Bromination of Vinylpyrazoles Ia-d. These compounds were brominated in the cold or at room temperature in CCl_4. The precipitated hydrobromides were removed from the reaction mixtures by filtration. The CCl_4 was removed from the mother liquors, and the residual bromination products were recrystallized from hexane or petroleum ether. In the case of vinylpyrazole Id the products were isolated by fractional precipitation with ether and purified by recrystallization or sublimation.

LITERATURE CITED

1. G. G. Skvortsova, E. S. Domnina, N. P. Glazkova, N. N. Chipanina, and N. I. Shergina, Zh. Obshch. Khim., 41, 623 (1971).
2. L. P. Makhno, Master's Dissertation, IGU, Irkutsk (1975).
3. I. Z. Finar and K. I. Saunders, J. Chem. Soc., No. 8, 3967 (1963).
4. C. Trofimenko, J. Am. Chem. Soc., 88, 5588 (1966).
5. N. N. Chipanina, N. A. Kazakova, L. A. Shestova, E. S. Domnina, G. G. Skvortsova, and Yu. L. Frolov, Zh. Prikl. Spektrosk., 23, 97 (1975).

RESEARCH IN THE CHEMISTRY OF PYRAZOLIDINE

XXIII.* STUDY OF THE REACTION OF 3,5-DIOXOPYRAZOLIDINES WITH β-NITROSTYRENE

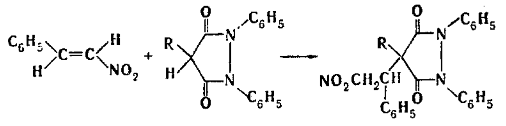
K. A. Sapozhnikova, A. S. Sopova,
and B. L. Moldaver

UDC 547.775'772.2

Products of Michael condensation containing a 1-phenyl-2-nitroethyl residue in the 4 position of the heteroring are formed in high yields in the reaction of equimolar amounts of 4-methyl-, 4-ethyl-, 4-isopropyl-, 4-butyl-, 4-isoamyl-, and 4-phenyl-1,2-diphenyl-3,5-dioxopyrazolidines and 1,2-diphenyl-3,5-dioxopyrazolidine with β-nitrostyrene under basic catalysis conditions. 1,2-Diphenyl-3,5-dioxopyrazolidine adds two equivalents of β-nitrostyrene when a twofold excess of the latter is present.

4-Monosubstituted and 4-unsubstituted 3,5-dioxopyrazolidines (DOP) are capable of adding compounds with an activated double bond – phenyl vinyl ketone [2] and azomethines [3] – to the 4-C atom of the heteroring. It is also known that arylnitroethylenes readily react with β-dicarbonyl compounds under the conditions of the Michael reaction [4-7]. The reaction of arylnitroethylenes with 1,2-diphenyl-DOP (DDP) and its 4-monosubstituted derivatives has not been studied.

We have studied the electrophilic addition of β-nitrostyrene (I) to 4-substituted DDP (IIa-g), as a result of which we obtained adducts of Michael condensation (IIIa-g) in 70-90% yields:



I IIa-g IIIa-g IV

II, III a $R = H$; b $R = CH_3$; c $R = C_2H_5$; d $R = iso\text{-}C_3H_7$; e $R = C_4H_9$;
f $R = iso\text{-}C_5H_{11}$; g $R = C_6H_5$; IV $R = C_6H_5CHCH_2NO_2$

Compound IIa also reacts with two equivalents of styrene I to give 4,4-bis(1-phenyl-2-nitroethyl)-DDP

---

* See [1] for communication XXII.

Leningrad Pharmaceutical-Chemistry Institute, Leningrad 197022. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 963-964, July, 1978. Original article submitted June 17, 1977.

