72. H. Wolfbauer, Monatsh., 25, 682 (1904).
73. H. K. Hall, J. Am. Chem. Soc., 78, 2717 (1956).
74. S. Holly and P. Sohár, Infravörös Spektroszkopia, Müszaki Könyvkiado, Budapest (1968), p. 110.

SYNTHESIS OF N-HETEROAROMATIC ONIUM BETAINES OF INDANE-1,3-DIONE

I. K. Raiskuma, G. G. Pukitis,
and O. Ya. Neiland

UDC 547.665

Betaines are formed in good yields in the reaction of N-heteroaromatic compounds with 2-dicyanomethyleneindane-1,3-dione oxide and its 4- and 5-halo derivatives in dioxane. The corresponding oxides were obtained by oxidation of 2-dicyanomethyleneindane-1,3-dione and its 4- and 5-substituted derivatives with hydrogen peroxide in dioxane. Data from the IR spectra of the compounds are presented.

Onium betaines in the indane-1,3-dione series were discovered recently. They have also recently been the subject of intensive study in view of their peculiar electrophysical and photoelectric properties [1] and their ability to form charge-transfer complexes (CTC) [2].

Several methods for the synthesis of N-heteroaromatic onium betaines of indane-1,3-dione are known. 2-N-Pyridiniaindane-1,3-dione betaine was first obtained in 1951 [3] by a method that seems of little interest for preparative purposes. Another method consisting in the reaction of indane-1,3-dione with pyridine and bromine was proposed in 1952 [4]. The reaction requires a large excess of the N-heteroaromatic base, and it is therefore of little promise for the preparation of indane-1,3-dione onium betaines from other heteroaromatic compounds that are less accessible than pyridine. In 1965 one of us [5] showed that cleavage of an indane-1,3-dione 2-phenyliodonium betaine in the presence of an N-heteroaromatic base is suitable for the preparation of indane-1,3-dione onium betaines. Somewhat later one of us [6] showed that indane-1,3-dione onium betaines can be obtained by reaction of phthalic anhydride with heteronia-substituted acetic acids in the presence of acetic anhydride and triethylamine.

The methods indicated above are not universal, and it therefore became necessary to develop a general method for the preparation of N-heteroaromatic indane-1,3-dione onium betaines. It occurred to us to use

TABLE 1. 2-Dicyanomethyleneindane-1,3-diones (I) and Corresponding Oxides (II)

Compound	X	Y	mp, °C (dec.)	Found, %			Empirical formula	Calculated, %			Yield, %
				C	H	N		C	H	N	
Ia	H	H	Lit. [7, 8]		—						—
Ib	Cl	H	250[a]	59,5	1,1	11,4	$C_{12}H_3ClN_2O_2$	59,4	1,2	11,6	70
Ic	H	Cl	248[b]	59,2	1,1	11,5	$C_{12}H_3ClN_2O_2$	59,4	1,2	11,6	70
Id	Br	H	265[b]	50,4	1,0	10,0	$C_{12}H_3BrN_2O_2$	50,2	1,1	9,8	65
IIa	H	H	204[c]	64,5	1,8	12,5	$C_{12}H_4N_2O_3$	64,3	1,7	12,5	92
IIb	Cl	H	208[d]	Cl 13,5	—	10,6	$C_{12}H_3ClN_2O_3$	Cl 13,7	—	10,8	88
IIc	H	Cl	212[e]	Cl 14,0	—	10,9	$C_{12}H_3ClN_2O_3$	Cl 13,7	—	10,8	88
IId	Br	H	207[c]	Br 26,0	—	9,2	$C_{12}H_3BrN_2O_3$	Br 26,4	—	9,2	85

---

[a] From dioxane–ethanol (1 : 1). [b] From dioxane. [c] From chlorobenzene. [d] From dioxane–benzene (1 : 2). [e] From dioxane–chloroform (1 : 2).

Riga Polytechnic Institute, Riga 226828. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 889-892, July, 1978. Original article submitted April 18, 1977; revision submitted December 5, 1977.

