[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Rearrangements During Oxidation of 1,1-Diarylethanes[1]

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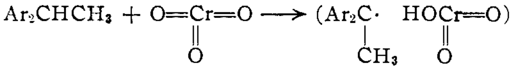
RECEIVED MAY 24, 1958

The formation of benzoic acids during the oxidation of 1,1-diarylethanes by means of chromic acid has been investigated. The formation of benzoic acids was observed only when substituents favoring free radical reactions were present, and the ratio of benzoic acids/benzophenones was shown to be dependent on the relative amount of oxidizing agent employed. Comparative oxidations of 1,2-diarylethanes, 1,1-diarylethylenes and stilbenes were also investigated.

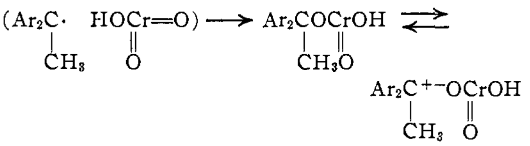
In the course of the oxidation of 1,1-di-(*p*-iodophenyl)-ethane (I) with chromic acid there was obtained[2] in addition to the expected *p,p'*-diiodobenzophenone also some *p*-iodobenzoic acid. Since the formation of the latter product is not expected in terms of the classical oxidation theory, the oxidation of 1,1-diarylethanes was subjected to closer scrutiny.

Repetition of the oxidation of I by means of chromic acid revealed that the yield of *p*-iodobenzoic acid was directly dependent on the ratio CrO_3/I (see Table I and Fig. 1). Since the oxidation of I to either *p*-iodobenzoic acid or *p,p'*-diiodobenzophenone requires the same amount of chromic acid (3.3 moles) it is of interest to note that the yield of *p*-iodobenzoic acid fits the straight line plot shown in Fig. 1 even when the amount of oxidizing agent is less than that required for the completion of the reaction.

Little is known about the mechanism of oxidation of hydrocarbons by chromic acid.[3] It is generally assumed that Cr(VI) is first reduced to Cr(IV) and such a two-electron change can be represented by equations 1 and 2.



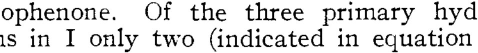
$$\mathrm{Ar_2CHCH_3} + \mathrm{O{=}\underset{O}{\underset{\|}{Cr}}{=}O} \longrightarrow (\mathrm{Ar_2\underset{CH_3}{\underset{|}{C}}\cdot}\quad \mathrm{HO\underset{O}{\underset{\|}{Cr}}{=}O}) \qquad (1)$$



$$(\mathrm{Ar_2\underset{CH_3}{\underset{|}{C}}\cdot}\quad \mathrm{HO\underset{O}{\underset{\|}{Cr}}{=}O}) \longrightarrow \mathrm{Ar_2\underset{CH_3}{\underset{|}{C}}O\underset{O}{\underset{\|}{Cr}}OH} \rightleftarrows \mathrm{Ar_2\underset{CH_3}{\underset{|}{C}}{}^{+-}O\underset{O}{\underset{\|}{Cr}}OH} \qquad (2)$$

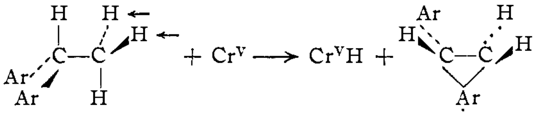
The organic portion of the reaction product would not be expected to rearrange since we deal here with tertiary and resonance-stabilized carbonium ion. Further oxidation of the solvated carbonium ion formed in 2 would produce the benzophenone and Cr(III) and thus represents the "normal" oxidation of I.

It is well recognized that Cr(VI) and Cr(IV) can undergo a disproportionation reaction to give Cr(V) and that the latter chromium species induces reactions involving free radicals.[4] The attack of Cr(V) upon I would be expected to cause an abstraction of a hydrogen atom in line with the usual behavior of hydrocarbons in the presence of radicals. In the molecule of I we can recognize four such hydrogen atoms susceptible to attack by Cr(V) and they can be divided into three classes. First, there is a tertiary hydrogen atom which, because of the resonance-stabilized residue, is most likely to be attacked (equation 3).



$$\mathrm{Ar_2\underset{H}{C}{-}CH_3} + \mathrm{Cr^V} \longrightarrow \mathrm{Ar_2\dot{C}{-}CH_3} + \mathrm{Cr^VH} \qquad (3)$$

The radical produced in this process is not likely to rearrange and probably is rapidly degraded to the benzophenone. Of the three primary hydrogen atoms in I only two (indicated in equation 4 by arrows) are located in positions which favor a concerted rearrangement of the aryl groups.



The rearrangement of the bridged radical shown in 4 can lead to the 1,2-diarylethane system which can then be degraded to the benzoic acid.

