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DECARBOXYLATION IN PROTON ACCEPTOR SOLVENTS

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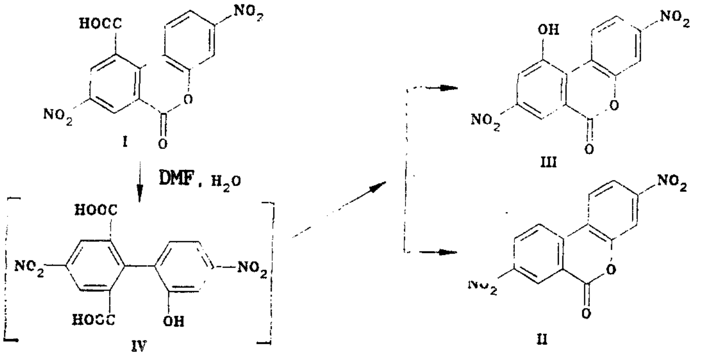
Heating 3,8-dinitro-10-carboxy-6H-dibenzo[b,d]pyran-6-one in DMSO, DMF, or HMPTA leads to decarboxylation and the replacement of the carboxyl group by a hydroxy group with the formation of 3,8-dinitro-6H-dibenzo[b,d]pyran-6-one and 3,8-dinitro-10-hydroxy-6H-dibenzo[b,d]pyran-6-one. The decarboxylation of 2,7-dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene in HMPTA is preceded by opening of the two lactone rings and the formation of a 1:4 molecular complex of 4,4'-dinitro-6,6'-dihydroxy-2,2'-dicarboxybiphenyl with HMPTA, whose structure was established by x-ray diffraction structural analysis.

In previous work [1], we showed that heating 3,8-dinitro-10-carboxy-6H-dibenzo[b,d]-pyran-6-one (I) in DMSO or DMF at reflux leads to decarboxylation and the replacement of the carboxyl group by a hydroxy group with the formation of 3,8-dinitro-6H-dibenzo[b,d]pyran-6-one (II) and 3,8-dinitro-10-hydroxy-6H-dibenzo[b,d]pyran-6-one (III).



A mixture of lactone I and acid IV, which may be seen as an intermediate, was isolated upon the slow evaporation of a solution of I in DMF at room temperature. In HMPTA, which is also a strong proton acceptor solvent, I undergoes ring opening almost immediately after entering solution by adding a water molecule with the formation of a 1:3 complex of hydroxy-acid IV with HMPTA. The same products are formed upon heating a solution of lactone I in HMPTA as upon heating in DMSO and DMF, namely, II and III.

The possibility of such reactions for other compounds containing lactone rings was indicated by the decarboxylation of 2,7-dinitro-5,10-dioxo-4,5,9,10-tetrahydro-4,9-dioxapyrene (V) synthesized according to our previous procedure [2]. Heating V in HMPTA at 100°C for 5 h gives decarboxylation product III in 63% yield. The two lactone rings in V are initially opened with the formation of a 1:4 molecular complex of 4,4'-dinitro-6,6'-dihydroxy-2,2'-dicarboxybiphenyl (DNCB) with HMPTA (VI) and then one carboxyl group is lost. Product III is readily acetylated by acetic anhydride with the formation of 3,8-dinitro-10-acetoxy-6H-dibenzo[b,d]pyran-6-one (VII).

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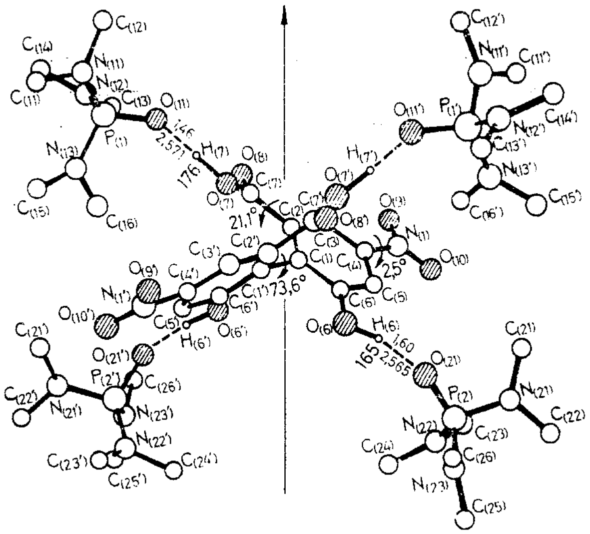
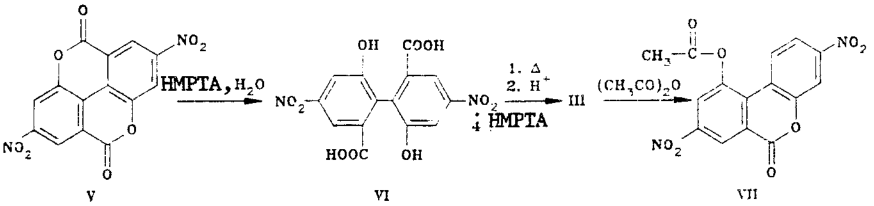


