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The Reactions of 1,3-Indandiones and 1,3(2*H*)-Phenalenediones with Lead Tetraacetate

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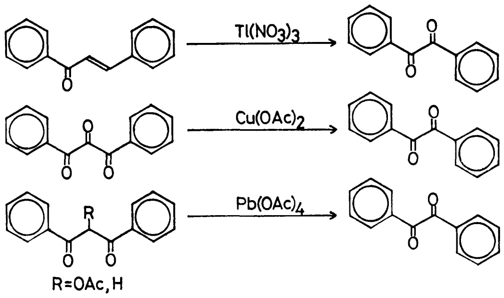
The reaction of 1,3-indandione with lead tetraacetate gave phthalic anhydride and 2,2-diacetoxy-1,3-indandione. The reaction of 2,2-dihydroxy-1,3-indandione gave phthalic anhydride. The reactions of 1,3(2*H*)-phenalenedione and 2,3-dihydroxy-1-phenalenone yielded acenaphthenequinone and 1,8-naphthalenedicarboxylic anhydride. The reactions of acenaphthenequinone and 2,2-dihydroxy-1,3-phenalenedione gave 1,8-naphthalenedicarboxylic anhydride with higher yields. The reactions of [2-^{14}C]-labeled compounds showed that the middle carbon atom was lost.

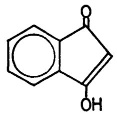
Mckillop and his co-workers[1)] have reported that the reaction of chalcones with thallium(III) nitrate gave benzils with the loss of one carbon atom. Roberts *et al.*[2)] reported that the decarbonylation of 1,3-diphenyl-1,2,3-propanetrione with cupric acetate in refluxing acetic acid yielded benzil with the loss of the center carbonyl group, as evidenced by the decarbonylation of the ^{14}C-labeled trione. Moriyama[3)] also reported that the oxidation of 2-acetoxy-1,3-diphenyl-1,3-propanedione-2-^{14}C with lead tetraacetate gave inactive benzil and active carbon dioxide, again indicating that the middle carbon was lost. However, the oxidation of β-hydroxychalcone-α-^{14}C with lead tetraacetate gave radioactive benzil (the relative specific radioactivity was 0.53) and carbon dioxide (the relative specific radioactivity was 0.06 as barium carbonate), thus suggesting that binary reaction mechanisms may operate in this case. We therefore examined the reactions of 1,3-indandiones and 1,3(2*H*)-phenalenediones with lead tetraacetate, which are cyclic analogues to the 1,3-diphenyl-1,3-propanediones, in the hope of clarifying the reaction pathways.

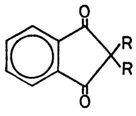


Scheme 1.

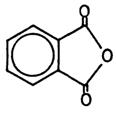
Results

When 1,3-indandione (I)[4)] was oxidized with lead tetraacetate in boiling benzene, two compounds (III(7%) and IV(12%)) were obtained. The NMR spectrum of III ($C_{13}H_{10}O_6$; mp 174—175 °C) indicated the presence of two acetoxyl groups [δ 2.14(s, 6H)] and aromatic protons [δ 7.98 (m, 4H)]. The IR spectrum of this compound suggested the presence of two carbonyl groups [ν_{max} 1745 (CO) and 1765 cm^{-1} (OAc)]. These spectroscopic properties indicated that this product has the structure of 2,2-diacetoxy-1,3-indandione. The second compound (IV) was found to be phthalic anhydride, which was identified by comparison of its IR spectrum and its melting point with those of an authentic specimen.


I



II=OH
III=OAc


IV

The yields of III and IV were slightly improved by increasing the amount of lead tetraacetate. These results are shown in Table 1.

The reaction of 2,2-dihydroxy-1,3-indandione (II)[5)] with lead tetraacetate in boiling benzene gave only IV (43%).

The reaction of 1,3(2*H*)-phenalenedione (VI)[6)] with lead tetraacetate in various molar ratios in boiling acetic acid gave two products (IX, mp 272—273 °C and X, mp 259—260 °C). IX and X were shown to be 1,8-naphthalenedicarboxylic anhydride and acenaphthenequinone respectively, by comparison of their melting points and their IR spectra with those of authentic specimens.

