The Acid-catalyzed Decomposition of α-Diazo β-Hydroxy Ketones

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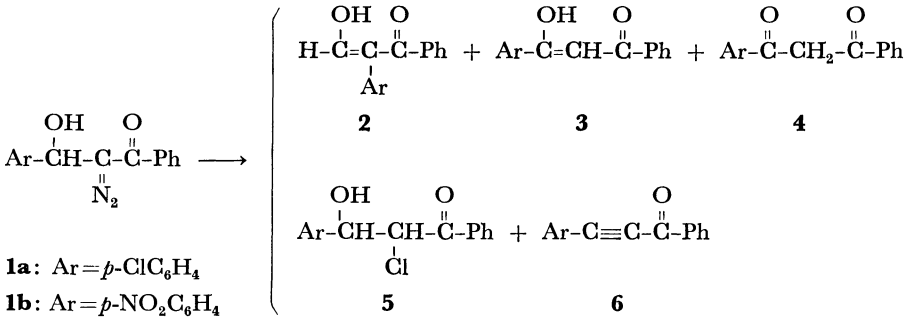
The proton acid-catalyzed decomposition of 3-aryl-2-diazo-3-hydroxy-1-phenylpropanone (**1**) gave aryl and hydrogen migration products. The former was the enol-form (**2**) of 2-aryl-3-phenyl-1,3-propanedione and the latter was the enol- (**3**) and keto-form (**4**) of 1-aryl-3-phenyl-1,3-propanedione. The product ratios, **2**/(**3**+**4**), were affected by the catalysts and solvents used. More polar solvents favored the formation of aryl migration products (**2**). On the other hand, the BF_3-catalyzed decomposition of **1** gave acetylenic ketones as main products along with **2**, **3**, and **4**. The TsOH-catalyzed decomposition of 2-diazo-3-hydroxy-3-phenyl-1-indanone, (cyclic α-diazo β-hydroxy ketone), gave 2-phenyl-1,3-indandione quantitatively through phenyl migration.

The acid-catalyzed decomposition of diazo compounds has been studied extensively from the synthetic and mechanistic view points.[1] However, only a few papers have been published on the acid-catalyzed decomposition of diazo carbonyl compounds bearing a hydroxyl group on the carbon atom adjacent to the diazomethyl-carbon. Wenkert and McPherson have reported the BF_3-catalyzed decomposition of α-diazo β-hydroxy esters and ketones to give the corresponding acetylenic esters and ketones.[2] Schöllkopf and his co-workers obtained ethyl 2-methyl-3-oxobutanoate as a methyl migration product in the HCl-catalyzed reaction of ethyl 2-diazo-3-hydroxy-3-methylbutanoate.[3] Similar observations were also reported by Disteldorf and Regitz in the BF_3- or HCl-catalyzed decomposition of 1-diazo-2-hydroxyethyldiphenylphosphine oxide.[4]

As an extension on the acid-catalyzed reaction of diazo carbonyl compounds,[5] we describe here the protonic or Lewis acids-catalyzed decomposition of 3-aryl-2-diazo-3-hydroxy-1-phenyl-1-propanones (**1**) to give aryl and hydrogen migration products and acetylenic ketones depending on the catalysts used.