TABLE 2. Heteroaromatic Onium Betaines (III)

Compound	Y	X	B	mp, °C (dec.) (crystalliza. solvent)	Crystal color	Found, %			Empirical formula	Calculated, %			IR spectrum at 1400-1800 cm^{-1} (absorption, %)	Yield, %
						C	H	N		C	H	N		
IIIa	H	H	Pyridine	257[a]	Yellow	75,0	4,0	6,2	$C_{14}H_9NO_2$	75,3	4,0	6,3	1625 (56); 1587 (61)	90
IVb	Cl	H	The same	240[a]	The same	65,0	3,0	5,3	$C_{14}H_8ClNO_2$	65,0	3,0	5,0	1658 (8); 1620 (26); 1584 (30)	72
IIIc	H	Cl	"	262[a]	"	64,8	3,1	3,1	$C_{14}H_8ClNO_2$	65,0	3,0	5,0		70
IIId	Br	H	"	242[a]	"			4,6	$C_{14}H_8BrNO_2$			4,6	1660 (11); 1614 (48); 1571 (41)	58
IIIe	H	H	Quinoline	233[a]	Orange-yellow	79,4	3,8	4,9	$C_{18}H_{11}NO_2$	79,1	4,0	5,1	1651 (28); 1625 (46); 1578 (55)	67
IIIg	Cl	H	The same	249[a]	The same	69,9	3,1	4,4	$C_{18}H_{10}ClNO_2$	70,2	3,3	4,6	1658 (8); 1620 (26); 1584 (30)	64
IIIh	H	H	Isoquinoline	232[a]	"	79,2	3,9	5,1	$C_{18}H_{11}NO_2$	79,1	4,0	5,1	1638 (29); 1621 (54); 1580 (60)	80
IIIi	H	H	4-Picoline	267[a]	"	76,2	4,6	5,9	$C_{15}H_{11}NO_2$	76,0	4,6	5,9	1657 (15); 1616 (45); 1571 (65)	83
IIIj	H	H	3-Picoline	225[a]	Yellow			6,0	$C_{15}H_{11}NO_2$			5,9	1643 (49); 1615 (75); 1570 (90)	83
IIIk	H	H	Pyrazole	188[a]	Dark red	68,1	3,2	13,1	$C_{12}H_8N_2O_2$	68,2	3,3	13,3	1710 (41); 1650 (43); 1604 (37)	70
IIIl	H	H	Imidazole	256[b]	Orange			13,1	$C_{12}H_8N_2O_2$			13,3	1661 (17); 1622 (36)	86
IIIm	H	H	4-Cyanopyridine	260[a]	Lemon yellow	72,7	3,3	11,3	$C_{15}H_8N_2O_2$	72,6	3,2	11,3	1614 (42); 1576 (54)	40
IIIn	H	H	Cinnoline	265[a]	Violet red			10,2	$C_{17}H_{10}N_2O_2$			10,2	1681 (23); 1635 (52); 1589 (50)	56
IIIo	H	H	4,4'-Dipyridyl	300[c]	Yellow	76,1	4,2	9,3	$C_{19}H_{14}N_2O_2$	76,0	4,0	9,3	1661 (17); 1621 (55); 1586 (62)	76
IIIp	H	H	Pyrazine	300[d]	Green yellow	70,0	3,6	12,4	$C_{13}H_8N_2O_2$	69,7	3,6	12,5	1651 (29); 1626 (58); 1590 (58)	32
IIIq	H	H	Thiazole	280[a]	Orange yellow	S 6,2		13,8	$C_{12}H_7NO_2S$	S 6,1		13,9	1642 (20); 1612 (36); 1578 (47)	70

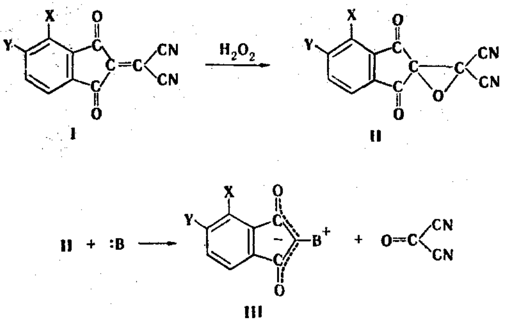
---

[a] From ethanol. [b] From water. [c] From dimethylformamide. [d] From dioxane.