When 2,3-dihydroxy-1-phenalenone (VIII)[6)] was oxidized with one equivalent of lead tetraacetate in boiling acetic acid, two compounds (IX and X) were obtained. However, when VIII was oxidized with three equivalents of lead tetraacetate, only IX was obtained.

The reaction of 2,2-dihydroxy-1,3-phenalenedione (VII)[7)] with lead tetraacetate in boiling acetic acid gave IX as the sole product.

Table 1. Oxidations of 1,3-indandione (I) and 2,2-dihydroxy-1,3-indandione (II) with lead tetraacetate in boiling benzene

Compound	Reaction conditions		Products		
	Molar ratio	Time (min)	(Isolated yield, %) III	IV	CO_2
I	1 : 2	20	4.8	3.4	a)
I	1 : 3	20	5.7	4.1	a)
I	1 : 4	20	6.8	12.0	29.6
II	1 : 1	20		23.4	a)
II	1 : 2	20		37.5	a)
II	1 : 3	20		43.2	17.0

a) Not measured.

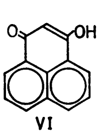
Table 2. Oxidation of 1,3(2*H*)-phenalenediones (VI, VII, VIII) and acenapquinone(X) with lead tetraacetate in boiling acetic acid

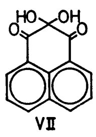
Compound	Reaction conditions		Products		
	Molar ratio	Time (min)	(Isolated yield, %) IX	X	CO_2
VI	1 : 1	10	a)	3.2	6.2
VI	1 : 2	10	a)	2.3	a)
VI	1 : 3	30	a)	1.8	a)
X	1 : 1	20	70		a)
VII	1 : 1	5	68		2.9
VII	1 : 2	5	68		a)
VII	1 : 3	15	62		a)
VIII	1 : 1	5	a)	14	a)
VIII	1 : 2	10	21		a)
VIII	1 : 3	15	62		57

a) Not measured.

The oxidation of acenaphthenequinone with one equivalent of lead tetraacetate in boiling acetic acid gave IX (70%) after 20 min. The yields of the products obtained by the above reactions are summarized in Table 2.

In order to establish the nature of the decarbonylation reaction, the reactions were repeated using [2-^{14}C]-labeled compounds, *i.e.*, [2-^{14}C]-I, [2-^{14}C]-II, [2-^{14}C]-VI, [2-^{14}C]-VII, and [2-^{14}C]-VIII. The results are summarized in Schemes 2 and 3.


VI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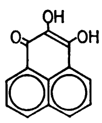
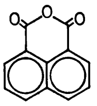
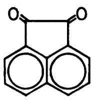
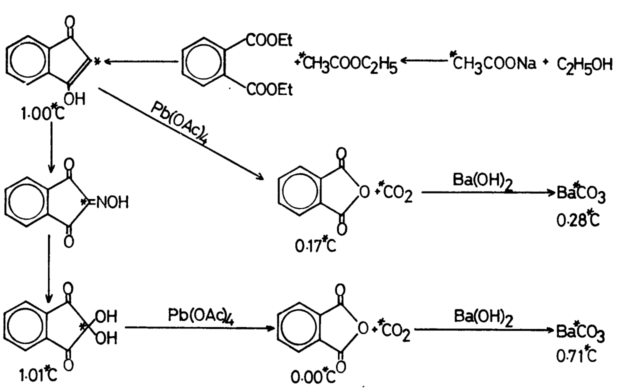

