrogen evolution ceased (3.5 h). The solvent was removed by distillation *in vacuo* at 10-12 mm and 15-20°C and then at 1 mm. The residue was dissolved in methylene chloride, and the solution was dried with anhydrous magnesium sulfate for 2 h. The solvent was removed by distillation, and the reaction mixture was recrystallized from 30 ml of methylene chloride. The precipitated colorless crystals of 5-oxo acid III [0.25 g (15%)] were separated and washed with cold methylene chloride. The solvent from the mother liquor was removed by distillation *in vacuo*, and the residue was chromatographed with a column packed with 40 g of silica gel to give (in the order of emergence from the column) the following compounds (compound, eluent, and yield given): diazirine VI, A, 0.20 g (12%); diazo compound I, B, 34 mg (2%); 5-oxo acid III, C, 0.70 g (43%); Meldrum acid II, ether, 85 mg (6%); malonic acid, ether, 62 mg (6%); tartramic acid, ether, 0.14 g (12%); a mixture of colored substances (TLC), methanol, 80 mg (not further investigated).

B) In Methanol. A solution of 1.70 g (0.01 mole) of diazo compound I was irradiated for 70 min, after which it was worked up as in the preceding experiment. After chromatography with a column packed with 50 g of silica gel, the following compounds were obtained (compound, eluent, and yield given): diazirine VI, A, 70 mg (4.5%); methyl ester IV, A, 1.10 g (64%); diazo compound I, B, 15 mg (1%); VII, C, 45 mg (2.5%); Meldrum acid II, C, 45 mg (3%); a mixture of substances, ether, 0.15 mg (according to TLC, the IR spectra, and potentiometric titration, the latter mixture contained malonic acid and other hydrolysis products).

The average yields of three to four experiments A and B are presented in Table 1.

2,2-Dimethyl-5-oxo-1,3-dioxolane-4-carboxylic Acid (III). This compound had mp 105-107°C (from CH_2Cl_2). IR spectrum (0.02 mole/liter in $CHCl_3$), cm^{-1}: 898 m, 991 m, 1096 w, 1131 s, 1152 w, 1270 s, 1385 m, 1392 m, 1606 w, 1743 s, 1779 s, 1804 vs, 2400-2600 broad m, 3505 w, 3605 w, and 3694 w. PMR spectrum (d_6-acetone, 0.4 mole/liter), δ: 1.62 (3H, s, CH_3), 1.66 (3H, s, CH_3), 5.13 (1H, s, CH), and 8.61 ppm (1H, s, OH). Found: C 45.0; H 5.1%; Э 161.4. $C_6H_8O_5$. Calculated: C 45.0; H 5.0%; 160.1.

Methyl 5-Oxo-2,2-dimethyl-1,3-dioxolane-4-carboxylate (IV). This compound had bp 70-73 °C (1mm) and mp 28-29°C. IR spectrum (0.02 mole/liter in $CHCl_3$), cm^{-1}: 896 m, 940 w, 996 m, 1023 w, 1098 w, 1153 s, 1262 s, 1281 m, 1384 m, 1392 m, 1604 w, 1762 vs, 1804 vs, 2962 w, and 3050 w. PMR spectrum ($CDCl_3$, 0.4 mole/liter), δ: 1.61 (3H, s, CH_3), 1.70 (3H, s, CH_3), 3.84 (3H, s, CH_3), and 4.91 ppm (1H, s, CH). Found: C 48.1; H 5.5. $C_7H_{10}O_5$. Calculated: C 48.3; H 5.7%.

6,6-Dimethyl-4,8-dioxo-5,7-dioxa-1,2-diazaspiro[2.5]oct-1-ene (VI). This compound had mp 82-83°C. IR spectrum (0.03 mole/liter in CCl_4), cm^{-1}: 920 s, 975 w, 1037 m, 1150 w, 1203 m, 1255 s, 1290 vs, 1387 m, 1397 m, 1745 w, 1775 vs, 1797 s, 2993 w, and 3015 w. PMR spectrum (0.4 mole/liter in $CDCl_3$), δ: 1.95 ppm (6H, s, $2CH_3$). Found: C 42.9; H 3.6; N 16.5%. $C_6H_6N_2O_4$. Calculated: C 42,4; H 3.6; N 16.5%.

4-Oxo-2,2-dimethyl-1,3-dioxolane (V). A 0,28-g sample of oxo acid III was heated in a sealed ampul at 170°C for 30 min. Workup gave dioxolane V in 97% yield (judged from the amount of CO_2 evolved) with bp 50-52°C (10 mm). IR spectrum (0.03 mole/liter in $CHCl_3$), cm^{-1}: 878 s, 981 m, 1072 m, 1123 s, 1278 vs, 1329 w, 1394 m, 1455 m, 1606 w, 1802 vs, 2872 w, 2944 w, and 2984 m. PRM spectrum (0.4 mole/liter in $CDCl_3$), δ: 1.57 (6H, s, $2CH_3$) and 4.31 ppm (2H, s, CH_2).