Results and Discussion

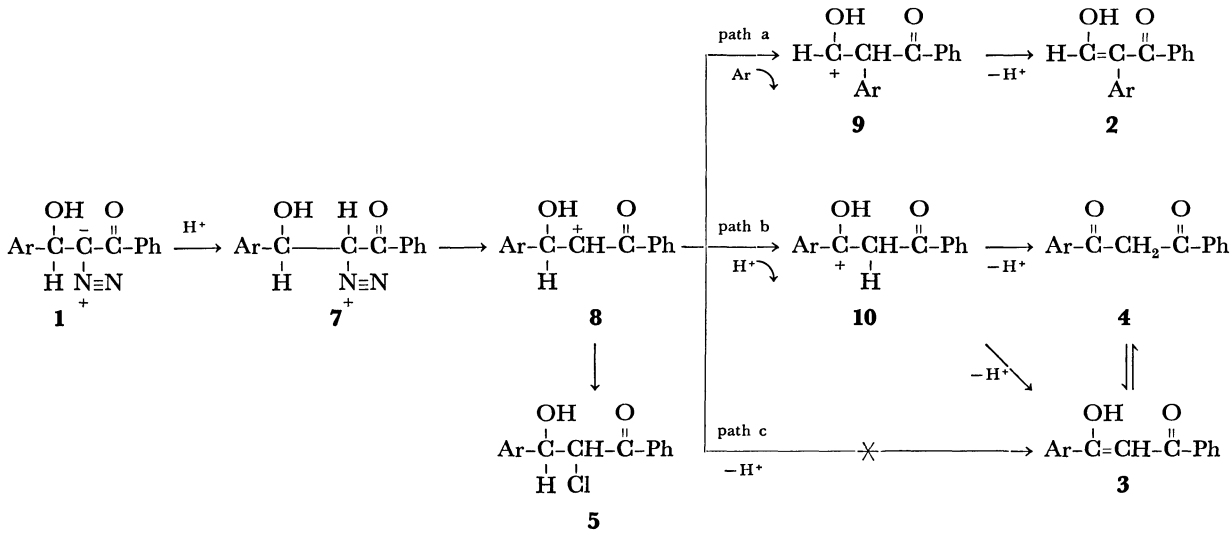
An acetonitrile solution of 3-(*p*-chlorophenyl)-2-diazo-3-hydroxy-1-phenyl-1-propanone (**1a**) was treated with a catalytic amount of acid at 30 °C. In the proton acid-catalyzed reaction, the major product was the enol-form (**2a**) of 2-(*p*-chlorophenyl)-1,3-propanedione accompanying the enol- (**3a**) and keto-form (**4a**) of 1-(*p*-chlorophenyl)-3-phenyl-1,3-propanedione. In the BF_3-catalyzed reaction, however, 3-(*p*-chlorophenyl)-1-phenyl-2-propyn-1-one (**6a**) was obtained as a major product along with **2a**, **3a**, and **4a**. 3-(*p*-Nitrophenyl)-2-diazo-3-hydroxy-1-phenyl-1-propanone (**1b**) also gave similar products, with a few differences in the product ratios. The main difference is that **2b** is still the main product in the BF_3-catalyzed reaction of **1b** contrary to the case of **1a**. The other point is that the yield of the chlorinated product (**5b**) is much higher than that of **5a** in the HCl- and $AlCl_3$-catalyzed reactions of **1b**. The results are summarized in Table 1.



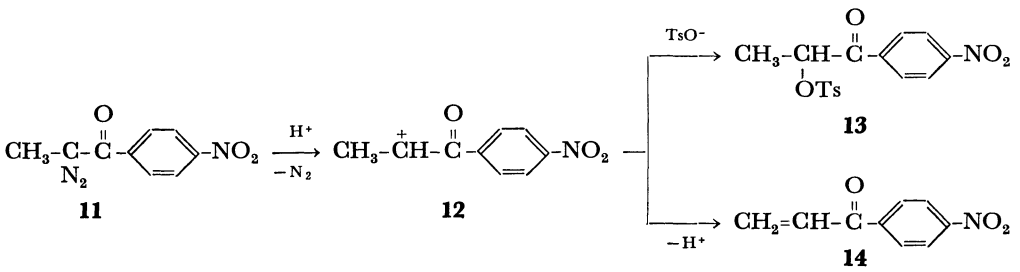
Scheme 1.

Table 1. Yields of products in the acid-catalyzed decomposition of **1** in acetonitrile at 30 °C

	Acid	**2**	**3**	**4**	**5**	**6**	**2**/(**3**+**4**)
1a	TsOH	84.3	3.0	8.0	—	—	7.7
	aq.HCl	76.1	5.5	2.6	14.5	—	9.4
	$AlCl_3$	68.8	8.0	3.1	18.8	—	6.2
	$BF_3(OEt_2)$	11.9	1.2	—	—	75.2	9.9
1b	TsOH	64.1	23.3	10.9	—	—	1.9
	aq.HCl	38.0	16.7	5.7	34.6	—	1.7
	$AlCl_3$	24.6	22.2	trace	47.1	—	1.1
	$BF_3(OEt)_2$	50.8	4.1	4.8	—	29.8	5.7



Scheme 2.