VIII


IX

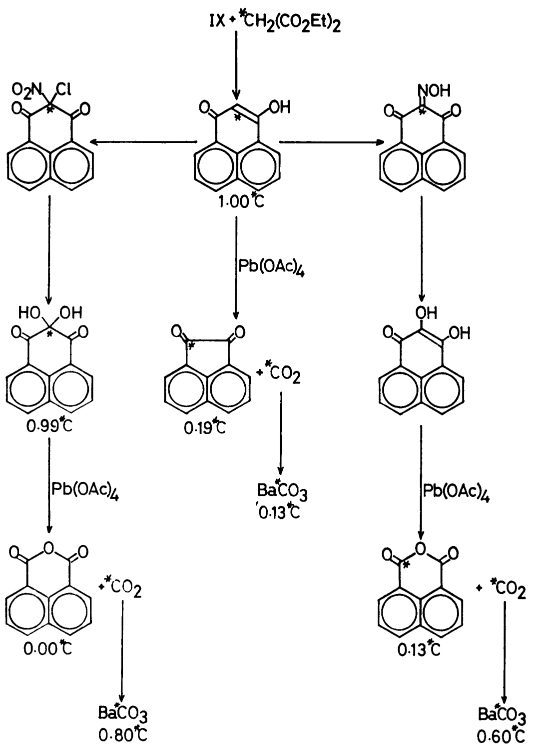

X

1,3-Indandione-2-^{14}C was synthesized by the reaction of diethyl phthalate with ethyl acetate-2-^{14}C. When 1,3-indandione-2-^{14}C was oxidized with lead tetraacetate, radioactive IV (the relative specific radioactivity was 0.17) and carbon dioxide (the relative specific radioactivity was 0.28 as barium carbonate) were obtained. On the other hand, the oxidation of 2,2-dihydroxy-1,3-indandione-2-^{14}C gave inactive IV and active carbon dioxide (the relative specific radioactivity was 0.71 as barium carbonate) (Scheme 2).

1,3(2*H*)-Phenalenedione-2-^{14}C was synthesized by the reaction of 1,8-naphthalenedicarboxylic anhydride with diethyl malonate-2-^{14}C. When 1,3(2*H*)-phenalenedione-2-^{14}C was oxidized with lead tetraacetate, radioactive X (the relative specific radioactivity was 0.19) and carbon dioxide (the relative specific radioactivity was 0.13 as barium carbonate) were obtained. When 2,3-dihydroxy-1-phenalenone-2-^{14}C was oxidized with lead tetraacetate, radioactive IX (the relative specific radioactivity was 0.13) and carbon dioxide the relative specific radioactivity was 0,60 as barium carbonate) were obtained. The oxidation of 2,2-dihydroxy-1,3-phenalenedione-2-^{14}C gave inactive IX and active carbon dioxide (the relative specific radiocativity was 0.80) (Scheme 3).



Scheme 2. Synthesis and decarbonylation reactions of 1,3-indandiones[2-^{14}C](the figures under the formulae refer to the specific activities of the compounds relative to 1,3-indandione).



Scheme 3. Synthesis and decarbonylation reactions of 1,3(2*H*)-phenalenediones[2-^{14}C](the figures under the formulae refer to the specific activities of the compounds relative to 1,3(2*H*)-phenalenedione).

Discussion

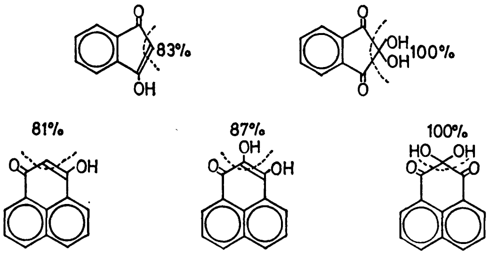
The conversion of I to III can readily be explained in terms of successive acetoxylations at the α-carbon adjacent to the carbonyl group. The conversion of I to IV involves the loss of 83% of C(2), suggesting that there may be binary reaction pathways.

In the case of the reaction of II with lead tetraacetate, the yield of IV was increased by increasing the molar ratio of the oxidant. From the tracer experiment, it was shown that the decarbonylation of C(2) is involved in the oxidation of II with lead tetraacetate, as indicated by the complete loss of the radioactivity.

When VI was oxidized with lead tetraacetate, the yield of X was decreased by increasing the molar ratio of the oxidant. It seems that X is an intermediate, as the oxidation of X with one equivalent of lead tetraacetate gave IX in better yield (70%). However a longer reaction time (20 min) was needed to consume the lead tetraacetate than in the case of VI. Therefore, we must eliminate the possibility that the reaction proceeds *via* X. The experiment on the ^{14}C-labeled compound showed that the reaction pathway involved the decarbonylation of C(2) atoms by 81%.

