PYROLYSIS OF AROMATIC CYCLIC DIAZOKETONES

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Abstract—The gas-phase pyrolyses of 2-diazo-1-indanone (**3**), 2-diazo-3-phenyl-1-indanone (**9**), 3-diazo-2-indolinone (**12**), 10-diazophenanthrene-9-one (**18**), and 2-diazoacenaphthene-1-one (**23**) have been reported. Indenone was isolated in 26–42 % yield from **3**; with methanol in the nitrogen stream, 2-methoxy-1-indanone was formed (24–32 %). Indenone formed 7*H*-benzo[*c*]fluoren-7-one upon standing. Pyrolysis of **9** led to 9-anthracenecarboxaldehyde (27 %) and anthracene (30 %). A mixture (10 %) of 2-indolinone and isoindigo was obtained from **12**. Pyrolysis of **18** gave (12–21 %) fluorene-9-carboxylic acid; with methanol in the stream, the methyl ester was formed in 20–26 % yield. Liquid-phase pyrolysis of **23** gave [$\Delta^{1,1}$]biacenaphthene-2,2'-dione. 75 %.

EXACT-MASS measurements taken from a mass spectrometer at high resolution have conclusively shown that the initial loss of 28 mass units from aromatic cyclic diazo-ketones is due solely to the loss of N_2, rather than CO.[2] The resulting ion may be a ketocarbene ion, it may rearrange directly to a ketoketene ion, or it may have a totally different structure. In most cases, the subsequent fragmentation of this ion, $(M.^+ - N_2)$, is the elimination of CO.

In the mass spectrum of 2-diazo-1,3-indanedione (**1**), the molecular ions eliminate N_2. This compound has also been pyrolyzed in the gas phase in the presence of methanol: a ketoketene was trapped and 2-carbomethoxybenzocyclobutenone (**2**) was isolated in 45–50% yield.[3]
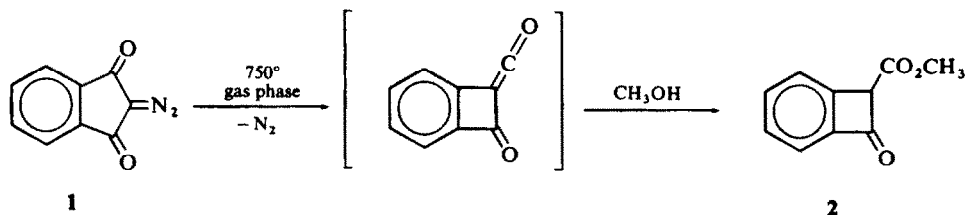
These results[2, 3] led us to hope that gas phase pyrolysis of aromatic cyclic diazo-ketones might lead to interesting products. We wish to report our results here.

RESULT AND DISCUSSION

Pyrolysis of 2-diazo-1-indanone (**3**). The gas-phase pyrolysis of **3** was carried out under reduced pressure in a stream of N_2 over a heated nichrome coil. The results are given in Table 1. When water vapor was in the stream of nitrogen, the major product was indenone (**4**), 26–42%. A minor product (0·5–3%) was anthracene (**5**). When methanol was present, 2-methoxy-1-indanone (**6**) was formed (24–32%). Polymeric material (2–8% by weight) was also formed.

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TABLE 1. RESULTS OF THE PYROLYSIS OF 2-DIAZO-1-INDANONE (3)

| Exp. no.	1	2	3	4
Amt 3 pyrolyzed, mg	302	102	127	190
Temp, °C	256	400	450	400
Nitrogen flow, l/min	0·25	0·35	0·30	0·25
Pressure, mm	20	10–14	10	12
Time, min.	180	180	300	390
Trapping agent	H_2O	H_2O	CH_3OH	CH_3OH
Amt 4, mg (%)	104 (41·9)	22 (26·2)	—	—
Amt 5 mg (%)	a	3 (2·6)	3 (2·1)	1 (0·5)
Amt 6, mg (%)	—	—	42 (32·3)	47 (24·1)