TABLE I

OXIDATION OF 0.00458 MOLE OF I WITH CHROMIC ACID[a]

No.	Mole CrO_3	Moles CrO_3/I	Yield, mole Acid	Yield, mole Ketone	Yield, mole Total	Ratio ketone/acid
1	0.0115	2.51	0.00007	0.00149	0.00156[b]	21.3
2	.020	4.37	.00058	.00252	.00310	4.35
3	.030	6.55	.00118	.00285	.00403	2.41
4	.030	6.55	.00118	.00398[c]	.00516[c]	1.41[c]
5[d]	.030	6.55	.00099	.00296	.00396[d]	2.98[d]
6	.040	8.73	.00188	.00239	.00427	1.27
7[e]	.046	10.0	.00234	.00198	.00432	0.84
8	.050	10.9	.00245	.00198	.00443	.81
9[f]	.050	10.9	.00219	.00175	.00394[f]	.80[f]
10	.052	11.4	.00252	.00172	.00424	.68
11[e]	.060	13.1	.00219	.00193	.00412	.88
12[e]	.070	15.3	.00238	.00150	.00388	.63
13	.078	17.0	.00243	.00098	.00341	.40

[a] See Experimental for conditions; reflux period 4 hours except where noted otherwise. [b] In this experiment 0.00139 mole of I was recovered. [c] Oxidation in presence of 0.00232 mole of *p,p'*-diiodobenzophenone; ratio ketone/acid calculated on basis of I alone. [d] Oxidation in presence of 0.409 g. of As_2O_3. [e] Reflux period of 2.25 hours. [f] Oxidation in presence of 1.004 g. of As_2O_3.

The above considerations explain the dependence of the yield of *p*-iodobenzoic acid on the excess of chromic acid in the oxidation mixture. Assuming a rapid conversion of Cr(VI) to Cr(IV) as the initial oxidation step, the rate of the "normal" degradation to the benzophenone is then dependent on the Cr(IV) concentration. The rate of the "abnormal" reaction, on the other hand, depends on the concentration of Cr(IV) as well as on the concentration of Cr(VI) since both species are needed to give Cr(V). The possibility that *p,p'*-diiodoben-

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[1] Presented at the A.C.S. Meeting in Miami, Fla., April, 1957. From the M.S. Thesis of J.F.D. Present address of H.H.S. to whom inquiries should be addressed: Universidad de Oriente, Santiago de Cuba, Cuba.

[2] H. H. Szmant and R. Yoncoskie, *J. Org. Chem.*, **21**, 78 (1956).

[3] W. A. Waters, "Organic Chemistry," H. Gilman, editor, Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 1202–1210.

[4] F. H. Westheimer and W. Watanabe, *J. Chem. Phys.*, **17**, 61 (1949).

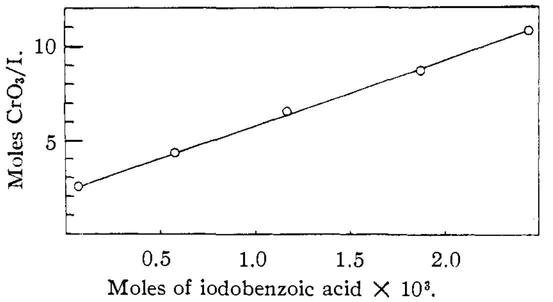

Fig. 1.—Yield of *p*-iodobenzoic acid *vs.* CrO_3/I.

zophenone is degraded to *p*-iodobenzoic acid was previously eliminated by control experiments.[2] An additional control experiment was now added on the assumption that while the benzophenone resists attack by Cr(VI) it may be degraded by the more reactive Cr(IV) and Cr(V) species formed during the oxidation process. However it was ascertained that the addition of *p,p'*-diiodobenzophenone to the mixture of I and CrO_3 gave the same yield of *p*-iodobenzoic acid that was produced in the absence of the ketone.

The above-mentioned explanation of the "abnormal" oxidation of 1,1-diarylethanes suggests that a free radical rather than an ionic intermediate is involved. This hypothesis is based on the observations that 1,1-diphenylethane[2] and especially 1,1-di-(*p*-anisyl)-ethane do not produce anything but the "normal" oxidation product; that is, benzophenone and *p,p'*-dimethoxybenzophenone, respectively. On the other hand, 1,1-di-(*p*-nitrophenyl)-ethane was shown to give as much as 30% of *p*-nitrobenzoic acid, and here too the yield of "abnormal" product seemed to depend on the excess of chromic acid employed (see Table II).