Scheme 3.

The difference between the behavior of proton acid and that of BF_3 may be attributed to the difference of the catalytic actions on the starting diazo ketones (**1**) as is described below.

In the proton acid-catalyzed reaction, the reaction may be initiated by protonation on the diazomethyl-carbon of **1** to give diazonium ion (**7**).[3,4] Successive elimination of nitrogen, aryl migration, and deprotonation lead to the enol ketone (**2**) through carbonium ion intermediate (**8** and **9**) (path a in Scheme 2). The hydrogen migration of **8** will afford diaroylmethane (**4**) and its enol-isomer (**3**) *via* deprotonation of intermediate (**10**) (path b in Scheme 2). Although direct deprotonation from the carbon attached by the hydroxyl group of **8** seems to give the enol-isomer (**3**) directly (path c in Scheme 2), this process can be excluded based on the results of the pinacol rearrangement of 1,1,2-triphenylethane-2-*d*-1,2-diol.[6]

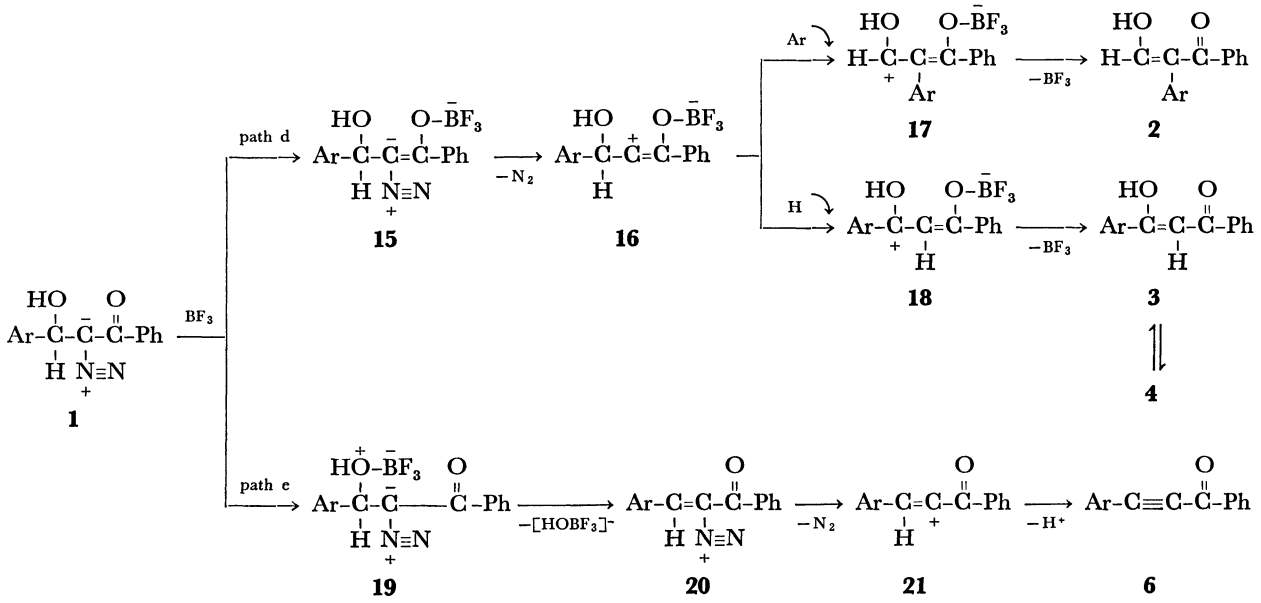
The HCl-catalyzed reaction of **1** gave 3-aryl-2-chloro-3-hydroxypropiophenone (**5**) along with **2**, **3**, and **4**. This chlorinated compound may be produced by the attack of chloride ion with its high nucleophilicity on the carbonium ion intermediate (**8**) in competition with the aryl and hydrogen migrations. The higher yield of chlorinated product (**5b**) in the reaction of **1b** than that of **5a** may be explained by the high positive charge density on carbonium carbon in **8b** caused by the electron attracting nitro group on the phenyl ring. The behavior of $AlCl_3$ was quite similar to that of hydrochloric acid. This may be due to hydrogen chloride produced by the reaction with moisture in the reaction system. However, no tosylate[7] corresponding to **5** was obtained in the reaction when *p*-toluenesulfonic acid was used as a catalyst. And neither oxazoles[5a] nor oxazolium salts,[8] which might be produced by the reaction of **8** with acetonitrile used as a solvent, were recognized in the reaction products.