$a$undetermined

These results show that 2-diazo-1-indanone does not undergo ring contraction upon pyrolytic loss of N_2. The ketocarbene can go to a stable molecule by insertion into the adjacent C–H bond to form 4 or by being trapped with methanol, as summarized in Scheme 1. None of 4 was isolated when methanol was present and no 2-hydroxy-1-indanone was isolated when water vapor was present in the stream of nitrogen.
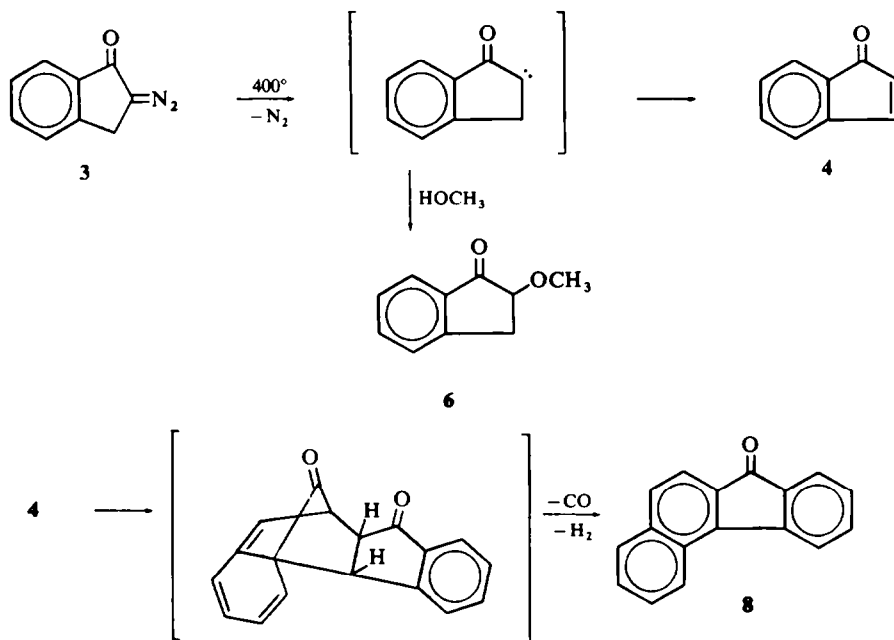
SCHEME 1

This is in contrast to the photolytic results. Photolysis has been used successfully as a method for the synthesis of strained bicyclic systems from diazoketones.[4] For example, the photolysis of 2-diazo-1-indanone (3) in aqueous tetrahydrofuran gave benzocyclobutene-1-carboxylic acid (7), resulting from addition of water to the ketene.[5]

3 $\xrightarrow[- N_2]{hv}$ [structure] $\xrightarrow[THF]{H_2O}$ [structure with CO_2H]

7
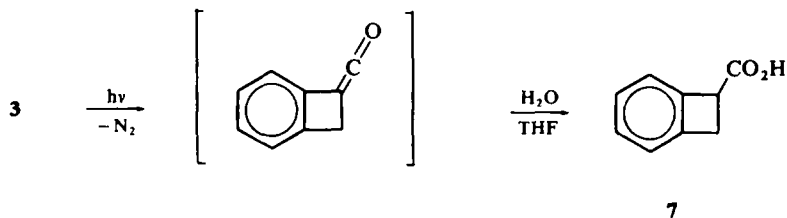
Marvel and Hinman have reported that indenone (**4**) polymerized at room temperature to give a white powdery material.[6] When our sample of indenone was reexamined after several weeks at room temperature, a powdery solid was present. The molecular ion was found at m/e 230 and loses CO followed by C_2H_2. This solid was different from the photodimers[7] of **4** and had different physical characteristics than the homopolymer of Marvel and Hinman.[6] The molecular weight, as determined by mass spectrometry, is 30 mass units less than the dimers of **4**.