TABLE II

OXIDATION OF 1,1-DI-(*p*-NITROPHENYL)-ETHANE WITH CHROMIC ACID[a]

No.	Mole CrO_3	Moles CrO_3/nitro compound	Reflux, hr.	Yield, mole Acid	Yield, mole Ketone	Yield, mole Total	Ratio ketone/acid
1	0.040	5.4	3	0.00024	0.00515	0.00539	21.5
2	.040	5.4	[b]	.00071	.00527	.00598	7.4
3	.060	8.1	[c]	.00123	.00417[d]	.00540	3.4
4[e]	.068	10.9[e]	[f]	.00185	.00252	.00407[e]	1.4

[a] Oxidation of 0.0074 mole of nitro compound in 50 ml. of acetic acid. [b] Reaction mixture heated gradually over 4 hours and then refluxed for 1 hour. [c] Reaction mixture stirred at room temperature for 20 hours, heated gradually to 100° over 4 hours, and then maintained at 100° for 2 hours. [d] In addition to the benzophenone there was isolated 0.03 g. of a neutral compound, m.p. 78–81°, which analyzed 57.71% C, 4.85% H and 7.70% N. [e] Only 0.00624 mole of nitro compound was used. [f] Reaction mixture maintained at 50° for 18 hours and then heated at 100° for 3.5 hours.

Thus it appears that the reaction represented by equation 4 requires the presence of an aryl group capable of stabilizing a free radical center. The present results are in line with the observed[5,6] relative susceptibilities of nitrobenzene, iodobenzene and benzene toward radical reactions which are reported to be 4.0:1.8:1.0, respectively. In accordance with this conclusion 1,1-di-(*p*-cyanophenyl)-ethane[2] should produce during oxidation with chromic acid also some *p*-cyanobenzoic acid since the relative susceptibility of benzonitrile to radical reactions is reported[7] to be 3.7 relative to that of benzene. This expectation is indeed realized[8] though a complicating factor in this case is the tendency of the cyano group to be partially hydrolyzed to the carboxamide group.

The postulated mechanism of the "abnormal" degradation of 1,1-diarylethanes suggests the requirement of a concerted abstraction of a hydrogen atom and the migration of a radical center stabilizing aryl group. The suggested requirement of a concerted process is based on the results obtained in oxidation experiments with 1,2-diarylethanes related to the mentioned 1,1-diarylethanes. *A priori* it may be assumed that 1,2-diarylethanes may also rearrange during oxidation with chromic acid and give as "abnormal" product the corresponding benzophenone. A number of experiments in which the aryl groups consisted of *p*-iodophenyl, *p*-nitrophenyl and *p*-anisyl failed to show the formation of the benzophenones. Consideration of the most favorable conformation of 1,2-diarylethanes (A in Fig. 2) shows the absence of hydrogen atoms, the removal of which could lead to a concerted migration of an aryl group. The most favorable conformation (A) in which the bulky aryl groups are farthest apart would have to change first to a less stable conformation (B in Fig. 2) before such a concerted aryl migration could take place. Also, the equilibrium

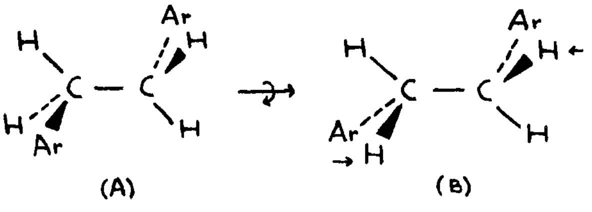

Fig. 2.—Conformations of 1,2-diarylethanes.

$$\mathrm{Ar{-}CH_2{-}\dot{C}H{-}Ar \rightleftarrows Ar_2CH{-}CH_2\cdot}$$

would hardly be expected to be displaced toward the righthand side in view of the greater stability of the secondary, resonance-stabilized radical as compared to the primary, resonance-nonstabilized radical.

The recent report[9] that the chromic acid oxidation of 2,3-di-(*p*-anisyl)-2-butene gave unexpectedly some *p,p'*-dimethoxybenzophenone prompted the examination of the oxidation of stilbenes containing iodo, nitro and methoxy groups in the *p,p'*-positions. The experiments with the iodo and nitro compounds did not indicate the formation of substituted benzophenones. In addition to the expected benzoic acids some of the experiments yielded partially oxidized products (benzils) or traces of unidentified neutral materials. However, the oxidation of *p,p'*-dimethoxystilbene gave a very small amount of the benzophenone. The Indian

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[5] R. L. Dannley, E. C. Gregg, Jr., R. E. Phelps and C. B. Coleman, THIS JOURNAL, **76**, 445 (1954).

[6] R. L. Dannley and E. C. Gregg, Jr., *ibid.*, **76**, 2997 (1954).

[7] D. R. Augood, J. I. G. Cadogan, D. H. Hey and G. C. Williams, *J. Chem. Soc.*, 3412 (1953).