When α-diazo-*p*-nitropropiophenone (**11**), instead of **1**, was treated with an equivalent amount of TsOH in acetonitrile at 0—5 °C, the reaction gave 1-(*p*-nitrobenzoyl)ethyl tosylate (**13**) as a main product in 69% yield accompanying a small amount (13%) of *p*-nitrophenyl vinyl ketone (**14**) without formation of the corresponding oxazoles (Scheme 3). Therefore, the preference of the migration of aryl group or hydrogen atom to the intermolecular nucleophilic attack of tosylate ions or the nitrogen atom of acetonitrile to the carbonium ion intermediate (**8**), as has been observed in the decomposition of **1**, seems to be attributable to the effect of hydroxyl group attached to the carbon atom adjacent to the diazo carbon.

As listed in Table 1, the yields of aryl migration products (**2**) were larger than those of hydrogen migration products (**3**+**4**). The results may be due to the difference of resonance stabilities in the transition states of aryl- and hydrogen-migrations. Moreover the product ratios, **2**/(**3**+**4**), in the reaction of **1b** (Ar=*p*-$NO_2C_6H_4$) were observed to be smaller than those in the reaction of **1a** (Ar=*p*-ClC_6H_4), suggesting that the migratory aptitude of *p*-nitrophenyl group is smaller than that of *p*-chlorophenyl group. The

Table 2. Solvent effect on the yields of products in the TsOH-catalyzed decomposition of **1a** at 30 °C

Solvent	μ(D)	ε	Products yield/% 2	3	4	2/(2+4)
Cyclohexane	0.00	2.02	46	38	14	0.9
CCl_4	0.00	2.24	44	22	16	1.2
Benzene	0.00	2.28	54	24	17	1.3
Dioxane	0.45	2.21	66	25	8	2.0
$C_2H_5OC_2H_5$	1.15	4.81	68	9	11	3.3
$CHCl_3$	1.15	4.81	68	9	11	3.4
$CH_3OCH_2CH_2OCH_3$	1.71	7.20	67	9	9	3.7
THF	1.75	7.58	66	7	11	3.7
CH_2Cl_2	1.14	8.93	71	7	8	4.7
CH_3CN	3.44	33.0	84	3	8	7.7

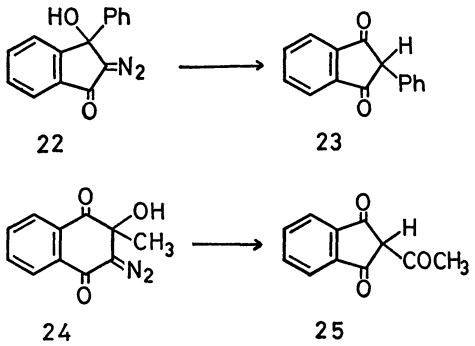


Scheme 4.

results further seem to accord with the view that the electron-withdrawing substituents reduce the migratory aptitude of aryl groups in the pinacol rearrangement.[9]

When the TsOH-catalyzed decomposition of **1a** was carried out in various solvents at 30 °C, it was recognized that the more polar solvents favored the migration of *p*-chlorophenyl group. In this case, the tendency of the migration of *p*-chlorophenyl in comparison to that of hydrogen, **2**/(**3**+**4**), seems to fit better to dielectric constant (ε) than to dipole moment (μ) (Table 2). The large migratory aptitude of aryl groups in polar solvent may be explained by the "principle of reactivity and selectivity relationship."[10] In other words, solvation stabilization of the carbonium ion intermediate (**8**) in polar solvents increases the amount of aryl migration products (**2**), owing to the large selectivity of **8** to the reaction paths (a and b).