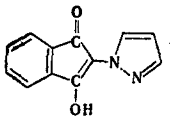
2-dicyanomethyleneindane-1,3-dione (Ia) [7, 8] for the preparation of the indicated compounds by oxidizing it to the corresponding oxide IIa, which, like tetracyanoethylene oxide [9], may give onium betaine III on reaction with an N-heteroaromatic base.

We carried out the oxidation of I in dioxane with hydrogen peroxide and obtained II (data on I and II are presented in Table 1).

It was found that the reaction of II with N-heteroaromatic bases takes place very readily in dioxane to give indane-1,3-dione onium betaines (III) [10] in excellent yields (see Table 2).



Compounds III are intensely yellow, are orange, or are red substances; this is associated with intramolecular charge transfer from the anionic part of the molecule to the onium substituent, during which the absorption is shifted bathochromically as the electron-acceptor properties of the onium substituent increase [11]. Groups of bands that are characteristic for the anionic form of β-diketones [12] are observed in the IR spectra of betaines III (Table 2). The assignment of the bands to the vibrations of definite C=O and C$\overset{-}{=}$C$\overset{-}{=}$C bonds is difficult because of the complex form of the vibrations due to equalization of the bond orders in the anionic system. Pyrazolium derivative IIIk for which normal wave numbers of the vibrations of the C=O and C=C bonds are observed in the IR spectra (Table 2) constitutes an exception to this generalization. Enol structure IV is therefore more likely for the pyrazolium derivative:



IV

As pointed out in [13], our research was concurrent with the research of the Junek group, which was able to obtain oxide II (X = Y = H) in 60% yield by oxidation of I (X = Y = H) and 2-N-pyridiniaindane-1,3-dione betaine (III, X = Y = H, and B = pyridine) by reaction of oxide II with pyridine in tetrahydrofuran. We obtained betaines III in considerably higher yields and demonstrated the extensive applicability of the reaction in our research [10].*

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with an IKS-14-A spectrometer.

5-Chloro-2-dicyanomethyleneindane-1,3-dione (Ib). A suspension of 1.44 g (0.008 mole) of 5-chloroindane-1,3-dione and 1.28 g (0.01 mole) of tetracyanoethylene in 10 ml of ethanol was stirred at room temperature for 30 min, as a result of which light-yellow plates of Ib precipitated. Compounds Ic,d were similarly obtained (Table 1).

2-Dicyanomethyleneindane-1,3-dione Oxide (IIa). A 4.16-g (0.02 mole) sample of Ia was dissolved in 200 ml of dioxane, and a solution of 3.7 ml of H_2O_2 (37%) in 5 ml of dioxane was added dropwise. The resulting solution gradually became colorless, after which it was diluted with a threefold volume of water and worked up to give colorless crystalline oxide IIa. Compounds IIb-d were similarly obtained (Table 1).

2-N-Pyridiniaindane-1,3-dione Betaine (IIIa). A mixture of 5 g (0.22 mole) of oxide IIa, 1.6 ml (0.2 mole) of pyridine, and 40 ml of dioxane was heated on a water bath for 5 min, after which it was cooled, as a result of which yellow acicular crystals of betaine IIIa precipitated. Betaines IIIb-q were similarly obtained (Table 2).

---

* The authors sincerely thank Yu. T. Rotberg for providing us with the 4- and 5-haloindanediones.