The data we have indicate that our compound is 7H-benzo[c]fluoren-7-one (**8**). The formation of **8** can be rationalized as occurring via a Diels–Alder dimerization of **4**, followed by loss of the carbonyl bridge and hydrogen. An analogous reaction has been reported to occur with thianaphthene-1,1-dioxide,[8] which is the sulfur analog of indenone.

Pyrolysis of 2-diazo-3-phenyl-1-indanone (**9**). The gas-phase pyrolyses of 2-diazo-3-phenyl-1-indanone (**9**) were carried out with water as a trapping agent, and also with methanol. In both cases, the major products were anthracene (**5**) and 9-anthracene-carboxaldehyde (**10**), Table 2. For example, at 400° with a flow rate of 0·30 1/min and a

TABLE 2. RESULTS OF THE PYROLYSIS OF 2-DIAZO-3-PHENYL-1-INDANONE (9)

Exp. no.	1	2	3	4
Amt 9 pyrolyzed, mg	550	131	148	208
Temp, °C	450	400	400	400
Nitrogen flow, 1/min	0·45	0·30	0·30	0·40
Pressure, mm	12	12	12	12
Time, min	430	190	210	210
Trapping agent	H_2O	CH_3OH	CH_3OH	CH_3OH
Amt 10, mg (%)	83 (17·1)	31 (27·0)	21 (16·1)	27 (14·7)
Amt 5, mg (%)	29 (6·9)	30 (30·1)	17 (15·1)	43 (27·2)

pressure of 12 mm with methanol in the stream, 27% of **10** and 30% of **5** were isolated from 0·131 g of **9**. 3-Phenylindenone, the 3-phenyl derivative of **4**, was not found.

A route to **10** from **9** is proposed in Scheme 2. The ketocarbene interacts with the phenyl group rather than undergoing C-H insertion into the benzylic C—H bond.

A similar insertion into an aromatic C—H bond has been observed in the formation of fluorene from (2-phenyl)phenyldiazomethane.[9] Anthracene could form directly from the intermediate as shown in Scheme 2 and/or from the pyrolytic decarbonylation of **10**.
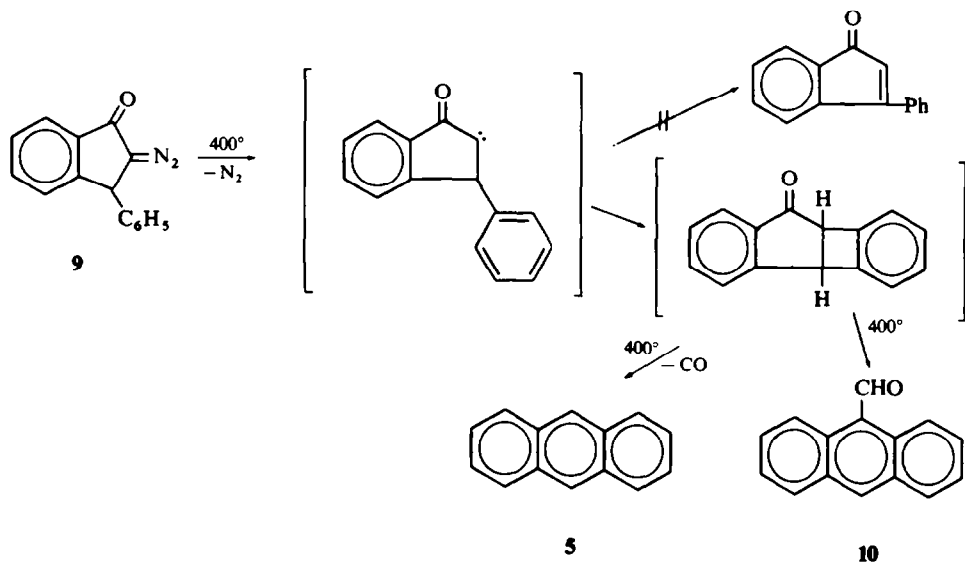
SCHEME 2

Also, the presence of very minor products was indicated by TLC. None was identified, although one, formed when methanol was present, had a molecular ion at m/e 238. This corresponds to the addition of methanol to the carbene or ketene intermediate formed upon loss of N_2 from 9. A metastable peak was present for the loss of CH_3O_2C, indicating that the compound might be 1-carbomethoxy-2-phenylbenzo-cyclobutene. Not enough material was available for full characterization.