[8] H. H. Szmant and J. M. Dixon, unpublished results.

[9] S. H. Zakeer, B. Singh, B. Bhushan, I. K. Kacker, K. Ramachandran, and N. S. Rao, *J. Chem. Soc.*, 1706 (1955).

workers[9] suggested that the formation of p,p′-dimethoxybenzophenone was probably due to the pinacol–pinacolone rearrangement of a glycol formed from an intermediate epoxide. It is likely that such a rearrangement could occur more easily in their tetrasubstituted ethylene glycol than in a disubstituted glycol which would be formed in the oxidation of our stilbene, and thus the smaller yield of the benzophenone in our experiment is justified. The exclusive formation of the benzophenone in the methoxy-substituted stilbene supports the suggested ionic mechanism of rearrangement.

In connection with the experiments involving stilbenes there was also carried out the analogous oxidation reactions with 1,1-diarylethylenes. The *p*,*p*′-dinitro and *p*,*p*′-dimethoxy compounds gave exclusively the expected benzophenones thus indicating the absence of any rearrangements. The *p*,*p*′-diiodo compound, on the other hand, gave in addition to the benzophenone also 14% of *p*-iodobenzoic acid. The unique behavior of the iodo compound is not understood at this time. It is possible that *p*,*p*′-diiodobenzophenone resists oxidative degradation under average reaction conditions[2] but that use of large excess of chromic acid causes a finite amount of breakdown to *p*-iodobenzoic acid. This preliminary conclusion seems to be supported by the observations (Table I) that the total yield of oxidation products of I passes through a maximum, and that the ratio *p*-iodobenzoic acid/*p*,*p*′-diiodobenzophenone gradually increases even after the total yield of oxidation products begins to decrease.

In the hope that rearrangements of 1,1-diarylethanes could be demonstrated in the course of a reaction well known to involve free radicals there was examined the behavior of 1,1-diarylethanes in the presence of N-bromosuccinimide (NBS) and benzoyl peroxide. The reaction with NBS was followed in each case by a treatment with pyridine to obtain the dehydrohalogenated product.

The reaction of I under the above-mentioned conditions gave a bromine-containing compound which is believed to be 1,1-di-(*p*-iodophenyl)-2-bromoethylene on the basis of its ultraviolet spectrum and oxidative degradation. Thus, while an undesired side-chain bromination was effected, it is clear that no rearrangement to a stilbene was obtained. It is noteworthy that this bromoölefin like the parent 1,1-di-(*p*-iodophenyl)-ethylene gave upon oxidation with chromic acid some *p*-iodobenzoic acid in addition to the expected *p*,*p*′-diiodobenzophenone. The reaction of 1,1-di-(*p*-nitrophenyl)-ethane with NBS followed by a treatment with pyridine gave only 1,1-di-(*p*-nitrophenyl)-ethylene demonstrating again absence of a rearrangement. The reaction of 1,1-di-(*p*-anisyl)-ethane with NBS was complicated by noticeable evolution of hydrogen bromide resulting from ring bromination known[10] to occur with benzene derivatives which are susceptible to electrophilic substitution. The product of the above reaction gave on oxidation a poor yield of *p*,*p*′-dimethoxybenzophenone and an unidentified bromine-containing acid, but the known *p*,*p*′-dimethoxystilbene could not be detected.

The failure to observe rearrangements during the reaction of I and its nitro and methoxy analogs with NBS can be explained by considering the relative stability of the succinimide radical as compared to the assumed Cr(V) species. As mentioned in the preceding discussion the formation of benzoic acids is thought to result from a secondary reaction which depends on the attack of Cr(V) on a primary hydrogen in a suitably substituted 1,1-diarylethane. The resonance-stabilized and thus relatively stable succinimide radical would be expected to be more selective and apparently limits itself to the attack upon the tertiary hydrogen. This reasoning is an extension of the conclusions[11] with regard to electrophilic substitution reactions of benzene derivatives in which the selectivity of orientation runs parallel with the relative stability of the attacking electrophilic reagent. The extraordinary selectivity of NBS in the bromination of allylic hydrogen atoms is well known.[12]

The NBS reaction was also extended to the 1,2-diarylethanes and only the expected stilbenes were obtained from the *p*-iodo and *p*-nitro compounds. 1,2-Di-(*p*-anisyl)-ethane again gave a more complex reaction and a small amount of a bromine-containing unidentified solid was isolated. The failure to observe rearrangement products from the reaction of 1,2-diarylethanes with NBS was not entirely unexpected in view of their classical behavior during the oxidation reactions with chromic acid.