Fig. 1. The structure of complex VI (the hydrogen bonds are given by dashed lines).



The composition and structure of complex VI were established by x-ray diffraction structural analysis. The configuration of molecular complex VI is represented in Fig. 1 (the hydrogen atoms of the benzene rings and methyl groups are not given). The bond lengths and angles of DNCB and HMPTA with their standard deviations are given in Tables 1 and 2. The DNCB molecule in the crystal is located at a special position (on the two-fold axis traversing the midpoint of the C($_1$)–C($_1$') bond). One acid molecule coordinates four solvent molecules. Two HMPTA molecules are found per one-half DNCB molecule in the independent section. Complex VI is formed due to the linkage of the hydroxyl and carboxyl groups of the DNCB molecule with phosphoryl group oxygen atoms of the solvent molecules by rather strong hydrogen bonds. Many such examples have been given in the literature, in which hydroxyl groups form hydrogen bonds with carboxylate groups, oxygen, halide anions, carbonyl oxygen atoms, and water oxygen atoms [3]. The binding of proton donor group occurs in the direction of the unshared pair of the electron acceptor and corresponds to a potential energy minimum of the system formed [4]. The geometric parameters of the OH...O(=P) and CO_2H...O(=P) bonds of complex VI formed as the result of opening of the lactone rings in V are as follows: O($_6$)...O($_{12}$) 2.565(5), O($_6$) – H($_6$) 0.98(4), H($_6$)...O($_{12}$) 1.60(5) Å, O($_6$)H($_6$)O($_{12}$) 165(3)°, O($_7$)...O($_{11}$) 2.571(5), O($_7$)–H($_7$) 1.11(5), H($_7$)...O($_{11}$) 1.46(5) A, O($_7$)H($_7$)O($_{11}$) 176(3)°. The parameters of the hydrogen bonds in complex VI are similar to the values obtained for the complex of 2',4,4',6-tetranitro-2-carboxylbiphenyl (TNCB) with DMSO (VIII) [5] (O...O, 2.494 Å). The existence of complexes VI and VIII indicates that both the decyclization and cyclization processes proceed through the formation of an intermediate molecular complex of the starting compound with the proton acceptor solvent. The lengths of the hydrogen bonds in the complex of 1,8-biphenylenediol with HMPTA (2.601 and 2.613 Å [6]) are similar to those obtained for complex VI. The hydrogen bonds in complexes VI and VIII are apparently sufficiently strong to affect the activity of the molecules involved in their formation but sufficiently weak to prevent their conversion to other compounds.

The planarity of the molecule formed breaks down as a result of the opening of both heterocycles in V due to steric hindrance arising between the functional groups at C($_2$), C($_2$), C($_6$), and C($_6$'). The planes of the C($_1$)–C($_6$) and C($_1$')–C($_6$') rings are twisted about the C($_1$)–C($_1$') single bond by 73.6° and are inclined toward this bond by 2.1°. The twist of the C($_7$)O_2H carboxyl group is 21.1° and the inclination of the C($_2$)–C($_7$) bond relative to