Photolysis of 2-diazo-3-phenyl-1-indanone (9) gave a similar result, the formation of 11.[10]

11
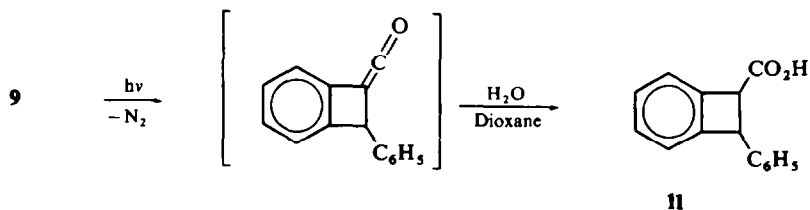
Pyrolysis of 3-diazo-2-indolinone (12). The products from the pyrolyses of 3-diazo-2-indolinone (12) in the absence of a trapping agent as well as with methanol present in the stream of N_2, were mainly polymeric materials. However, approximately 10% of a mixture of 2-indolinone (13) and isoindigo (14) was isolated by TLC. Compound 13 reacts vigorously with $SOCl_2$ in absence of solvent to give 14.[11] Thus it is possible that at least some of 14 was formed on TLC by acid catalysis of silica gel.

13
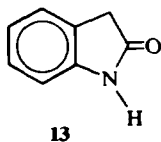
Heterocyclic analogs of the diazoindanones do not undergo ring contraction upon photolysis or pyrolysis. For example, the N-methyl derivative (15) of 3-diazo-2-indolinone (12) gave products arising from the ketocarbene intermediate when photolysed in the presence of various trapping agents.[12] In a similar manner, sealed-tube pyrolysis of 12 at 300° gave isoindigo (14), the dimer of the ketocarbene.[13]
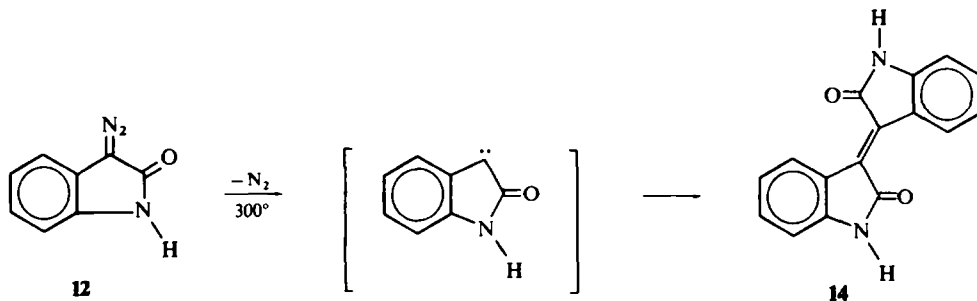
2-Diazo-3-ketothianaphthane-1,1-dioxide (16) photolyzes to give a ketocarbene which abstracts two hydrogen atoms from the trapping agent (methanol) to give 3-ketothianaphthane-1, 1-dioxide (17).[14] Also, there is evidence that 16 gives 17 thermally upon introduction into the ion source of a mass spectrometer.[2] The formation of 13 from 12 is similar to the formation of 17 from 16.