Experimental[13]

1,1-Di-(*p*-iodophenyl)-ethane was prepared as previously described.[2]

1,2-Di-(*p*-iodophenyl)-ethane.—A suspension of 50 g. of 1,2-diphenylethane and 112 g. of silver nitrate in 500 ml. of concd. sulfuric acid and 150 ml. of water was stirred rapidly and cooled to 5°. Iodine, 150 g., was added over a period of 1 hour. The mixture was stirred at 25° for two days and then poured into water. The solid was filtered and extracted with benzene. The benzene solution was concentrated to give a 25% yield of the desired product which upon crystallization from ethyl acetate was obtained as white, granular crystals, m.p. 152–153° (lit.[14] m.p. 152°).

1,1-Di-(*p*-nitrophenyl)-ethane.—1,1-Diphenylethane, 40 g., was added slowly to a rapidly stirred mixture of 230 ml. of red fuming nitric acid (sp. gr. 1.59) and 20 ml. of water. The temperature was maintained below 10° during the addition and then the mixture was allowed to come to room temperature. The mixture was poured into water and extracted with benzene. The benzene extract was concentrated to yield 42% of the desired product, pale yellow needles, m.p. 110.5–112°.

Anal. Calcd. for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; N, 10.29. Found: C, 61.86; H, 4.62; N, 10.10.

1,2-Di-(*p*-nitrophenyl)-ethane was prepared by air oxidation of *p*-nitrotoluene.[15]

1,1-Di-(*p*-anisyl)-ethane was prepared by treating a mixture of anisole, paraldehyde and concd. hydrochloric acid with hydrogen chloride.[16]

1,2-Di-(*p*-anisyl)-ethane was prepared by hydrogenating *p*,*p*′-dimethoxystilbene,[17] 0.85 g., in 200 ml. of ethyl acetate

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[10] N. Büu-Hoi, *Ann.*, **556**, 1 (1944).

[11] H. C. Brown and W. H. Bonner, This Journal, **76**, 605 (1954).

[12] C. Djerassi, *Chem. Revs.*, **43**, 295 (1948).

[13] All melting points are uncorrected. Microanalyses by Drs. Strauss and Weiler, Oxford, England.

[14] K. Elbs and A. Jaroslawzer, *J. prakt. Chem.*, **88**, 94 (1900).

[15] H. O. House, *Org. Syntheses*, **34**, 35 (1954).

[16] R. Quelet, *Bull. soc. chim., France*, **7**, 196 (1940).

[17] P. Rumpf and Gillois, *ibid.*, **22**, 1348 (1955).

in the presence of Raney nickel for 22 hours at 60 pounds pressure. The product had m.p. 126–127° (lit.[18] m.p. 125°).

1,1-Di-(*p*-iodophenyl)-ethanol.—A solution of 11 g. of *p,p*-diiodobenzophenone in benzene was added to 0.05 mole of methylmagnesium iodide in 150 ml. of ether. The reaction mixture was hydrolyzed and the organic portion was concentrated to yield 43% of the desired alcohol. The product was crystallized from methanol to give white crystals, m.p. 118–119°.

Anal. Calcd. for $C_{14}H_{12}OI_2$: C, 37.37; H, 2.69; I, 56.4. Found: C, 37.25; H, 2.58; I, 56.3.

1,1-Di-(*p*-iodophenyl)-ethylene.—The above alcohol, 2.0 g., was refluxed in 30 ml. of acetic anhydride for 1 hour. The resulting solution was flash distilled to yield a brown solid which was crystallized from methanol to give a 70% yield of white crystals, m.p. 97–98°.

Anal. Calcd. for $C_{14}H_{10}I_2$: C, 38.92; H, 2.33; I, 58.7. Found: C, 39.05; H, 2.50; I, 58.7.

***p,p'*-Diiodostilbene.**—A mixture of 1.6 g. of 1,2-di-(*p*-iodophenyl)-ethane, 2.9 g. of NBS and 0.1 g. of benzoyl peroxide was refluxed in 200 ml. of carbon tetrachloride for 1 hour. The reaction mixture was filtered and the filtrate was concentrated to dryness. The residue was dissolved in 25 ml. of pyridine and the solution was refluxed for 1 hour. The reaction mixture was poured into water and filtered. The solid was crystallized from benzene to give a 24% yield of the desired stilbene, m.p. 260–262° (lit.[19] m.p. 257–259°).

1,1-Di-(*p*-nitrophenyl)-ethylene.—A mixture of 3.0 g. of 1,1-di-(*p*-nitrophenyl)-ethane, 6.0 g. of NBS and 0.2 g. of benzoyl peroxide, was refluxed in 150 ml. of carbon tetrachloride for 2 hours. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was refluxed with 40 ml. of pyridine for 1.5 hours and the mixture was then poured into water to give the desired olefin in 75% yield as pale yellow needles from methanol, m.p. 175–176.5°.