LITERATURE CITED

1. Structures and Tautomeric Transformations of β-Dicarbonyl Compounds [in Russian], Zinatne, Riga (1977), p. 361.
2. G. G. Pukitis, I. K. Raiskuma, and O. Ya. Neiland, Summaries of Papers Presented at the Third All-Union Conference on Charge-Transfer Complexes and Ion-Radical Salts [in Russian], Zinatne, Riga (1976), p. 79.
3. D. P. Vitkovskii and M. M. Shemyakin, Zh. Obshch. Khim., 21, 547 (1951).
4. W. H. Stafford, J. Chem. Soc., 581 (1962).
5. O. Ya. Neiland, M. A. Sile, and B. Ya. Karele, Izv. Akad. Nauk Latv. SSSR, Ser. Khim., No. 2, 217 (1965).
6. O. Ya. Neiland and A. P. Pavars, USSR Author's Certificate No. 228,669; Byul. Izobr., No. 32 (1968).
7. S. Chatterjee, J. Chem. Soc., B, No. 11, 1170 (1967).
8. H. Junek and H. Sterk, Tetrahedron Lett., 24, 4309 (1968).
9. Y. Kobayashi, T. Kutsuma, and R. Morinaga, Chem. Pharm. Bull. (Tokyo), 19, 2106 (1971).
10. O. Ya. Neiland and I. K. Raiskuma, USSR Author's Certificate No. 537,067; Byul. Izobr., No. 44, 72 (1976).
11. V. É. Kampar and O. Ya. Neiland, Izv. Akad. Nauk Latv. SSR, Ser. Khim., No. 6, 727 (1975).
12. Structures and Tautomeric Transformations of β-Dicarbonyl Compounds [in Russian], Zinatne, Riga (1977), p. 142.
13. H. Junek, D. Hermetter, and H. Fischer-Colbrie, Angew. Chem., 86, 380 (1974).

C NUCLEOSIDES

II.* PREPARATION OF 2-β-D-RIBOFURANOSYLBENZOTHIAZOLE, 5-β-D-RIBOFURANOSYLTETRAZOLE, AND 5-β-GLYCOSYL-1,3,4-OXADIAZOLE DERIVATIVES

I. Farkas, I. F. Szabo,
R. Bognar, and L. Sziladi

UDC 547.963.32

The conversion of 5-β-D-ribofuranosyl cyanides to the corresponding 2-β-ribofuranosylbenzothiazoles (under the influence of 2-aminothiophenol) and to 5-β-glycosyltetrazoles (by reaction with sodium azide and ammonium chloride) is described. It is shown that acylation of the latter structures with acetic anhydride or benzoyl chloride is a convenient method for the synthesis of 5-β-glycosyl-1,3,4-oxadiazoles.

We have previously reported [1] the possibility of conversion of acylated β-D-ribo-, β-D-xylo-, and β-D-galactopyranosyl cyanides to the corresponding 2-β-glycosylbenzothiazoles by the action of 2-aminothiophenol and to 5-β-glycosyltetrazoles by means of a mixture of sodium azide and ammonium chloride. In the present paper we report the use of these reactions for 5-β-D-ribofuranosyl cyanides (I) and the conversion of 5-β-glycosyltetrazoles to 5-β-glycosyl-1,3,4-oxadiazoles.

Up until now C-glucosyloxadiazoles have been described in the literature only in a few cases. Thus several "inverse" 2-phenyl-C-glycosyl-1,3,4-oxadiazoles have been synthesized from aldehydodialdose derivatives by a different method, and 2-amino-5-(β-DL-ribofuranosyl)-1,3,4-oxadiazole has been synthesized by oxidation of 3,4-O-isopropylene-2,5-anhydro-DL-allose semicarbazone with lead tetraacetate [3]. Several 3-β-D-ribofuranosyl-1,2,4-oxadiazole derivatives [4] and acyclic compounds with structures similar to those

---

*See [1] for communication I.

Department of Organic Chemistry, Lajos Kossuth University. Group for Research on the Chemistry of Antibiotics, Hungarian Academy of Sciences, Debrecen N-4010. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 893-896, July, 1978. Original article submitted June 17, 1977.