TABLE 1. Bond Lengths (Å) in DNCB and HMPTA

Bond	d	Bond	d	Bond	d
$C_{(1)}-C_{(2)}$	1,391(5)	$N_{(1)}-O_{(9)}$	1,207(7)	$P_{(2)}-O_{(12)}$	1,472(3)
$C_{(1)}-C_{(6)}$	1,409(4)	$N_{(1)}-O_{(10)}$	1,200(6)	$P_{(2)}-N_{(21)}$	1,619(3)
$C_{(2)}-C_{(3)}$	1,389(5)	$P_{(1)}-O_{(11)}$	1,474(2)	$P_{(2)}-N_{(22)}$	1,628(4)
$C_{(3)}-C_{(4)}$	1,372(5)	$P_{(1)}-N_{(11)}$	1,635(4)	$P_{(2)}-N_{(23)}$	1,625(3)
$C_{(4)}-C_{(5)}$	1,371(6)	$P_{(1)}-N_{(12)}$	1,633(3)	$N_{(21)}-C_{(21)}$	1,441(8)
$C_{(5)}-C_{(6)}$	1,378(6)	$P_{(1)}-N_{(13)}$	1,615(4)	$N_{(21)}-C_{(22)}$	1,472(6)
$C_{(1)}-C_{(1')}$	1,496(7)	$N_{(11)}-C_{(11)}$	1,468(8)	$N_{(22)}-C_{(23)}$	1,443(7)
$C_{(2)}-C_{(7)}$	1,506(5)	$N_{(11)}-C_{(12)}$	1,438(7)	$N_{(22)}-C_{(24)}$	1,476(7)
$C_{(6)}-O_{(6)}$	1,353(4)	$N_{(12)}-C_{(13)}$	1,442(6)	$N_{(23)}-C_{(25)}$	1,450(6)
$C_{(7)}-O_{(7)}$	1,307(5)	$N_{(12)}-C_{(14)}$	1,461(5)	$N_{(23)}-C_{(26)}$	1,461(6)
$C_{(7)}-O_{(8)}$	1,209(5)	$N_{(13)}-C_{(15)}$	1,431(6)		
$C_{(4)}-N_{(1)}$	1,466(6)	$N_{(13)}-C_{(16)}$	1,472(7)		

TABLE 2. Bond Angles ω(°) in DNCB and HMPTA

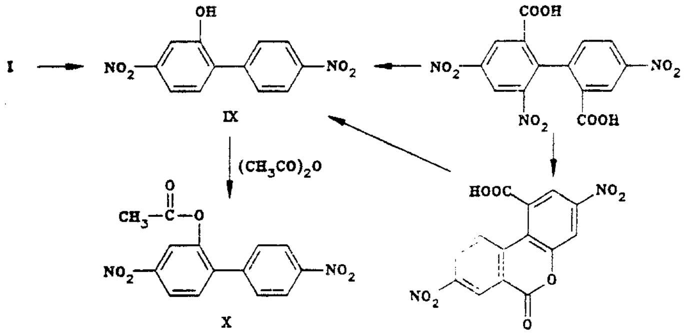
Angle	ω	Angle	ω	Angle	ω
$C_{(1)}C_{(2)}C_{(3)}$	120,2(3)	$C_{(6)}C_{(1)}C_{(1')}$	116,9(3)	$C_{(15)}N_{(13)}C_{(16)}$	111,8(4)
$C_{(2)}C_{(3)}C_{(4)}$	118,2(4)	$C_{(1)}C_{(6)}O_{(6)}$	117,0(3)	$O_{(12)}P_{(2)}N_{(21)}$	108,5(2)
$C_{(3)}C_{(4)}C_{(5)}$	123,5(4)	$C_{(5)}C_{(6)}O_{(6)}$	122,8(3)	$O_{(12)}P_{(2)}N_{(22)}$	117,1(2)
$C_{(4)}C_{(5)}C_{(6)}$	118,3(3)	$O_{(11)}P_{(1)}N_{(11)}$	111,1(2)	$O_{(12)}P_{(2)}N_{(23)}$	110,1(2)
$C_{(5)}C_{(6)}C_{(1)}$	120,2(3)	$O_{(11)}P_{(1)}N_{(12)}$	110,5(2)	$N_{(21)}P_{(2)}N_{(22)}$	106,8(2)
$C_{(6)}C_{(1)}C_{(2)}$	119,5(3)	$O_{(11)}P_{(1)}N_{(13)}$	111,9(2)	$N_{(21)}P_{(2)}N_{(23)}$	111,0(2)
$C_{(1)}C_{(2)}C_{(7)}$	123,7(3)	$N_{(11)}P_{(1)}N_{(12)}$	106,3(2)	$N_{(22)}P_{(2)}N_{(23)}$	103,2(2)
$C_{(3)}C_{(2)}C_{(7)}$	116,1(3)	$N_{(11)}P_{(1)}N_{(13)}$	106,9(2)	$P_{(2)}N_{(21)}C_{(21)}$	123,5(3)
$C_{(2)}C_{(7)}O_{(7)}$	116,0(3)	$N_{(12)}P_{(1)}N_{(13)}$	109,9(2)	$P_{(2)}N_{(21)}C_{(22)}$	122,7(3)
$C_{(2)}C_{(7)}O_{(8)}$	121,0(4)	$P_{(1)}N_{(11)}C_{(11)}$	124,0(4)	$C_{(21)}N_{(21)}C_{(22)}$	112,3(4)
$O_{(7)}C_{(7)}O_{(8)}$	123,0(3)	$P_{(1)}N_{(11)}C_{(12)}$	119,4(4)	$P_{(2)}N_{(22)}C_{(23)}$	121,6(4)
$C_{(3)}C_{(4)}N_{(1)}$	118,1(4)	$C_{(11)}N_{(11)}C_{(12)}$	116,1(5)	$P_{(2)}N_{(22)}C_{(24)}$	118,8(4)
$C_{(5)}C_{(4)}N_{(1)}$	118,4(3)	$P_{(1)}N_{(12)}C_{(13)}$	120,4(3)	$C_{(23)}N_{(22)}C_{(24)}$	113,8(4)
$C_{(4)}N_{(1)}O_{(9)}$	118,9(4)	$P_{(1)}N_{(12)}C_{(14)}$	123,8(3)	$P_{(2)}N_{(23)}C_{(25)}$	126,5(3)
$C_{(4)}N_{(1)}O_{(10)}$	118,5(5)	$C_{(13)}N_{(12)}C_{(14)}$	114,2(3)	$P_{(2)}N_{(23)}C_{(26)}$	119,5(3)
$O_{(9)}N_{(1)}O_{(10)}$	122,6(5)	$P_{(1)}N_{(13)}C_{(15)}$	127,3(3)	$C_{(25)}N_{(23)}C_{(26)}$	112,8(4)
$C_{(2)}C_{(1)}C_{(1')}$	123,5(3)	$P_{(1)}N_{(13)}C_{(16)}$	120,5(3)		