The oxidation of VIII with one equivalent of lead tetraacetate gave both IX and X, but that with three equivalents of lead tetraacetate gave only IX (62%). The experiment on the ^{14}C-labeled compound again indicated that the decarbonylation of C(2) was involved by 87% in this case.

The oxidation of VII gave IX (68%) without redox disproportionation, which was reported to occur in the reactions of VII[6] in boiling water or at high temperature, and completed by one equivalent of the oxidant. This reaction pathway involved the complete loss of C(2) atoms as shown by the tracer experiment (Scheme 4).



Scheme 4. The loss of the carbon (2-position) in 1,3-diones.

The above data indicate that the reaction pathway for the oxidation of the 1,3-diones and the enediol are fairly complicated ones, as indicated by the presence of the portion of the radioactivity in the product.

In the case of trione, on the other hand, on change in the yields of IV in the oxidation of II was observed when acetic acid was used as a solvent. The oxidations of VIII required only one equivalent of the oxidant and lost the C(2) completely. The above two facts suggest that the radical mechanism is favored in this case. However, no conclusive evidence is available to distinguish the radical and ionic mechanisms which operate in the reaction.

Experimental

The NMR spectra were recorded for the deuteriochloroform and trifluoroacetic acid solutions with a Hitachi R 24 NMR spectrometer, with tetramethylsilane as an internal reference. The IR spectra were recorded for the chloroform solution and KBr disk with a JASCO IRA-1 grating spectrometer. The melting points were determined with a Yanagimoto hot-stage apparatus. The radioactivities were recorded, for samples crystallized to a constant specific radioactivity, with an Aloka liquid scintillation spectrometer. The scintillator consisted of DPO(6 g), POPOP (0.275 g), and naphthalene (Dojin Laboratories, Kumamoto) dissolved in dioxane. Barium carbonate samples were suspended in a gel made up with 4% W/V CAB-O-SIL (Beckmann Instruments Inc., U.S.A.). Sample counts were repeated twice; the maximum observed error was within 0.5%.

Oxidations of 1,3-Indandiones with Lead Tetraacetate. The typical procedure of the oxidation of 1,3-indandiones is as follows. A mixture of 1,3-indandione (2 mmol), lead tetraacetate (4—8 mmol), and benzene (30 ml) was heated under reflux for the period of time shown in Table 1. Nitrogen was passed through the reaction mixture, and the evolved gases were passed into saturated aqueous barium hydroxide, aqueous potassium permanganate, and again saturated aqueous barium hydroxide. The precipitated barium carbonate was collected by centrifugation, washed with water, and dried. After the removal of insoluble materials by filtration, the benzene was evaporated *in vacuo* and the products were purified on TLC with chloroform as an eluting solvent. I gave 2,2-diacetoxy-1,3-indandione (III), mp 174—175 °C, 6.8%, (Found: C, 59.34; H, 3.99%. Calcd for $C_{13}H_{10}O_6$: C, 59.54; H, 3.84%, δ: 7.98 (m, 4H) and 2.14 (s, 6H, OAc), ν_{max}: 1745 and 1750 cm^{-1}), phthalic anhydride (IV) (mp 130—131 °C) and carbon dioxide. II yielded IV (mp 130—131 °C) and carbon dioxide.

*Oxidation of 1,3(2*H*)-Phenalenediones with Lead Tetraacetate.* A typical procedure of the oxidation of 1,3(2*H*)-phenalenediones is as follows. A mixture of 1,3(2*H*)-phenalenedione (2 mmol), lead tetraacetate (2—6 mmol), and hot acetic acid (30 ml) was heated under reflux for a period of time shown in Table 2. The carbon dioxide which evolved was converted to barium carbonate as described previously. After the removal of the acetic acid *in vacuo*, the residue was treated with 2M hydrochloric acid (60 ml) and extracted with chloroform. The chloroform solution was dried over sodium sulfate and evapolated under reduced pressure, and the products were separated on TLC with chloroform as an eluting solvent, giving the 1,8-naphthalenedicarboxylic anhydride (IX) (mp 272—273 °C) and/or acenaphthenequinone (X) (mp 259—260 °C). VII yielded IX (mp 272—273 °C) and carbon dioxide. VIII yielded IX (mp 272—273 °C), carbon dioxide and/or X (mp 259—260 °C).