Pyrolysis of 10-*diazophenanthrene-9-one* (18). The gas phase pyrolyses (Table 3) of

TABLE 3. RESULTS OF THE PYROLYSIS OF 10-DIAZOPHENANTHRENE-9-ONE (18)

| Exp. no.	1	2	3	4	5
Amt 18 pyrolyzed, mg	182	108	181	182	161
Temp, °C	400	400	450	450	450
Nitrogen flow, 1/min	0·35	0·40	0·25	0·70	0·25
Pressure, mm	9	10	7·5	10	4
Time, min	300	390	220	1440	490
Trapping Agent	CH_3OH	CH_3OH	CH_3OH	none	none
Material unsublimed, mg	89	45	101	66	121
Amt 21, mg (%)[a]	89 (28·0)	31 (16·4)	[b]	[b]	[b]
Amt 19, mg (%)	39 (22·5)	27 (26·2)	35 (20·2)	—	—
Amt 20, mg (%)	—	—	—	39 (21·0)	20 (12·2)

[a] This was isolated from the unsublimed material.
[b] Undetermined.

10-diazophenanthrene-9-one (18) gave products formed after ring contraction to a ketene. When methanol was present, the product was 9-carbomethoxyfluorene (19), 20–26%. In the absence of methanol, the product which was isolated was fluorene-9-carboxylic acid (20), 12–21%. Acid (20) was probably formed by addition of water to the ketene upon workup.

The pyrolysis of 18 was complicated by the fact that 18 decomposed in the sublimation region of the pyrolysis apparatus to a purple material (21), 16–28%. The mass

18   **19**

20
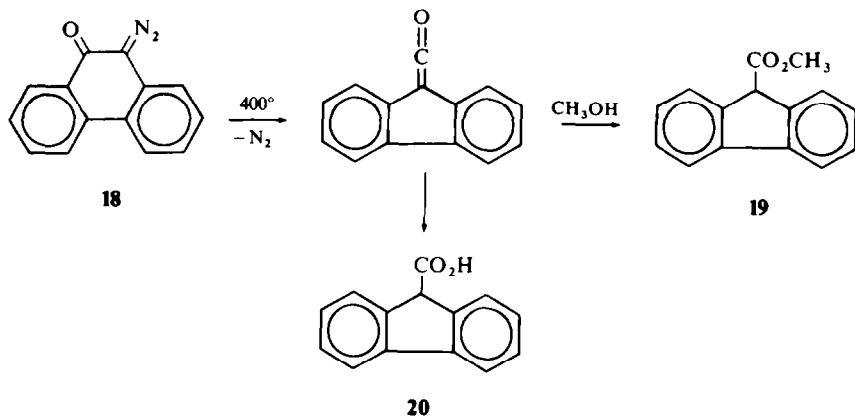
spectrum of **21** corresponds to a $C_{28}H_{16}O_2$ compound, the molecular ions of which lose CO. The formula $C_{28}H_{16}O_2$ is twice the formula of the intermediate ketene formed upon loss of N_2 from **18**. The structure of **21** has not been identified. However, its melting point and IR spectrum are different from those reported for **22**.[15] When **18** was heated at 130° for 6 hr, a 48·7% yield of **21** was isolated.

22
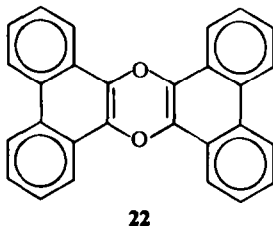
Pyrolysis of 2-diazoacenaphthene-1-one (**23**). Nothing but tarry polymer was isolated from the gas-phase pyrolysis of 2-diazoacenaphthene-1-one (**23**). However, when **23** was heated at 160° for 3 hr in a round-bottomed flask, 75% of [$Δ^{1,1}$]biacenaphthene-2,2'-dione (**24**) was isolated. Compound **24** presumably forms from an intermediate ketocarbene which dimerizes.