Anal. Calcd. for $C_{14}H_{10}N_2O_4$: C, 62.20; H, 3.73; N, 10.35. Found: C, 62.07; H, 3.72; N, 10.10.

***p,p'*-Dinitrostilbene** was prepared as described above from the corresponding ethane and NBS in 35% yield, m.p. 286–288° (lit.[20] m.p. 288°).

1,1-Di-(*p*-anisyl)-ethylene and ***p,p'*-dimethoxystilbene** were prepared as described in the literature.[17]

Oxidation Reactions.—All oxidations experiments were carried out by refluxing the solution of the desired compound in acetic acid and in the presence of reagent grade chromic acid. The reaction mixture was poured on ice and extracted with benzene. The benzene extracts were in turn extracted with 10% sodium hydroxide. Acidification of the alkaline extracts gave the carboxylic acids, while the residual benzene solutions yielded the neutral oxidation products.

A. **1,1-Di-(*p*-iodophenyl)-ethane.**—The various oxidation experiments using 0.00458 mole of I in 50 ml. of glacial acetic acid are summarized in Table I. The products of the oxidation experiments, *p,p'*-diiodobenzophenone, m.p. 237–238°, and *p*-iodobenzoic acid, m.p. 268–270°, were identified by means of melting points and mixture melting points.

Determination of Recovery of *p,p'*-Diiodobenzophenone and *p*-Iodobenzoic Acid from Oxidation Mixtures.—Mixtures of 1 g. each of the ketone and acid were refluxed in 50 ml. of acetic acid in the presence of 3 g. of chromic acid for periods of 15 minutes and 4 hours. In four experiments the recovery of *p*-iodobenzoic acid and *p,p'*-diiodobenzophenone was 88.5–93 and 48.7–52.7%, respectively. In another experiment 2 g. of ketone alone was refluxed for 3.25 hours in 50 ml. of acetic acid in the presence of 4 g. of chromic acid. The reaction mixture was worked up as described above to give 80% of original ketone and traces of acid.

B. **1,2-Di-(*p*-iodophenyl)-ethane.**—A mixture of 0.00458 mole of iodo compound and 0.040 mole of chromic acid in 75 ml. of acetic acid was refluxed for 3.5 hours. The reaction mixture yielded 0.00282 mole of *p*-iodobenzoic acid and 0.33 g. of a neutral compound, m.p. 252–253°, suspected to be *p,p'*-diiodobenzil (m.p. reported[21] 255°). An attempted benzilic acid rearrangement failed with the latter compound.

In another experiment, the iodo compound, 0.00685 mole, was treated with 0.120 mole of chromic acid in 80 ml. of acetic acid, and the mixture was heated to initiate the reaction and then warmed on a steam-bath for 2 hours. From the reaction mixture there were isolated 0.00525 mole of *p*-iodobenzoic acid and 0.013 g. of a neutral compound, m.p. 195–217°, which failed to give a 2,4-dinitrophenylhydrazone.

C. **1,1-Di-(*p*-nitrophenyl)-ethane.**—The oxidation experiments utilizing 0.0074 mole of the nitro compound in 50 ml. of acetic acid are summarized in Table II. The products of the reaction, *p,p'*-dinitrobenzophenone, m.p. 188–189°, and *p*-nitrobenzoic acid, m.p. 238–240°, were identified by their characteristic melting points.

D. **1,2-Di-(*p*-nitrophenyl)-ethane.**—The nitro compound, 0.0110 mole, chromic acid, 0.070 mole, and 50 ml. acetic acid were refluxed for 4 hours. The mixture yielded 0.0123 mole of *p*-nitrobenzoic acid and traces of an unidentified neutral solid, m.p. 153°.

In another experiment, 0.00735 mole of nitro compound, 0.080 mole of chromic acid and 250 ml. of acetic acid were stirred at room temperature for 20 hours, heated on a steam-bath for 4 hours, and finally refluxed for 2 hours. The mixture yielded 0.0072 of *p*-nitrobenzoic acid and traces of an unidentified solid, m.p. 50–60°.

E. **1,1-Di-(*p*-anisyl)-ethane.**—The compound, 0.00802 mole, and 0.045 mole of chromic acid, were mixed with 50 ml. of acetic acid and the mixture was stirred at room temperature for 18 hours and then worked up in the usual manner. There was obtained 0.00567 mole of *p,p'*-dimethoxybenzophenone, m.p. 141–143°, and no acidic product could be detected.