Oxidation of Acenaphthenequinone (X). A mixture of acenaphthenequinone (2 mmol), lead tetraacetate (2 mmol), and acetic acid (30 ml) was heated under reflux for 20 min. After cooling, the crystals which precipitated were collected by filtration, giving IX (mp 272—273 °C).

1,3-Indandione-2-^{14}C. Into a mixture of diethyl phthalate (72 g) and powdered sodium (14.3 g) was dropped ethyl acetate-2-^{14}C (70 g) (which was prepared from acetic-2-^{14}C acid (250 μCi, Radiochemical Centre, Amersham, England) in absolute ethyl alcohol (1.43 g) over a period about 90 min). The material in the flask was refluxed gently during the addition of ethyl acetate mixture. The heating was continued for 6 h, and ether (30 ml) was added after cooling. As much of the sodium salt as possible was collected on a filter and then washed with ether, using as small a volume as possible. The total yield of the dry, yellow sodium salt was 55 g (71%). The sodium salt (55 g) was added to hot water (750 ml). The solution was cooled to 70 °C and under vigorous agitation the sodium salt was decomposed with a sulfuric acid solution (three parts of concentrated sulfuric acid and one part of water) (50 ml). The mixture was cooled to 15 °C and filtered. The 1,3-indandione thus obtained was a pale yellow solid (mp 127—

129 °C, 29 g, 61.3%, specific radioactivity 0.176 μCi/mmol).

2,2-Dihydroxy-1,3-indandione-2-^{14}C. To 1,3-indandione-2-^{14}C (5 g) dissolved in dilute sodium hydroxide (200 ml) was added sodium nitrite (2.5 g); then the mixture was cooled to 0 °C. Hydrochloric acid was added dropwise until the solution became distinctly acidic, whereupon the ice-bath was removed and the mixture was stirred for 30 min at room temperature. The solution was filtered and a yellow amorphous powder (5.9 g, 100%) was obtained. The oxime was recrystallized from acetic acid and formed yellowish green plates; mp 200—201 °C (decomp.). A mixture of selenious acid and the oxime (5 g) was refluxed for 3 h, and the clear solution was cooled to room temperature and saturated with sulfur dioxide. The solid which separated was filtered off and the filtrate was concentrated by distillation to *ca.* 50 ml and filtered. The filtrate was boiled with active carbon, filtered again, concentrated to 20 ml, and allowed to stand at room temperature. The crude 2,2-dihydroxy-1,3-indandione-2-^{14}C was filtered, and the mother liquor was concentrated to obtain a second crop; total yield 3.7 g (73%). It was purified by recrystallization from hot water with the aid of active carbon. Long colorless prisms of 2,2-dihydroxy-1,3-indandione-2-^{14}C were obtained, mp 241—243 °C (decomp.). The specific radioactivity was 0.178 μCi/mmol.

1,3(2H)-Phenalenedione-2-^{14}C. To a stirred mixture of diethyl malonate-2-^{14}C (75 ml, 250 μCi, Radiochemical Centre, Amersham, England) and 1,8-naphthalenedicarboxylic anhydride (25 g) was added zinc chloride (25 g); then the mixture was heated to *ca.* 170—175 °C for 6 h. The cooled reaction mass, after the addition of hot water (50 ml), was crushed to a powder and filtered. The residue was stirred with aqueous ammonia (one part of ammonia and four parts of water, 250 ml) for 15 min, and filtered. The filtrate was treated with active carbon, again filtered, and acidified with acetic acid. The solution was allowed to stand at room temperature for one hour, and filtered. The crystals obtained were washed with water, mp 254 °C (decomp.) (20.0 g, 81%, specific radioactivity 0.369 μCi/mmol).