23   **24**
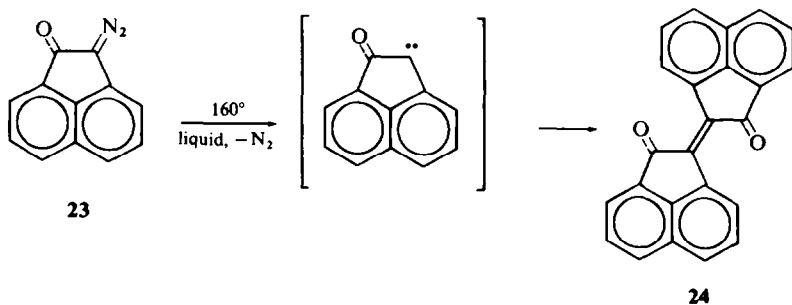
Pyrolysis of naphthalene-2-diazo-1-oxide (**25**) in boiling xylene gave both a ring-contracted ketene intermediate and a ketocarbene intermediate which reacted together to give a ketene ketal, 2-indenylidenenaphtho[1,2]-1,3-dioxide.[16] Photolysis

of **25** led to indene-1-carboxylic acid which reacted with starting material to give an azo dye.[17, 18] Photolysis of substituted benzene-2-diazo-1-oxides did not lead to ring contraction, but rather to 1,3-dipolar addition.[19, 20] For example, tetrachlorobenzene-2-diazo-1-oxide **(26)** reacted with substituted olefins to give the corresponding dihydrotetrachlorobenzofurans.[20] Pyrolysis of **26** gave the same results.[21]

The reactions of the carbene anthronylidene, prepared from 10-diazo-9,10-dihydro-9-oxoanthracene by photolysis in solution, have been studied.[22] The carbene added to double bonds of olefins, giving spiranes. Products resulting from abstraction of hydrogen atoms were also isolated.

The products formed in the pyrolyses of these diazoketones may be rationalized as arising via a ketocarbene intermediate or via a ring-contracted ketene intermediate. Compounds **1**[3] and **18** give exlusively ring contraction upon gas-phase pyrolysis. This contraction may be concurrent with loss of N_2 or may be subsequent to the formation of the ketoketene. On the other hand, the ketocarbenes from **3**, **9**, **12** and **23** either do not undergo ring contraction to ketenes or are trapped before they rearrange.

In general, upon pyrolysis, diazoketones form ketocarbenes which react with and/ or without rearrangement in protic solvents.[4] If there is a C—H bond alpha to the diazo group, unsaturated ketones can form. Other possible reactions are intra-molecular insertion and dimerization. In the products of the pyrolyses of these aromatic cyclic diazoketones, we see evidence for all these types of reactions, but from each compound under a given set of conditions, products from only one type of reaction are isolated.

EXPERIMENTAL

M.ps were determined by the open capillary method and are reported uncorrected. IR spectra were obtained from a Perkin Elmer 137 or a Perkin Elmer 700 spectrophotometer. NMR spectra were obtained from a Varian A-60A spectrometer using TMS as an internal standard. The mass spectra were obtained at medium resolution from an Atlas CH4 (direct probe, 70 eV) or an AEI MS902 (direct probe, 70 eV) mass spectrometer.

The pyrolysis apparatus and procedure have been described and used on other studies.[23-27]

The diazoketones were prepared by methods previously described: 2-diazo-1-indanone **(3)**,[5b] 2-diazo-3-phenyl-1-indanone **(9)**,[10] 3-diazo-2-indolinone **(12)**[5a] 10-diazophenanthrene-9-one **(18)**,[5a] and 2-diazoacenaphthene-1-one **(23)**.[5a]

Pyrolysis of 2-diazo-1-indanone **(3)**. In a typical experiment, 0·365 g of **3** was sublimed into the pyrolysis zone with a pressure of 10–14 mm and a N_2 flow rate of 0·35 l/min. The wire was heated to 400°. Water vapor was present in the stream of N_2, acting as a trapping agent. The sample was sublimed for 5 hr, after which the heating was terminated. At that time, 0·263 g of **3** remained unsublimed, i.e., 0·102 g had been led through the pyrolysis zone. This starting material which remained was compared with another sample of **3** in order to verify that the sample has not decomposed prior to sublimation into the pyrolysis zone.