F. **1,2-Di-(*p*-anisyl)-ethane.**—A mixture of 0.00244 mole of the compound, 0.025 mole of chromic acid and 50 ml. of acetic acid was stirred at room temperature for 23 hours and then refluxed for 30 minutes. The reaction mixture yielded 0.0022 mole of *p*-anisic acid and 0.00066 mole of *p,p'*-dimethoxybenzil, m.p. 133°, which was characterized as its disemicarbazone, m.p. 252–253°.

G. ***p,p'*-Diiodostilbene.**—A mixture of 0.0087 mole of the compound, 0.020 mole of chromic acid and 50 ml. of acetic acid was stirred at room temperature for 18 hours and then heated on a steam-bath for 3.5 hours and finally refluxed for one hour. The reaction mixture yielded 0.00081 mole of *p*-iodobenzoic acid and traces of an unidentified solid, m.p. 205°.

H. **1,1-Di-(*p*-nitrophenyl)-ethylene.**—A mixture of 0.00158 mole of the compound, 0.010 mole of chromic acid and 25 ml. of acetic acid was refluxed for 1.5 hours. The mixture yielded 0.00143 mole of *p,p'*-dinitrobenzophenone and no acidic product could be detected.

In another experiment a mixture of 0.00482 mole of the compound, 0.030 mole of chromic acid and 50 ml. of acetic acid was stirred for 20 hours at room temperature and then refluxed for 2 hours. The reaction mixture yielded 0.00423 mole of *p,p'*-dinitrobenzophenone and no acidic products could be detected.

I. ***p,p'*-Dinitrostilbene.**—A mixture of 0.00519 mole of the compound, 0.060 mole of chromic acid and 80 ml. of acetic acid was stirred at room temperature for 18 hours, heated on a steam-bath for 2 hours, and finally refluxed for 2.5 hours. The mixture yielded 0.00497 mole of *p*-nitrobenzoic acid and traces of an unidentified neutral solid which melted over a wide range up to 90°.

J. **1,1-Di-(*p*-anisyl)-ethylene.**—A mixture of 0.00732 mole of the compound, 0.035 mole of chromic acid and 50 ml. of acetic acid, was stirred at room temperature for 36 hours. The reaction mixture yielded 0.00570 mole of *p,p'*-dimethoxybenzophenone and no acidic product could be detected.

K. ***p,p'*-Dimethoxystilbene.**—A mixture of 0.00399 mole of the compound, 0.020 mole of chromic acid and 40 ml. of acetic acid was stirred at room temperature for 1.5 hours and then refluxed for 30 minutes. From the reaction mixture there were isolated 0.00215 mole of *p*-anisic acid, 0.07 g. of an unidentified neutral solid, m.p. 207–209°, traces of *p,p'*-dimethoxybenzophenone, and trace amounts of *p,p'*-dimethoxybenzil, m.p. 133°, characterized as its disemicarbazone, m.p. 252–253°.

L. **1,1-Di-(*p*-iodophenyl)-ethylene.**—A mixture of 0.00254 mole of the compound, 0.023 mole of chromic acid

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[21] C. Willgerodt, *J. prakt. Chem.*, **86**, 283 (1898).

and 50 ml. of acetic acid was stirred at room temperature for 4 hours and then refluxed for 1.5 hours. The reaction mixture yielded 0.00056 mole of *p*-iodobenzoic acid and 0.00142 mole of *p,p'*-diiodobenzophenone.

Reaction of I with NBS.—A mixture of 2.0 g. of I, 3.6 g. of NBS, 0.2 g. of benzoyl peroxide and 100 ml. of carbon tetrachloride was refluxed for 2 hours. The mixture was filtered and the filtrate concentrated to dryness. The residue was dissolved in 25 ml. of pyridine and the solution was refluxed for 1 hour, poured into water and filtered. The resulting solid was crystallized from benzene to give 1.8 g. of compound, m.p. 150–151°, believed to be 1,1-di-(*p*-iodophenyl)-2-bromomethylene.

Anal. Calcd. for $C_{14}H_9I_2Br$: C, 32.91; H, 1.78; Br, 15.64; I, 49.67. Found: C, 33.28; H, 1.88; Br, 15.28; I, 49.70.

The ultraviolet spectrum of the above compound in 95% ethanol shows a maximum at 255 mμ (ε 31,000) and shoulders at 235 (ε 18,000) and 270 mμ (ε 24,000). This spectrum compares favorably with that determined for 1,1-di-(*p*-iodophenyl)-ethylene in 95% ethanol which exhibits a maximum at 255 mμ (ε 31,000) and a shoulder at 233 mμ (ε 17,000). The oxidation of 1.8 g. of the above compound with 7.5 g. of chromic acid and 75 ml. of acetic acid gave 0.23 g. of *p*-iodobenzoic acid and 0.23 g. of *p,p'*-diiodobenzophenone.