0009-3122/78/1407-0776$07.50

TABLE 1. Products of Reaction of β-Nitrostyrene with DOP

Compound	Synthetic conditions			mp, °C[a]	R_f	Found, %			Empirical formula	Calc., %			Yield, %
	amount of starting comp., mole	amt. of solvent, ml	reaction time, h			C	H	N		C	H	N	
IIIa	0,01	130	30	146—147	0,14	68,4	4,3	10,4	$C_{23}H_{19}N_3O_4$	68,8	4,7	10,5	70[b]
IIIb	0,01	60	24[c]	132—134	0,16	69,7	5,2	10,0	$C_{24}H_{21}N_3O_4$	69,4	5,1	10,1	84
IIIc	0,01	40	10[c]	165—167	0,22	69,2	5,4	9,6	$C_{25}H_{23}N_3O_4$	69,9	5,4	9,8	65
IIId	0,01	100	14[c]	186—188	0,28	69,8	5,7	9,2	$C_{26}H_{25}N_3O_4$	70,4	5,6	9,2	70
IIIe	0,004	50	10 min	191—192	0,33	70,9	5,9	9,2	$C_{27}H_{30}N_4O_6$	70,9	5,9	9,2	88[d]
IIIf	0,005	17	15 min	179—181	0,38	71,6	5,9	8,9	$C_{28}H_{29}N_3O_4$	71,3	6,1	8,9	86
IIIg	0,001	40	5[c, e]	212—214	0,45	72,7	5,1	8,6	$C_{29}H_{23}N_3O_4$	72,9	4,9	8,8	94
IV	—	—	—	190—192	0,25	67,7	4,9	9,9	$C_{31}H_{26}N_4O_6$	67,6	4,7	10,2	60

---

[a] From ethanol. [b] The yield was 59% in anhydrous methanol and 70% in anhydrous ethanol (at 49°C for 2 h). [c] The excess benzene was removed by distillation at the end of the reaction. [d] The yield was 80% in anhydrous methanol (at 20°C for 40 min), 88% in anhydrous ethanol (at 20°C for 8 min), and 88% when the reaction components were fused (at 40°C for 5 min). [e] The reaction was carried out at 70°C.

(IV), which was also obtained from β-nitrostyrene and IIIa. We could not isolate IV in high yield, probably because of steric hindrance.

Bands characteristic for dioxo form DOP at 1750 and 1720 cm^{-1} are observed in the IR spectra of derivatives III and IV. The unconjugated nitro group is responsible for the presence of intense asymmetrical and symmetrical stretching vibrations at 1550 and 1350 cm^{-1}.

Absorption with a maximum at 238-240 nm (log ε 4.5-4.7) similar to the absorption observed for fixed dioxo form of DOP II is characteristic for the UV spectra of III in ethanol. An absorption maximum at 265 nm (log ε 4.7), which is shifted hypsochromically to 240 nm (log ε 4.5) when the ethanol solution is acidified, is characteristic only for IIIa, which is capable of enolization.

A multiplet at 5.1 ppm (2H) and a doublet of doublets at 4.1 ppm (1H), are observed in the PMR spectra of III; this indicates nonequivalence of the protons of the methylene group.

EXPERIMENTAL

The individuality of the compounds was confirmed by chromatography on Silufol UV-254 plates in chloroform with development in UV light. The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrophotometer. The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with a Varian EM-360A spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard. The properties of the synthesized compounds are presented in Table 1.

4-Substituted 4-(1-Phenyl-2-nitroethyl)DDP (IIIa-g). An equimolar amount of I and 0.01 g of triethylamine were added to a solution of the appropriate II (10 mmole) in anhydrous benzene, and the mixture was allowed to stand at 20°C. The resulting white crystalline precipitate was removed by filtration. When product III was quite soluble in benzene, the excess solvent was removed by distillation at the end of the reaction. The reaction conditions and properties of IIIa-g are presented in Table 1.

4,4-Bis(1-phenyl-2-nitroethyl)-DDP (IV). A) A heated (to 40°C) solution of 0.25 g (1 mmole) of IIa and 0.01 g of triethylamine in 40 ml of anhydrous methanol was added dropwise to a solution of 0.3 g (2 mmole) of I in 20 ml of anhydrous methanol, and the mixture was refluxed. After 7 h, the crystalline precipitate was removed by filtration to give 0.35 g (65%) of IV.

B) A 0.25-g (1 mmole) sample of IIa was dissolved at 40°C in 50 ml of anhydrous benzene, 0.3 g (2 mmole) of I and 0.01 g of triethylamine were added, and the mixture was maintained at 20°C for 12 h. Workup gave 0.33 g (60%) of IV.