TLC showed the presence of three major products (silica gel G, 8″ × 8″ plates, benzene). The fastest moving band (R_f 0·9) was scraped off the plate and eluted with benzene. The product (3 mg) was identified as **5**: mp 211–215° (lit.[28] 216°); mixed mp, undepressed. Mass spectrum: m/e 178, mol. ion. This product had the same retention time as commercially-prepared anthracene, and a different retention time than that of phenanthrene.

The second band (R_f 0·4, broad and yellow) was eluted with benzene, and the soln was distilled. A yellow oil was isolated (22 mg) and identified as **4**: bp 60–65°, 1 mm (lit.[6] 61–63°, 0·9 mm): IR (CH_2Cl_2), 1715 cm^{-1} (lit. 1715 cm^{-1},[6] 1713 cm^{-1}.[29]). Mass spectrum: m/e (rel. intensity), 130 (100), 102 (51), 76 (16), and 51 (20). Upon standing at room temp for several weeks, our indenone decomposed and gave a powdery

solid from which was obtained **8**: oxime, mp 201–203° (lit.[30] 202°) (lit.[31] 215°); IR (CH$_2$Cl$_2$), 1710 cm^{-1} (lit.[32] 1712 cm^{-1}); mass spectrum, m/e 230 (mol. ion).

The third band remained at the origin and had a dark orange colour. This polymeric material was not examined further.

The results of this and another pyrolysis using water as a trapping agent are given in Table 1. Table 1 also contains the results of two experiments in which MeOH was used as a trapping agent. With MeOH, three bands were obtained on the thin layer plate; one was the dark orange polymeric material at the origin and another was anthracene. The third band gave a yellow oil, identified as **6**: IR (CH$_2$Cl$_2$) 1725 cm^{-1} (lit.[33] 1720 cm^{-1}); NMR (CD$_3$COCD$_3$, TMS), δ 7·2 (4H, m), 4·30 (1H, t), 3·65 (3H, s), and 3·35 (2H, d); mass spectrum, m/e 162 (mol. ion); dinitrophenylhydrazone, mp 254–256° (lit.[33] 253·5°).

Pyrolysis of 2-diazo-3-phenyl-1-indanone (**9**). The pyrolysis experiments are summarized in Table 2. They were carried out and worked up in a similar manner to that described above for **3**. Three major bands were obtained on the TLC plates. One of these remained at the origin and was not worked with further. The fastest moving band (R_f 0·9) was identified as **5** by direct comparison with an authentic sample. The second band (R_f 0·7) was eluted with benzene, evaporated to dryness, and recrystallized from dilute AcOH. Yellow-orange needles of **10** were obtained: mp 104–105° (lit.[28] mp 104–105°); partial NMR (CDCl$_3$) δ 11·3 (lit.,[34] δ 11.4); IR (CH$_2$Cl$_2$), 1670 cm^{-1} (lit.,[35] 1667 cm^{-1}); mass spectrum, m/e 206, mol. ion.

The presence of other products from the experiments in which MeOH was present was indicated by minor bands in the chromatogram. These minor bands from pyrolyses 2–4 (Table 2) were scraped off, combined, eluted and rechromatographed. All bands except one contained only trace amounts of material. This band gave 2 mg of a yellow solid which has not been identified: mass spectrum, m/e (rel. intensity), 238 (13), 179 (100), and 178 (56); metastable for 238 → 179.

Pyrolysis of 3-diazo-2-indolinone (**12**). It is necessary to heat **12** at a temp below 100° when subliming it into the pyrolysis zone. Excessive heating results in a mild explosion, and the entire apparatus becomes coated with a black substance.