Reaction of 1,1-Di-(*p*-anisyl)-ethane with NBS.—A mixture of 2.0 g. of the compound, 4.0 g. of NBS and 0.2 g. of benzoyl peroxide was refluxed in 100 ml. of carbon tetrachloride for 1 hour. Hydrogen bromide was evolved during the reaction. The mixture was filtered and the filtrate was concentrated to dryness. The residue was heated with 25 ml. of pyridine for 2 hours and the mixture worked up in the usual way to give 1.8 g. of a compound, m.p. 94–95°.

Anal. Calcd. for $C_{16}H_{14}O_2Br_2$: C, 48.30; H, 3.54; Br, 40.2. Found: C, 48.36; H, 3.55; Br, 40.0.

The oxidation of 1.0 g. of the above compound with 2.0 g. of chromic acid gave 0.026 g. of an unidentified acid, m.p. 172–176°, which depressed the m.p. of *p*-anisic acid, and 0.14 g. of *p,p'*-dimethoxybenzophenone.

Reaction of 1,2-Di-(*p*-anisyl)-ethane with NBS.—A mixture of 0.2 g. of the compound, 0.6 g. of NBS and 0.05 g. of benzoyl peroxide was refluxed in 50 ml. of carbon tetrachloride for 1.5 hours. Hydrogen bromide was evolved during the reaction. The reaction mixture was worked up in the usual way to give traces of an unidentified solid, m.p. 198–201°, which depressed the m.p. of *p,p'*-dimethoxystilbene and which gave a positive test for bromine (sodium fusion).

PITTSBURGH, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUQUESNE UNIVERSITY]

Hydrazones of Nitrophenyl and Pyridyl Aldehydes and Ketones. New Preparation of *o*-Nitrobenzophenones and Differences in Behavior of *o*-Nitrobenzophenone and *o*-Nitrophenyl Mesityl Ketone[1]

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RECEIVED MAY 24, 1958

The preparation of a series of hydrazones of nitrobenzaldehydes, nitrobenzophenones, pyridine carboxaldehydes and pyridyl phenyl ketones is described. A new method of preparation of *o*-nitrobenzophenones was developed. Complex replacement reactions of *o*-nitrobenzophenones are discussed in terms of conformational differences.

The continuation of the study of the Wolff–Kishner reaction[2] required a series of hydrazones of the isomeric nitrobenzaldehydes, nitrobenzophenones, pyridine carboxaldehydes and pyridyl phenyl ketones. The preparation of the aldehydes and ketones required for this purpose did not offer any difficulties except in the case of *o*-nitrobenzophenone (I).

Our attempts to prepare I by the Friedel–Crafts reaction of *o*-nitrobenzoyl chloride and benzene gave black, resinous materials in agreement with the experiences of previous investigators.[3] Because of the failure of the Friedel–Crafts reaction involving *o*-nitrobenzoyl chloride, it has been customary to prepare I by the oxidation of *o*-nitrodiphenylmethane[4,5] and by the ferric chloride-catalyzed reaction of *o*-nitrobenzoyl chloride and benzene.[3] Since the latter reaction gives only a yield of 17% of I, and the former involves several steps, it was decided to apply the acylation procedure discovered recently in this Laboratory[6,7] to the synthesis of I.

The mixture of *o*-nitrobenzoic acid, trifluoroacetic anhydride and benzene failed to give I. This result is not unexpected for two reasons. Firstly, it is known[8] that this acylation procedure is only applicable to electron-rich systems. Secondly, the use of an acid containing an electron-withdrawing substituent would be expected to inhibit the dissociation of the mixed anhydride to give the acylonium ion necessary for the reaction. The use of additional catalysis by means of boron trifluoride[6,7] proved to be successful for the preparation of I and the related *o*-nitrophenyl anisyl and mesityl ketones. While the yield of I under the optimum conditions encountered so far is not better than that obtained by the ferric chloride-catalyzed acylation,[3] our procedure is nevertheless advantageous because of its simplicity and the recovery of unreacted *o*-nitrobenzoic acid. The yields of *o*-nitrophenyl anisyl and mesityl ketones by our procedure were 25 and 75%, respectively, and this represents a great improvement over the previously reported[3] yields of 1.5 and 7%, respectively.

Numerous experiments using *o*-nitrobenzoic acid, trifluoroacetic anhydride, boron trifluoride and either benzene, anisole or mesitylene, proved that the reaction conditions were of utmost importance. Addition of the aromatic substrate to the red solution of the complex formed between the mixed anhydride and boron trifluoride gave immediate

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(1) From Ph.D. thesis of C.M.H., 1956. Present address of H.H.S. where inquiries should be addressed: Universidad de Oriente, Santiago de Cuba, Cuba.

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