the aromatic ring is 2.0°. The bond in the hydroxyl group $C(_6)-O(_6)$ is tilted by 1.3°. The $N(_1)O(_2)$ groups at $C(_4)$ and $C(_4{}')$ are twisted by an angle of 2.5°, while the $C(_4)-N(_1)$ bond is inclined toward the ring plane by 1.3°. The lengths of the bonds in the carboxyl group in the DNCB molecule in complex VI (C–C, 1.506; C=O, 1.209; C–O(H), 1.307 Å) are the same as in the TNCB molecule (1.506, 1.199, and 1.308 Å, respectively [5]). This finding supports our hypothesis postulating some ionization of this group in complex VIII [5]. The $C(_6)-O(_6)$ bond length (1.353 Å) in the hydroxyl group is similar to the corresponding parameter of monosubstituted phenol derivatives with different substituent arrangements (1.343 Å for the ortho [7], 1.366 and 1.362 Å for the meta [8], and 1.361 Å for the para positions [9]) and complexed 1.8-phenylenedion (1.351 and 1.353 Å [6]). The inequality of the exocyclic bond angles $C(_1)C(_6)O(_6)$ and $C(_5)C(_6)O(_6)$ (117.0 and 122.8°) arises upon the formation of a directed hydrogen bond by the hydroxyl group [7-9] and is a consequence of bending of the C–O bond orbitals due to the repulsion of the H(O) and carbon atom of the aromatic system bound to the other OH group [9].

In the series of polar aprotic solvents, HMPTA and DMSO have the highest solvating capacity due to the ability of the oxygen atom to offer electrons to cations or accept them from anions [10]. The slight extension of the P=O bonds in HMPTA to 1.473 Å (the standard bond length is 1.46 Å [11]) and contraction of the mean P–N and N–C bond lengths to 1.626 and 1.455 Å (standard P–N, 1.65 Å [11], Csp^3–N, 1.47 Å) also indicate ionization of HMPTA molecules in complex VI. The coordination of the bonds of the phosphorus atoms in HMPTA molecules differs somewhat from ideal tetrahedral; the range of the OPN and NPN bond angles are 108.5-117.1° and 103.2-111.0°, respectively. Similar geometric parameters were found in other complexes and adducts of HMPTA [12-15]. The observed deviations of the bond lengths of the molecular fragments from standard values in the CO_2H and OH groups in the TNCB molecule, which acts as a proton donor, and of the P–O, P–N, and N–C bonds in the HMPTA molecules, which act as proton acceptors, indicate their mutual ionization upon the formation of complex VI.