Hydrolysis of Oxo Acid III. The hydrolysis of a 0.23-g sample of III was carried out with stirring in 10 ml of a mixture of $CHCl_3-H_2O$ (5:1) and CF_3COOH (0.2 ml) at room temperature for 3 days. Removal of the volatile components *in vacuo* (8-10 mm) and washing of the residue with chloroform (two 10-ml portions) gave 0.16 g (94%) of tartramic acid with mp 146-148°C (from ether). According to the data in [17], this compound had mp 141-142°C and 156-158°C. PMR spectrum (d_6-acetone, 0.4 mole/liter), δ: 4.71 (1H, s, CH) and 8.5 ppm (3OH).

Reaction of Oxo Acid III with Diazomethane. A 50-ml sample of a standard ether solution of diazomethane (from 3 g of nitrosomethylurea) was added at 0°C to a solution of 1.32 g of the reaction mixture (after irradiation of 1.36 g of diazo compound I) in 20 ml of ether, and the resulting mixture was allowed to stand for 30 min. After the usual workup and vacuum distillation, the yield of methyl ester IV was 0.88 g (63%, based on diazo compound I).

LITERATURE CITED

1. V. A. Nikolaev, O. V. Zhdanova, and I. K. Korobitsyna, Zh. Org. Khim., 18, 559 (1982).
2. H. Meier and K.-P. Zeller, Angew. Chem., Int. Ed., 14, 32 (1975).
3. F. Weygand and H. S. Bestmann, Angew. Chem., 72, 535 (1960).
4. J. Shafer, P. Baronowsky, R. Laursen, F. Finn, and F. H. Westheimer, J. Biol. Chem., 241, 421 (1966).
5. D. C. Richardson, M. E. Hendrick, and M. Jones, J. Am. Chem. Soc., 93, 3790 (1971).
6. I. Hayasi, T. Okada, and M. Kawanisi, Bull. Chem. Soc., Jpn., 43, 2506 (1970).
7. S. L. Kammula, H. L. Tracer, P. B. Shevlin, and M. Jones, J. Org. Chem., 42, 2931 (1977).
8. M. Jones, W. Ando, M. E. Hendrick, A. Kulczycki, P. M. Howley, K. F. Hummel, and D. S. Malament, J. Am. Chem. Soc., 94, 7469 (1972).
9. T. Livingshouse and R. V. Stevens, J. Am. Chem. Soc., 100, 6479 (1978).
10. R. V. Stevens, G. S. Bissacchi, L. Goldsmith, and C. E. Strouse, J. Org. Chem., 45, 2708 (1980).
11. I. K. Korobitsyna and V. A. Nikolaev, Zh. Org. Khim., 12, 1251 (1976).
12. J. Apjok, M. Bartok, R. A. Karakhanov, and N. I. Shuikin, Usp. Khim., 38, 72 (1969).
13. J. E. G. Barnett and P. W. Kent, Nature, 192, 556 (1961).
14. M. Farines and J. Soulier, Bull. Soc. Chim. France, No. 1, 332 (1970).
15. L. Bellamy, New Data on the IR Spectra of Complex Molecules [Russian translation], Mir, Moscow (1971).
16. M. Regitz and D. Stadler, Ann., 678, 214 (1965).
17. Dictionary of Organic Compounds, 4th Edition, Vol. 5, London (1965), p. 2946.

TRICYANOVINYLATION OF PHENOXAZINE AND PHENOTHIAZINE

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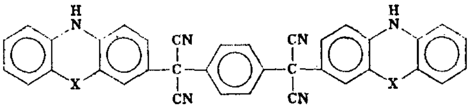
UDC 547.867.8'869.2:541.124

In the reaction of tricyanoethylene (TCE) with phenoxazine in DMF at 100°C, in addition to the principal reaction product — viz., 3-(tricyanovinyl)phenoxazine — 3-dicyanomethylene-3H-phenoxazine and 3-phenoxazinyl-3-(3H-phenoxazinylene)-cyanomethane are formed in small amounts. The latter two compounds were also obtained from phenoxazine and dibromomalononitrile. Phenothiazine reacts similarly with tetracyanoethylene. A reaction scheme is proposed, and in this scheme the formation of side products is explained by significant electron transfer in the tetracyanoethylene—heterocycle system. For the first time, 1,6 cleavage of HCN was detected, in which (in contrast to the known 1,6 cleavage of HCN from carbon atoms) the hydrogen is split out from the nitrogen atom.

In a previous study of the reaction of 7,7,8,8-tetracyanoquinodimethane (TCQD) with phenoxazine and phenothiazine it was found that the formation of a product of 1,6 addition to the quinoid system of TCQD (the principal product in the reaction of TCQD with anilines, phenols, pyrroles, and indoles) is observed only as an intermediate step [1]. The reaction results in the formation of I.



X=O, S

I

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