In the BF_3-catalyzed reaction, two kinds of initial attack of BF_3 are expected. When the initial attack of BF_3 occured on the carbonyl-oxygen atom of **1**, the reaction will proceed to give diazonium ion intermediate (**15**),[5,11] from which two kinds of enol ketones (**2** and **3**) and β-diketone (**4**) may be derived *via* carbonium ion intermediates (**16**, **17**, and **18**) in a similar manner as described above (path d in Scheme 4). If the initial attack of BF_3 took place on hydroxyl-oxygen atom of **1** to afford oxonium ion intermediate (**19**), diarylpropynones (**6**)[2,12] will be given via intermediates (**20** and **21**) (path e in Scheme 4). Although the path e is the main path of the reaction of **1a**, the electron attracting nitro group retards the path e in the reaction of **1b** to give the small amount of **6b**.



Scheme 5.

In another experiment, the TsOH-catalyzed decomposition of 2-diazo-3-hydroxy-3-phenyl-1-indanone (**22**) was carried out in order to compare with that of acyclic α-diazo β-hydroxy ketones. The reaction led to 2-phenyl-1,3-indandione (**23**) quantitatively without formation of the corresponding tosylate. In this reaction, the phenyl migration was observed also. However, Moore and his co-workers showed that the acid-catalyzed decomposition of 2-diazo-3-hydroxy-3-methyl-1,4-(2*H*,3*H*)-naphthalenedione (**24**) gave 2-acetyl-1,3-indandione (**25**) caused by ring contraction in a quantitative yield without methyl migration products.[13] The ring size seems to exert an influence on the course of the acid-catalyzed decomposition of cyclic α-diazo β-hydroxy ketones.

Experimental

All melting points were measured with a Yanagimoto Melting Point Apparatus and are not corrected. The IR spectra were measured on a JASCO IR Spectrometer model IR-G. NMR spectra were recorded in $CDCl_3$ solution at 60 MHz on a Varian Spectrometer model EM-360 using TMS as an internal standard.

Materials. *3-Aryl-2-diazo-3-hydroxy-1-phenyl-1-propanones (**1**)* were prepared by the reaction of α-diazoacetophenone and corresponding benzaldehydes according to the method described by Wenkert.[14] The obtained α-diazo β-hydroxy ketones were purified by recrystallization from benzene-heptane.

1a (Ar=*p*-ClC_6H_4): mp 126—127 °C; IR (KBr) 3350 (OH), 2070 (diazo), 1600 cm^{-1} (diazo C=O); ^{1}H-NMR ($CDCl_3$) δ 3.97 (d, 1H, OH, *J*=3.6 Hz), 6.14 (d, 1H, CH, *J*=3.6 Hz), 7.23—7.73 (m, 9H, arom). Found: C, 63.01; H, 3.82; N, 9.77%. Calcd for $C_{15}H_{11}O_2N_2Cl$: C, 62.84; H, 3.87; N, 9.77%.

1b (Ar=*p*-$NO_2C_6H_4$): mp 120—121 °C; IR (KBr) 3360 (OH), 2060 (diazo), 1600 (diazo C=O), 1515, 1340 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ 4.15 (d, 1H, OH, *J*=3.8 Hz), 6.30 (d, 1H, CH, *J*=3.8 Hz), 7.38—7.95 (m, 9H, arom). Found: C, 60.63; H, 3.83; N, 13.91%. Calcd for $C_{15}H_{11}O_4N_3$: C, 60.60; H, 3.73; N, 14.14%.

*α-Diazo-*p*-nitropropiophenone (**11**)* was synthesized by the reaction of *p*-nitrobenzoyl chloride with an excess of diazoethane in the presence of an equimolar amount of triethylamine at 0 °C under vigorous stirring.[15] Mp 106—107 °C; IR (KBr) 2070 (diazo), 1610 (diazo C=O), 1510, 1340 cm^{-1} (NO_2). Found: C, 52.47; H, 3.47; N, 20.75%. Calcd for $C_9H_7O_3N$: C, 52.68; H, 3.44; N, 20.48%.