The decarboxylation of dinitrodioxapyrene V upon heating in DMSO or DMF at reflux proceeds very slowly. The reaction rate increases upon the addition of solid alkali to the reaction solutions but its completion requires 10-12 h. The yield of III is 47-53%. The yield of III upon heating dinitrodioxapyrene V in aqueous alkali does not exceed 5-7%.

The reaction proceeds more extensively under the standard decarboxylation conditions involving heating of a quinoline solution of lactone I at reflux in the presence of copper. Compound I is converted to 4,4'-dinitro-2-hydroxybiphenyl (IX). This compound was obtained under the indicated conditions from 4,4',6-trinitrodiphenoic acid.and 3,8-dinitro-1-carboxy-6H-dibenzo[b,d]pyran-6-one. Heating IX in acetic anhydride at reflux leads to acetylation with the formation of 4,4'-dinitro-2-acetoxybiphenyl (X).



Heating dinitrodioxapyrene V in quinoline at reflux in the presence of copper leads to the formation of a complex product mixture, which is difficult to separate.

Thus, ordinary reactive proton acceptor solvents such as DMSO, DMF, and HMPTA may be recommended for carrying out reactions, proceeding with loss of a carboxyl group. HMPTA is the most efficient in this series.

EXPERIMENTAL

The IR spectra were taken on a Perkin—Elmer 580 spectrometer in KCl pellets. The reactions were carried out in DMSO, DMF, and HMPTA. The purity of the reaction products was monitored by thin-layer chromatography on Silfuol UV-254 plates.

The x-ray diffraction analysis was carried out on a Syntex $P\bar{1}$ automatic diffractometer using Mo radiation, graphite monochromator, and $\theta/2\theta$ scanning to $2\theta_{max} = 48°$. The unit cell parameters of the light yellow, monoclinic crystals of VI are as follows: $a = 22.021(7)$, $b = 13.403(4)$, $c = 19.538(7)$ Å, $\gamma = 80.05(2)°$, $V = 5680(3)$ Å^3, $M = 1081$ ($C_{14}H_8N_2O_{10}\cdot 4C_6H_{18}N_3OP$), space group $A2/a$, $Z = 4$, $d_{calc} = 1.264$ g/cm^3. The intensities of 1968 reflections with $I \geq 2\sigma(I)$ were used for interpreting the structure by the direct method and refined to R 0.036 (taking account of all the hydrogen atoms). The coordinates of the atoms (except for the methyl group hydrogen atoms) are given in Table 3. All the calculations were carried out using the Nicolet P3 SHELXTL and XTL programs. The elemental analysis data for carbon, hydrogen, and nitrogen corresponded to the calculated values.

3,8-Dinitro-10-carboxy-6H-dibenzo[b,d]pyran-6-one (I), $C_{14}C_6N_2O_8$. A. A sample of 3.1 ml (0.03 mole) 30% H_2O_2 was added dropwise to a suspension of 3.14 g (0.01 mole), 2,7-dinitro-4-carboxyfluorenone in 21 ml (0.4 mole) sulfuric acid (d 1.83) over 20 min maintaining the temperature at 20°C. The light yellow solution formed was stirred for 1 h and poured onto 100 g ice. The precipitate was filtered off, washed with water, and dried to give 3.08 g (93%) I as light yellow crystals, mp 237-238°C [16] (from acetic acid), R_f 0.51 (7:1 benzene—acetone). IR spectrum: 3400-2900, 1760 (C=O), 1730 (C=O), 1620, 1595, 1530 (NO_2), 1380, 1320 (NO_2), 1270, 1260, 1230, 1180, 1140, 1115, 1010, 980, 930, 905, 890, 835, 805, 800, 795, 750, 730 cm^{-1}.

B. A sample of 1.63 ml (0.042 mole) nitric acid (d 1.51) was added dropwise with ice cooling to a solution of 4.48 g (0.02 mole) 4-carboxyfluorenone in 175 ml (1.4 mole) sulfuric acid (d 1.83) and stirred at room temperature for 1 h. Then, 10.3 ml (0.1 mole) 30% H_2O_2 was added at a rate such that the temperature did not rise above 30°C. The mixture was stirred for 1 h and poured onto 300 g ice. The precipitate was filtered off, washed with water, dried, and recrystallized from acetic acid to give 5.7 g (86% relative to 4-carboxyfluorenone) I, identical to the sample obtained by procedure A.