2,3-Dihydroxy-1-phenalenone-2-^{14}C. 1,3(2*H*)-Phenalenedione-2-^{14}C (9.8 g) was dissolved in dilute sodium hydroxide (5%, 200 ml). After the addition of sodium nitrite (3.8 g), the mixture was cooled to 0 °C. Hydrochloric acid (17%) was added dropwise until the solution became distinctly acidic, whereupon the ice-bath was removed and the mixture was stirred for 30 min at room temperature. The solution was filtered and then washed with water and dried in *vacuo*, yielding the oxime (11.25 g, *ca.* 100%). The oxime (2.25 g) was dissolved into a mixture of acetic acid (10 ml), formalin (6.5 ml, 40%), and hydrochloric acid (2 ml). The mixture was refluxed for 4 h, and the solution was cooled and water (30 ml) was added. The solution was filtered to obtain 2,3-dihydroxy-1-phenalenone-2-^{14}C (1.7 g, 80%, mp 256 °C (xylene)). The specific radioactivity could not be obtained because of the deep coloration of the sample solution.

2,2-Dihydroxy-1,3-phenalenedione-2-^{14}C. A mixture of 1,3-(2*H*)-phenalenedione-2-^{14}C (1.96 g), sodium chloride (0.7 g), acetic acid (20 ml), and nitric acid (5 ml) was heated at 100 °C and stirred for 10 min. After cooling, the precipitates were collected, washed with ether, and dried. This gave 2-chloro-2-nitro-1,3-phenalenedione-2-^{14}C (1.8 g, 69%). The compound (1.0 g) was heated in nitrobenzene (10 ml) at 140 °C for 15 min; then the solution was cooled and the precipitates were washed with ether. This gave 2,2-dihydroxy-1,3-phenalenedione-2-^{14}C (0.62 g, 81%, mp 263 °C (decomp.), specific radioactivity 0.367 μCi/mmol).

Oxidation of [2-^{14}C]-Compounds by Lead Tetraacetate. [2-^{14}C]-Compounds were oxidized by the method described previously for the oxidation of the unlabeled compounds.

1,3-Indandione-2-^{14}C (292 mg) gave phthalic anhydride, mp 129—131 °C (35.6 mg, 12%, specific radioactivity 0.030 μCi/mmol), and carbon dioxide, which was converted to barium carbonate (116.7 mg, 29.6%, specific radioactivity 0.048 μCi/mmol).

2,2-Dihydroxy-1,3-indandione-2-^{14}C (356 mg) gave phthalic anhydride, mp 129 °C (127.7 mg, 43.2%, no radioactivity), and carbon dioxide, which was converted to barium carbonate (67.5 mg, 17%, specific radioactivity 0.124 μCi/mmol).

1,3(2*H*)-Phenalenedione-2-^{14}C (329 mg) gave acenaphthenequinone, mp 260 °C (11.5 mg, 3.2%, specific radioactivity 0.071 μCi/mmol), and carbon dioxide, which was converted to barium carbonate (24.3 mg, 6.2%, specific radioactivity 0.049 μCi/mmol).

2,3-Dihydroxy-1-phenalenone-2-^{14}C (424 mg) gave 1,8-naphthalenedicarboxylic anhydride, mp 274 °C (247.3 mg, 62.4%, specific radioactivity 0.049 μCi/mmol), and carbon dioxide, which was converted to barium carbonate (225.5 mg, 57%, specific radioactivity 0.222 μCi/mmol).

2,2-Dihydroxy-1,3-phenalenedione-2-^{14}C (456 mg) gave 1,8-naphthalenedicarboxylic anhydride, mp 274 °C (270 mg, 68%, no radioactivity), and carbon dioxide, which was converted to barium carbonate (11.47 mg, 2.9%, specific radioactivity 0.299 μCi/mmol).

References

1) A. Mckillop and B. Swan, *Tetrahedron Lett.*, **1970**, 5281.

2) J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 618 (1951).

3) K. Kurosawa and A. Moriyama, *Bull. Chem. Soc. Jpn.*, **47**, 2717 (1974).

4) W. O. Teeters and R. L. Shriner, *Ber.*, **55**, 3026 (1933).

5) S. Egashira, *Nippon Kagaku Zasshi*, **75**, 308 (1954).

6) B. Eistert, W. Eifler, and H. Göth, *Chem. Ber.*, **101**, 2162 (1968).

7) B. Eistert and O. Ganster, *Chem. Ber.*, **102**, 198 (1969).