C) A 0.4-g (1 mmole) sample of IIIa was dissolved in 10 ml of anhydrous benzene at 60°C, 0.45 g (3 mmole) of I and 0.01 g of triethylamine were added, and the mixture was maintained at 20°C for 10 h. The solvent was then removed, and the residue was chromatographed with a column filled with silica gel (elution with chloroform). The chloroform was removed from the eluate, and the residue was treated with ethanol and purified on a porous plate in an ether chamber to give 0.07 g (8%) of product.

LITERATURE CITED

1. B. L. Moldaver, V. V. Zverev, M. P. Papirnik, M. E. Aronzon, and Yu. P. Kitaev, Khim. Geterotsikl. Soedin., No. 3, 403 (1974).
2. E. Hannig, Arch. Pharm., 298/68, 441 (1963).
3. N. S. Kozlov and L. G. Ryzhkina, Dokl. Akad. Nauk Belorussk. SSR, 12, 47 (1968).
4. V. V. Perekalin and A. S. Sopova, Zh. Obshch. Khim., 24, 513 (1954).
5. V. V. Perekalin and K. S. Parfenova, Zh. Obshch. Khim., 30, 388 (1960).
6. E. M. Danilova and V. V. Perekalin, Zh. Obshch. Khim., 35, 1708 (1965).
7. M. J. Kamlet and D. J. Glover, J. Am. Chem. Soc., 78, 4556 (1956).

REACTION OF o-DIAMINOANTHRAQUINONES WITH MALONIC ESTER

V. A. Loskutov, A. V. Konstantinova,
and E. P. Fokin

UDC 547.785.5'892

The reaction of 1,2- and 2,3-diaminoanthraquinones with malonic ester was studied. It was established that the reaction products are N-ethoxymalonyl-o-diaminoanthraquinones and their heterocyclic derivatives – 1H-2-ethoxycarbonylmethylanthraimidazolediones. N-Ethoxymalonlyl-2,3-anthraquinone undergoes cyclization to 1H-2,3,4,5-tetrahydroanthra[2,3-b]-1,4-diazepine-2,4,7,12-tetraone when it is heated with sodium methoxide in absolute methanol, whereas 2-N-ethoxymalonyl-1,2-diaminoanthraquinone undergoes cyclization to 1H-2-ethoxycarbonylmethylanthra-1,2-d]imidazole-6,11-dione.

In [1] we showed that a monoacylation product – N-ethoxymalonyl-2,3-diaminonaphthaquinone – rather than a cyclic diamide – naphthoquinonediazepine-2,4-dione [2] – is formed in the reaction of 2,3-diaminonaphthoquinone with malonic ester. In the present research we studied the reaction of 1,2- and 2,3-diaminoanthraquinones (I and II) with malonic ester. The reaction is interesting from a synthetic point of view, since it may open up a pathway to the preparation of new heterocyclic derivatives of anthraquinone.

In contrast to 2,3-diaminonaphthoquinone [1], complex mixtures of products, which can be separated by chromatography on silica gel, are formed when diamines I and II are heated with excess malonic ester. We isolated monoacyl derivative III (30%) and a cyclization product – 2-carbethoxymethylimidazole V (32%) – from the mixture obtained in the reaction of diamine I with malonic ester. In the case of diamine II, in addition to monoacyl derivative IVa and imidazole VI, we observed the formation of appreciable amounts (26%) of diacylation product IVb.

The structures of the compounds obtained are confirmed by the analytical and spectral data (see Table 1). The IR spectra of III-VI contain absorption bands that confirm the presence of carbonyl groups of a quinone, amide (1640-1680 cm^{-1}), and an ester (1720-1740 cm^{-1}), as well as NH_2 and (or) NH groups (3150-3450 cm^{-1}). In addition to signals of protons of an anthraquinone ring at 7-8 ppm and NH groups, the PMR spectra contain a triplet and quartet of an ethyl group (1.20 and 4.00-4.15 ppm); the singlet at 3.55 or 4.00-4.10 ppm (in the case of V and VI) corresponds to the protons of the methylene group of a carbethoxymethyl fragment.

The proof of the structures of 1,2-diaminoanthraquinone derivatives III and V, for which products with isomeric structures is possible, is based on the following analogies. The chemical shifts of the amide

---

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk 630090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 965-968, July, 1978. Original article submitted June 29, 1977.

0009-3122/78/1407-0778$07.50