TABLE 3. Coordinates of the P Atoms ($\times 10^5$), C, N, and O Atoms ($\times 10^4$) and H Atoms ($\times 10^3$)

Atom	x	y	z	Atom	x	y	z
$C_{(1)}$	2381(2)	4510(2)	3436(2)	$N_{(12)}$	236(1)	8394(2)	1288(2)
$C_{(2)}$	1848(2)	4370(3)	3094(2)	$N_{(13)}$	1043(2)	8898(3)	2179(2)
$C_{(3)}$	1636(2)	3455(3)	3148(2)	$C_{(11)}$	1463(3)	9821(5)	924(4)
$C_{(4)}$	1976(2)	2696(3)	3528(2)	$C_{(12)}$	1348(3)	8353(5)	1204(3)
$C_{(5)}$	2502(2)	2803(3)	3875(2)	$C_{(13)}$	−139(2)	7707(4)	1564(3)
$C_{(6)}$	2702(2)	3720(3)	3840(2)	$C_{(14)}$	−117(2)	9299(3)	970(2)
$C_{(7)}$	1479(2)	5157(3)	2639(2)	$C_{(15)}$	587(2)	9634(4)	2507(3)
$N_{(1)}$	1765(2)	1717(3)	3561(3)	$C_{(16)}$	1606(3)	9650(5)	2596(3)
$O_{(6)}$	3208(1)	3908(2)	4176(1)	$P_{(2)}$	38792(5)	17648(8)	54903(6)
$O_{(7)}$	1770(1)	5859(2)	2406(1)	$O_{(12)}$	3755(1)	2391(2)	4870(2)
$O_{(8)}$	951(1)	5115(2)	2490(2)	$N_{(21)}$	4095(2)	597(2)	5261(2)
$O_{(9)}$	1294(2)	1623(3)	3271(2)	$N_{(22)}$	3312(2)	1782(3)	6028(2)
$O_{(10)}$	2066(2)	1043(3)	3880(3)	$N_{(23)}$	4406(1)	2157(2)	5949(2)
$H_{(3)}$	128(1)	339(2)	291(2)	$C_{(21)}$	3921(4)	191(5)	4622(3)
$H_{(5)}$	271(2)	230(3)	412(2)	$C_{(22)}$	4360(3)	−203(4)	5744(3)
$H_{(6)}$	339(2)	326(3)	438(2)	$C_{(23)}$	2891(2)	1071(5)	5975(3)
$H_{(7)}$	152(2)	643(4)	205(3)	$C_{(24)}$	3043(3)	2750(5)	6355(4)
$P_{(1)}$	9644(5)	82726(7)	14879(5)	$C_{(25)}$	4527(3)	1956(5)	6670(3)
$O_{(11)}$	1240(1)	7194(2)	1554(1)	$C_{(26)}$	4898(2)	2575(4)	5610(3)
$N_{(11)}$	1292(2)	8812(3)	872(2)				

3,8-Dinitro-6H-dibenzo[b,d]pyran-6-one (II) and 3,8-dinitro-10-hydroxy-6H-dibenzo[b,d]pyran-6-one (III), $C_{13}H_6N_2O_7$. A. A solution of 3.3 g (0.01 mole) I in 100 ml HMPTA was heated for 2 h at 100°C, cooled to room temperature, and poured into a mixture of 300 g of ice and 10 ml concentrated hydrochloric acid. The precipitate was filtered off, washed with water, and dried to give 2.61 g of a substance, which was dissolved in 7:1 benzene—acetone and placed on a 40 × 1500 mm column packed with silica gel (40 × 100 μm). The column was eluted with 7:1 benzene—acetone. The first fraction after distillation of the solvent and recrystallization from acetic acid gave 0.83 g (29%) II as light yellow crystals, mp 211.5-212°C [16]. The second fraction gave 1.52 g (50%) III as light yellow crystals, mp 291.5-292.5°C (dec., from acetic acid), R_f 0.5 (7:1 benzene—acetone). IR spectrum: 3300-2900, 1730 (C=O), 1600, 1525 (NO_2), 1295, 1350 and 1335 (NO_2), 1320, 1300, 1240, 1200, 1160, 1135, 1105, 960, 905, 900, 850, 835, 790, 785, 740 cm^{-1}.