*2-Diazo-3-hydroxy-3-phenylindanone (**22**)* was synthesized by the triethylamine-catalyzed isomerization of 2-benzoyl-α-diazoacetophenone, which was prepared by the reaction of DCC-complex of 2-benzoylbenzoic acid with an excess of diazomethane,[16] according to the method of Burkoth.[17] Mp 179—180 °C; IR (KBr) 3280 (OH), 2090 (diazo), and 1662 cm^{-1} (diazo C=O). Found: C, 71.71; H, 3.60; N, 11.26%. Calcd for $C_{15}H_{10}O_2N_2$: C, 71.99; H, 4.03; N, 11.20%.

Acid Catalysts. Reagent grade chemicals were used as catalyst without further purification.

All solvents were purified by distillation over appropriate drying reagents just before use.

General Procedure of the Acid-catalyzed Decomposition of α-Diazo β-Hydroxy Ketones. To a solution of diazo ketone (**1**; 2 mmol) in an appropriate solvent (30 ml) were added an acid catalyst (0.2—0.4 mmol) under vigorous magnetic stirring at 30 °C. After evolution of N_2 ceased the reaction mixture was poured into 50 ml of water and the products were extracted with ether (20 ml) three times. The ether extract was column-chromatographed on silica gel after usual work-up.

2a (Ar=*p*-ClC_6H_4): mp 132—133 °C; $FeCl_3$ test, positive; IR (KBr) 3054 (OH), 1584 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 7.12 (ABq, 4H, arom), 7.32 (s, 5H, Ph), 8.59 (d, 1H, =CH, *J*=4.8 Hz), and 16.93 (d, 1H, enol-OH); Found: C, 69.59; H, 4.24%. Calcd for $C_{15}H_{11}O_2Cl$: C, 69.64; H, 4.29%.

2b (Ar=*p*-$NO_2C_6H_4$): mp 144—146 °C; $FeCl_3$ test, positive; IR (KBr) 3000 (OH), 1595 (C=O), 1525, 1340 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ 7.16—8.22 (m, 9H, arom), 8.66 (s, 1H, =CH), 13.00 (broad s, 1H, enol-OH). Found: C, 66.74; H, 4.08; N, 5.27%. Calcd for $C_{15}H_{11}O_4N$: C, 66.91; H, 4.12; N, 5.20%.

3a (Ar=*p*-ClC_6H_4): mp 90—92 °C; $FeCl_3$ test, positive; IR (KBr) 3050 (OH), 1490 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 6.76 (s, 1H, =CH), 7.13—8.05 (m, 5H, Ph), 7.68 (ABq, 4H, arom), 17.80 (broad s, 1H, enol-OH). Found: C, 69.55; H, 4.53%. Calcd for $C_{15}H_{11}O_2Cl$: C, 69.64; H, 4.29%.

3b (Ar=*p*-$NO_2C_6H_4$): mp 166—167 °C; $FeCl_3$ test, positive; IR (KBr) 3100 (OH), 1585 (C=O), 1510, 1340 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ 6.90 (s, 1H, =CH), 7.38—8.08 (m, 9H, arom), 17.10 (broad s, 1H, enol-OH). Found: C, 66.47; H, 4.12; N, 5.26%. Calcd for $C_{15}H_{11}O_4N$: C, 66.91; H, 4.12; N, 5.20%.

4a (Ar=*p*-ClC_6H_4): mp 108—110 °C; IR (KBr) 1685 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 4.66 (s, 2H, CH_2), 7.16—8.11 (m, 9H, arom). Found: C, 69.58; H, 4.30%. Calcd for $C_{15}H_{11}O_2Cl$: C, 69.64; H, 4.29%.

4b (Ar=*p*-$NO_2C_6H_4$): mp 121—122 °C; IR (KBr) 1680 (C=O), 1518, 1348 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ 4.60 (s, 2H, CH_2), 7.26—8.16 (m, 9H, arom). Found: C, 67.00; H, 4.15; N, 5.28%. Calcd for $C_{15}H_{11}O_4N$: C, 66.91; H, 4.12; N, 5.20%.