In a typical experiment, 0·250 g of **12** was pyrolyzed at 550°, 16 mm, and at a N$_2$ flow rate of 0·60 l/min with the presence of MeOH as a trapping agent. After 6 hr the pyrolysis was stopped; 0·0925 g of unsublimed material remained, which was identical with an authentic sample of **12**. The work-up gave 0·092 g of crude pyrolysis product. Preparative TLC (silica gel G, 8″ × 15″ plates, CHCl$_3$) showed the presence of many bands and a major band at the origin which could not be eluted with MeOH and was not investigated further.

A red-orange band (R_f 0·2) was eluted with MeOH and contained 13 mg of product: IR (CHCl$_3$) 1700, 1625, 1465 cm^{-1}. Mass spectrum at 95°, m/e 133, mol. ion; raising the temp to 310° resulted in the disappearance of the peak at m/e 133 and the appearance of a second molecular ion at m/e 262. Comparison with authentic samples of **13** and **14**, the latter prepared by a known method,[11] indicated that the red-orange band was a mixture of these two compounds. TLC behaviour, IR spectra, and mass spectra were compared. If all 13 mg were 2-indolinone, the yield would be 9·9%. The remainder of the bands in the chromatogram (a red-violet band and several fluorescent bands) contained traces of material (< 1 mg). Diisatinazine was prepared by the method of Borsche and Meyer,[36] but comparison showed that it was not present in any of the TLC bands.

Pyrolysis of 10-diazophenanthrene-9-one (**18**). The results of five experiments are given in Table 3. Upon termination of the pyrolyses, material was recovered which had not sublimed into the pyrolysis zone. This material was purple and had different TLC properties than **18**. TLC indicated that it was a single compound: mp 300°; IR (CH$_2$Cl$_2$), 1680, 1650, 1600 cm^{-1}; mass spectrum, m/e (rel. intensity), 384 (100), 356 (4·5). Calc for C$_{28}$H$_{16}$O$_2$, mol. ion, m/e 384 (100), M + 1 (30·8), M + 2 (5·1); Found, mol. ion m/e 384 (100), M + 1 (31), M + 2 (5.4). The structure of this compound has not been identified.

One product was isolated from the traps after the pyrolysis zone. When MeOH was present in the nitrogen stream, this product was **19**: mp 64–65·5° (lit.,[37] 65–66°); IR (CH$_2$Cl$_2$), 1730 cm^{-1}; mass spectrum, mol. ion. m/e 224. In the absence of a trapping agent, the product was **20**: mp 229–230° (lit.,[37] 225–226°) IR (KBr), 3030, 1720 cm^{-1} (lit.,[38] 3030, 1720 cm^{-1}); mass spectrum, m/e 166, mol. ion. The water most likely came from moisture in the air and from undried solvents used in the workup. The N$_2$ stream had been dried.

Compound **18** (166 mg) was heated at 130° for 6 hr at atmospheric pressure in a round-bottomed flask. The product was 141 mg of the C$_{28}$H$_{16}$O$_2$ compound (48·7%).

Pyrolysis of 2-diazoacenaphthene-1-one (**23**). When **23** was heated at 160° for 3 hr at atmospheric pressure in a round-bottomed flask, 333 mg of **23** gave 301 mg of crude pyrolysis product. TLC (silica gel G, 3″ × 1″

slides, CH_2Cl_2) showed three bands. The first remained at the origin and was not investigated. The second (R_f 0·2) was starting material. The third spot (R_f 0·4) was pink and was collected from a column of alumina eluted with CH_2Cl_2. Recrystallization of this material from MeOH gave 192 mg of 24: recrystallized from MeOH, mp 277° (chars), 284° (melts) (lit.[39] 287–288°), (lit.[40] 300°): IR (nujol), 1700 cm^{-1}: mass spectrum, m/e 332 (mol. ion), yield 37·3%: 75% based on reacted starting material.

Pyrolysis of 23 in the gas phase gave a black tar from which nothing could be isolated.

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