B. A solution of 3.28 g (0.01 mole) V in 100 ml HMPTA was heated for 5 h at 100°C, cooled to room temperature, and poured into a mixture of 300 g of ice and 10 ml concentrated hydrochloric acid. The precipitate was filtered off, washed with water, and recrystallized from acetic acid to give 1.9 g (63%) III, identical to the sample obtained by procedure A.

C. A sample of finely ground potassium hydroxide powder was added to a solution of 6.56 g (0.02 mole) V in 150 ml DMSO and heated at reflux for 5 h. The solution was cooled to room temperature and poured into a mixture of 200 g ice and 25 ml concentrated hydrochloric acid. The precipitate was filtered off, washed with water, and recrytallized from acetic acid to give 3.62 g (60%) III, identical to the samples obtained by the above procedures.

D. A sample of 20 g copper powder was added to a solution of 6.56 g (0.02 mole) V in 200 ml quinoline and heated at reflux for 2 h. The reaction mixture was cooled to room temperature and filtered to remove the slurry. The filtrate was poured into 250 ml 5% hydrochloric acid. The precipitate was filtered off, washed with water, and recrystallized from acetic acid to give 2.68 g III.

The slurry was treated with two 100-ml portions of DMF. The extracts were combined, evaporated to a volume of 25-30 ml, and diluted with water. The precipitate was filtered off, washed with water, and recrystallized from acetic acid to give 0.64 g III. The total yield of III was 3.32 g (55%).

3,8-Dinitro-10-acetoxy-6H-dibenzo[b,d]pyran-6-one (VII), $C_{15}H_8N_2O_8$. A solution of 6.04 g (0.02 mole) III in 100 ml acetic anhydride was heated at reflux for 1 h, cooled to room temperature, and poured onto 300 g ice. The precipitate was filtered off, washed with water, and dried to give 5.81 g (84.4%) VII as pale yellow crystals, mp 215-216°C (from acetic acid), R_f 0.33 (benzene). IR spectrum: 3400, 3100, 1780 ($COCH_3$), 1760 (CO_2), 1600, 1525 (NO_2), 1450, 1350, 1330 (NO_2), 1315, 1295, 1280, 1245, 1205, 1175, 1145, 1125, 1100, 1020, 960, 925, 900, 890, 850, 830, 785, 740, 725 cm^{-1}.

4,4'-Dinitro-2-hydroxybiphenyl (IX), $C_{12}H_8N_2O_5$. A. A sample of 5 g copper powder was added to a solution of 3.77 g (0.01 mole) 4,4',6-trinitrodiphenoic acid in 100 ml quinoline and heated at reflux for 2 h. The hot reaction mixture was filtered to remove the slurry. The filtrate was cooled to room temperature and poured into 150 ml 5% hydrochloric acid. The precipitate was filtered off, washed with water, and recrystallized from acetic acid to give 1.32 g (51%) IX as pale yellow crystals, mp 228.5-229.5°C, R_f 0.7 (5:1 benzene-acetone). IR spectrum: 3530, 1600, 1515 (NO_2), 1485, 1435, 1400, 1350 (NO_2), 1305, 1270, 1260, 1190, 1120, 1100, 1090, 1010, 945, 855, 815, 765, 740, 725 cm^{-1}.

B. Product IX was also obtained by this method from 3,8-dinitro-1-carboxy-6H-dibenzo [b,d]pyran-6-one and from I in 67 and 60% yield, respectively.

4,4-Dinitro-2-acetoxybiphenyl (X), $C_{14}H_{10}N_2O_6$. A solution of 5.2 g (0.02 mole) IX in 50 ml acetic anhydride was heated at reflux for 1 h, cooled to room temprature, and poured into a mixture of 200 g ice and 10 ml concentrated hydrochloric acid. The precipitate was filtered off, washed with water, and dried to give 5.32 g (88%) X as pale yellow crystals, mp 150-151°C (from acetic acid), R_f 0.3 (benzene). IR spectrum: 3450, 3100, 1780 (C=O), 1600, 1520 (NO_2), 1480, 1400, 1350 (NO_2), 1200, 1175, 1135, 1110, 1090, 1010, 950, 910, 875, 860, 835, 815, 740 cm^{-1}.

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