5a (Ar=*p*-ClC_6H_4): mp 125—126 °C; IR (KBr) 3350 (OH), 1650 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 5.08 (d, 1H Cl-CH), 5.16 (q, 1H, O-CH), 16.63 (d, 1H, enol-H). Found: C, 61.23; H, 3.90%. Calcd for $C_{15}H_{12}O_2Cl_2$: C, 61.04; H, 4.10%.

5b (Ar=*p*-$NO_2C_6H_4$): mp 139—140 °C; IR (KBr) 3350 (OH), 1650 (C=O), 1510, 1350 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ 5.03 (d, 1H, Cl-CH), 5.30 (q, 1H, O-CH), 16.46 (d, 1H, enol-OH). Found: C, 59.10; H, 3.66; N, 4.61%. Calcd for $C_{15}H_{12}O_4NCl$: C, 58.93; H, 3.96; N, 4.58%.

6a (Ar=*p*-ClC_6H_4): mp 107—109 °C; IR (KBr) 2200 (C≡C), 1630 cm^{-1} (C=O); ^{1}H-NMR ($CDCl_3$) δ 7.23—8.28 (m, 9H, arom). Found: C, 74.36; H, 3.80%. Calcd for $C_{15}H_9OCl$: C, 74.85; H, 3.77%.

6b (Ar=*p*-$NO_2C_6H_4$): mp 154—156 °C; IR (KBr) 2210 (C≡C), 1630 (C=O), 1528, 1352 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ 7.50—8.54 (m, arom). Found: C, 71.61; H, 3.67; N, 5.58%. Calcd for $C_{15}H_9O_3N$: C, 71.71; H, 3.61: N, 5.57%.

*p-Toluenesulfonic Acid-catalyzed Decomposition of α-Diazo-*p*-nitropropiophenone (**11**).* To a solution of **11** (0.41 g, 2 mmol) in an acetonitrile (10 ml) was added an equimolar amount of $TsOH \cdot H_2O$ (0.38 g, 2 mmol) in small portions at 0—5 °C under vigorous stirring. After evolution of N_2 ceased the reaction mixture was poured into 50 ml of cold water and the organic layer was extracted with each 30 ml of ether three times. Combined ether solution was dried over $MgSO_4$ and separated with silica gel column chromatography. Major product was characterized to 1-(*p*-nitrobenzoyl)ethyl tosylate (**13**): white crystals; 0.48 g, 69%;

mp 146—147.5 °C; IR (KBr) 1685 (C=O), 1520, 1345 (NO_2), 1365, 1195 cm^{-1} (SO_2); ^{1}H-NMR ($CDCl_3$) δ 1.60 (d, 3H, CH_3 J=6.6 Hz) 2.43 (s, 3H, CH_3), 5.68 (q, 1H, CH, J=6.6 Hz), and 7.2—8.4 (two pairs of ABq, 8H, arom). Found: C, 54.95; H, 4.27; N, 4.12%. Calcd for $C_{16}H_{15}O_6NS$: C, 55.01; H, 4.33; N, 4.01%. The minor product was determined to *p*-nitrophenylvinylketone (**14**): 0.046 g, 13%; mp 87—87.5 °C; IR (KBr) 1645 (enone), 1490, 1320 cm^{-1} (NO_2); ^{1}H-NMR ($CDCl_3$) δ 6.03 (dd, 1H, Hx), 6.42 (dd, 1H, Hb (*cis* to Hx), 9.13 (dd, 1H Ha (*trans* to Hx)) and 8.0—8.4 (ABq, 4H, arom), (Jab=16.0, Jax=10.0, and Jbx=2.0 Hz). Found: C, 60.95; H, 4.07; N, 7.59%. Calcd for $C_9H_7O_3$: C, 61.01; H, 3.98; N, 7.91%.

p-*Toluenesulfonic Acid-catalyzed Decomposition of 2-Diazo-3-hydroxy-3-phenyl-1-indandione (**22**).* To an acetonitrile solution (10 ml) of **22** (0.500 g, 2 mmol) was added a catalytic amount of $TsOH \cdot H_2O$ at room temperature. Pouring the reaction mixture into 50 ml of water gave a white crystalline product (**23**) in quantitative yields. The structure was determined by the comparison of its IR spectra with that of authentic sample prepared by the alkali-catalyzed reaction of 3-benzylidenephthalide.[18]

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